15 Cereals and Cereal Products

15.1 Foreword

15.1.1 Introduction

Cereal products are amongst the most important staple foods of mankind. Nutrients provided by bread consumption in industrial countries meet close to 50% of the daily requirement of carbohydrates, one third of the proteins and 50–60% of vitamin B. Moreover, cereal products are also a source of minerals and trace elements.
The major cereals are wheat, rye, rice, barley, millet and oats. Wheat and rye have a special role since only they are suitable for bread-making.

15.1.2 Origin

The genealogy of the cereals begins with wild grasses (*Poaceae*), as shown in Fig. 15.1. Barley (*Hordeum vulgare*), probably one of the first cereals grown systematically, was known as early as 5000 B.C. in Egypt and Babylon. Also, the bearded wheat cultivars from the groups Einkorn (*Triticum monococcum*) and Emmer (*T. dicoccum*), with diploid (genome formula: AA, $2n = 14$) and tetraploid (AABB, $2n = 28$) sets of chromosomes, (the chromosome number of the wheat genome is $n = 7$), were found among cultivated plants that were widely spread in temperate zones of Euroasia during the neolithic period. These cultivars are becoming extinct. Only the durum form of Emmer (*T. turgidum durum*, hard wheat, AABB), at 10% of the total wheat grown, has a significant role. The hexaploid (AABBDD, $2n = 42$) wheats derived from spelt are grown worldwide as bread cereals. The A genome of the spelts is closely related to that of Einkorn (*T. monococcum*). The origin of the B genome is unknown. It probably comes from species of the genus *Aegilops* and the D genome from *Aegilops squarrosa*.
Two varieties are derived from the spelts, bare wheat (soft wheat, *T. aestivum*) and bearded spelt (*T. spelta*). The low yield and the additional dehusking procedure led to the fact that soft wheat (called "wheat" below) gained more acceptance than spelt. As late as the middle of the 19th century, 15–20 times more spelt than wheat was grown in Southern Germany. Since the 1980s, however, demand for spelt has increased, especially in the natural food market. To compensate for the disadvantages with respect to the yield and the baking properties, wheat cultivars are crossed with the spelt. Such varieties differ from pure spelt in their gliadin pattern, which can be determined by HPLC (cf. 15.2.1.3.1).
Rice (*Oryza sativa*) and corn (*Zea mays*) have been cultivated for 5000 years, first in tropical Southeast Asia and then in Central and South

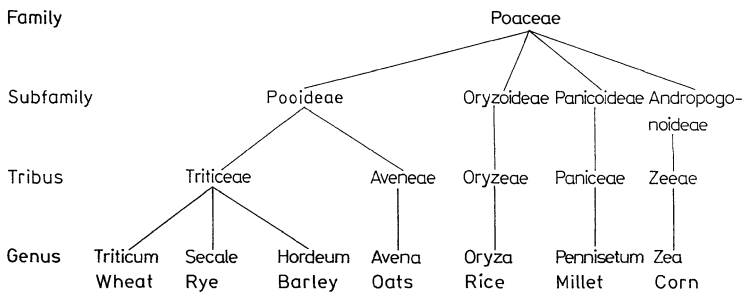


Fig. 15.1. Evolutionary development (phylogeny) of cereals

America. Cereals designated as millet have had a role from antiquity in subtropical and tropical regions of Asia and Africa. True millet from the subfamilies *Eragrostoideae* and *Panicoideae*, to which many regionally important cultivars belong (for instance, *Eragrostis tef, Eleusine coracan, Echinochloa frumentacea, Pennisetum glaucum, Setaria italica*), is distinguished from sorghum (*Sorghum bicolor*), which belongs to the subfamily *Andropogonoideae* and is cultivated worldwide.

Rye (*Secale cereale*) and oats (*Avena sativa*) are so-called secondary culture plants. Initially hardy and unwanted escorts of cultivated plants, they prospered and established themselves in northern regions with unfavorable climates. Their high tolerance for unfavorable climates surpassed that of both wheat and barley. Rye and oats have been cultivated for millenia.

Breeders have for many years attempted to combine the baking quality of wheat with the hardiness of rye. *Triticale*, the man-made hybrid of wheat and rye, does not yet fulfill this aim, hence its economic significance is low.

15.1.3 Production

Cereals are of great importance as raw materials for production of food and feed. Accordingly, they are grown on close to 60% of cultivated land in the world. Wheat production takes up the greatest part of land cultivated with cereals (Table 15.1) and wheat is produced in the largest quantity (Table 15.2). Wheat surplus producers are the USA, Canada, Argentina, Australia, and France. In the Federal Republic of Germany (FRG), winter wheat (92%) and spring wheat (8%) are both cultivated. The rise of cereal production in the world is shown in Table 15.3. The yields per hectare vary greatly from one country to another (Table 15.4). Due to an intensive effort in breeding and crop production programs, the yields per hectare in the FRG are very high and are surpassed by only a few countries, e. g., Holland. The FRG utilized 25.7×10^6 tons of cereals in 1976/77, of which 38% was bread and 62% feed cereals.

Table 15.1. Land cultivated with a cereal crop as % of the world total area under cereal cultivation (1979: 7.6×10^8 ha)

Cereal	1966	1976	1984	1988	1990	1996
Wheat	30.6	31.5	34.5	31.2	32.7	32.4
Rice	18.8	19.2	21.9	20.9	20.6	21.2
Corn	15.5	15.9	19.3	18.2	18.3	19.7
Millet	15.4[a]	15.6[a]	12.3[a]	5.7	5.3	5.1
Sorghum				6.6	6.3	6.6
Barley	12.2	11.9	11.7	10.8	10.1	9.4
Oats	4.5	3.8	3.8	3.2	3.1	2.4
Rye	2.4	2.1	2.6	2.3	2.3	1.6

[a] Sum of millet and sorghum.

15.1.4 Anatomy – Chemical Composition, a Review

Cereals, in contrast to forage grasses, form a relatively large fruit, termed a caryopsis, in which the fruit shell is strongly bound to the seed shell. The kernel size, which is expressed as grams per 1000 kernels (Table 15.5), is not only dependent on the kind of cereal but on the cultivar and crop production techniques, hence it varies widely.

In oats, barley, and rice the front and back husks are fused together with the fruit. In contrast, threshing separates wheat and rye kernels from the husks as bare seed.

The major constituents of seven kinds of cereal are fairly uniform (Table 15.6). Noteworthy variations are the higher lipid content in oats and a lower fiber content in millet and rice. The available carbohydrates consist mainly of starch. Oats are especially rich in nonstarch polysaccharides (cf. 15.2.4.2). These cereals also differ in their vitamin B content (Table 15.6).

Fruit and seed coats enclose the nutrient tissue (endosperm) and germ in the kernel (Fig. 15.2). Botanically the endosperm consists of the starchy endosperm (70–80% of the kernel; Table 15.7) and the aleurone layer, which, with exception of barley, is a single cell layer.

The aleurone layer is rich in protein and also contains fat, enzymes and vitamins (Table 15.8 and 15.9). The proteins, of which half are water-soluble, appear as granules in the aleurone cells. They have no influence on the baking properties

Table 15.2. Cereal production in 2006 (1000 t)

Continent	Wheat	Rice, paddy	Barley	*(Corn)* Maize	Rye
World	605,946	634,606	138,643	695,228	13,261
Africa	25,096	21,131	6133	46,260	39
America, Central	3345	1179	875	24,788	–
America, North	84,575	8787	13,925	276,866	484
America, South and Caribbean	22,636	24,564	3024	91,778	38
Asia	272,185	576,518	22,441	203,025	1107
Europe	191,378	3459	89,048	76,742	11,574
Oceania	10,075	148	4072	558	20

Continent	Oats	Millet	Sorghum	Cereals, grand total
World	23,101	31,781	56,485	2,221,119
Africa	226	17,788	26,113	145,892
America, Central	153	1	5831	36,176
America, North	4963	300	7050	397,456
America, South and Caribbean	1247	16	10,973	154,677
Asia	1630	12,891	10,691	1,102,274
Europe	14,377	751	658	403,644
Oceania	658	35	1001	17,176

[a] World production = 100%.

Country	Wheat
China	104,470
India	69,350
USA	57,298
Russian Fed.	45,006
France	35,367
Canada	27,277
Germany	22,428
Pakistan	21,277
Turkey	20,010
UK	14,735
Iran	14,500
Argentina	14,000
Ukraine	14,000
∑(%)[a]	76

Country	Rice
China	184,070
India	136,510
Indonesia	54,400
Bangladesh	43,729
Vietnam	35,827
Thailand	29,269
Myanmar	25,200
Philippines	15,327
Brazil	11,505
Japan	10,695
∑(%)[a]	86

Country	Barley
Russian Fed.	18,154
Germany	11,967
Ukraine	11,316
France	10,412
Canada	10,005
Turkey	9551
Spain	8318
UK	5239
USA	3920
Australia	3722
China	3430
Denmark	3270
Poland	3161
Iran	3000
∑(%)[a]	76

Country	*(Corn)* Maize
USA	267,598
China	145,625
Brazil	42,632
Mexico	21,765
India	14,710
Argentina	14,446
France	12,902
Indonesia	11,611
Italy	9671
Canada	9268
∑(%)[a]	79

Country	Rye
Russian Fed.	2965
Germany	2644
Poland	2622
Belarus	1072
Ukraine	920
China	783
Canada	302
Turkey	246
USA	183
Spain	159
∑(%)[a]	90

Country	Oats
Russian Fed.	4880
Canada	3602
USA	1361
China	1160
Poland	1035
Finland	1029
Spain	918
Germany	830
UK	728
Ukraine	700
Sweden	635
Australia	633
∑(%)[a]	76

Table 15.2. Continued

Country	Millet	Country	Sorghum	Country	Cereals, grand total
India	10,100	Nigeria	9866	China	445,355
Nigeria	7705	India	7240	USA	346,562
Niger	3200	USA	7050	India	239,130
China	1821	Mexico	5487	Russian Fed.	76,866
Burkina Faso	1199	Sudan	5203	Indonesia	66,011
Mali	1060	China	2490	France	61,813
Sudan	792	Argentina	2328	Brazil	59,017
Uganda	687	Ethiopia	2313	Canada	50,895
Russian Fed.	600	Brazil	1556	Bangladesh	45,010
Chad	590	Burkina Faso	1554	Germany	43,475
				Vietnam	39,648
				Turkey	34,598
				Ukraine	33,698
				Argentina	33,556
				Thailand	33,146
				Pakistan	32,839
				Mexico	31,959
∑(%)[a]	87	∑(%)[a]	80	∑(%)[a]	75

Table 15.3. World production of cereals 1948–2006 (10^6 t)

Year	Amount	Year	Amount
1948	683	1988	1742
1956	789	1989	1881
1964	1019	1990	1955
1968	1180	1996	2050
1976	1456	2004	2239
1984	1802	2006	2221

of wheat. Millers regard the aleurone layer as part of the bran.

The starchy endosperm is the source of flour. Its thin-walled cells are packed with starch granules which lie imbedded in a matrix which is largely protein. A portion of these proteins, the gluten proteins, is responsible for the baking properties of wheat. The concentrations of the proteins and some other constituents (vitamins and minerals) decrease from outer to inner cells of the endosperm. The germ is separated from the endosperm by the scutellum. The germ is rich in enzymes and lipids (Table 15.8). Table 15.9 shows that wheat milling, when starchy endosperm cells are separated from germ and bran, results in a substantial loss of B-vitamins and minerals.

15.1.5 Special Role of Wheat–Gluten Formation

After addition of water a viscoelastic cohesive dough can be kneaded only from wheat flour. The resulting gluten, which can be isolated as a residue after washing out the dough with water, removing starch and other ingredients, is responsible for plasticity and dough stability.

Gluten consists of 90% protein (cf. 15.2.1.3), 8% lipids and 2% carbohydrates. The latter are primarily the water-insoluble pentosans (cf. 15.2.4.2.1), which are able to bind and hold a significant amount of water, while the lipids (cf. 15.2.5) form a lipoprotein complex with certain gluten proteins. In addition, enzymes such as proteinases and lipoxygenase are detectable in freshly isolated gluten.

The gluten proteins, in association with lipids, are responsible for the cohesive and viscoelastic flow properties of dough. Such rheological properties give the dough gas-holding capacity during leavening and provide a porous, spongy product with an elastic crumb after baking.

Rye and other cereals can not form gluten. The baking quality of rye is due to pentosans and to some proteins which swell after acidification (cf. 15.4.2.2) and contribute to gas-holding properties.

Table 15.4. Yield per hectare in year 2000/2001/2002/2003/2004/2006 (dt/ha)

	Wheat	Rye	Corn	Rice
Germany	72.8/78.8/68.1/65.0/81.7/72.0	49.3/61.3/50.3/42.9/61.3/49.1	92.1/88.4/93.8/72.4/ 90.9/80.3	-.- / -.- / -.- / -.- / -.-/ -.-
Argentina	24.9/22.4/20.3/25.3/25.4/25.5	14.4/13.3/14.0/ 9.5/ 9.5/11.5	54.3/54.5/61.7/64.7/ 64.6/59.0	47.8/57.0/57.5/54.0/62.8/70.6
Australia	18.2/21.1/ 9.1/20.7/17.0/ 8.8	6.4/ 6.4/ 6.4/ 6.4/ 5.7/ 5.7	49.4/46.6/55.1/59.4/ 49.6/50.0	82.6/92.8/79.5/95.2/82.3/63.0
China	37.4/38.1/37.8/39.3/42.0/44.6	15.3/13.4/14.5/22.7/21.0/35.1	46.0/47.0/49.3/48.1/ 51.5/53.7	62.6/61.5/61.9/60.6/62.6/62.6
France	71.2/66.2/74.5/62.5/75.8/67.4	46.1/40.8/48.6/40.3/50.5/45.7	90.8/85.6/89.8/71.2/ 89.8/85.6	58.4/53.6/56.9/56.1/57.1/55.3
India	27.8/27.1/27.6/26.2/27.1/26.2	-.- / -.- / -.- / -.- / -.-/ -.-	18.2/20.0/16.4/19.8/ 20.0/19.4	28.5/31.2/28.9/30.8/30.5/31.2
Russian Fed.	16.1/20.6/20.7/17.0/19.8/19.5	15.8/18.8/19.9/18.6/15.4/17.1	21.2/18.1/28.6/32.2/ 40.4/36.3	34.9/34.9/37.7/31.5/37.7/43.9
Turkey	22.4/20.3/21.0/20.9/22.3/21.5	17.7/15.7/17.0/17.1/18.5/16.5	41.4/40.0/42.0/50.0/ 42.9/58.6	60.3/61.0/60.0/57.2/50.0/87.0
USA	28.3/27.1/23.7/29.7/29.0/28.3	17.8/17.2/15.5/17.0/16.9/16.5	85.9/86.7/81.6/89.2/100.7/93.6	70.4/72.8/73.7/74.5/77.8/76.9
World	27.2/27.5/26.8/27.1/29.1/28.0	20.4/23.6/23.0/21.8/25.2/22.1	42.8/44.2/43.5/44.4/ 49.1/48.2	38.9/39.4/39.1/39.1/40.0/41.1

Table 15.5. Average thousand kernel weight of cereals (g)

Wheat	37	Oats	32
Rye	30	Barley	37
Corn	285	Millet	23
Rice	27		

15.1.6 Celiac Disease

Wheat, rye and barley can cause celiac disease in genetically predisposed persons; the role of oats in this disease is uncertain. Celiac disease affects both infants and adolescents, and in adults it is also called sprue. It is associated with a loss of villous structure of the intestinal mucosa; epithelial cells exhibit degenerative changes and nutrient absorption functions are severly impaired. Incidence of the disease varies, e. g., 0.1% of the children are affected in central Europe and 0.3% in Ireland. The prolamin fractions of wheat, barley or rye are the cause of the disease, which is therefore eliminated by a change of diet to rice, millet or corn.

15.2 Individual Constituents

The role of constituents is of particular interest in the processing of wheat and rye into bakery products.

15.2.1 Proteins

15.2.1.1 Differences in Amino Acid Composition

The proteins of different cereal flours vary in their amino acid composition (Table 15.10). Lysine content is low in all cereals. Methionine is also low, particularly in wheat, rye, barley, oats and corn. Both amino acids are significantly lower in flour than in muscle, egg or milk proteins. By breeding, attempts are being made to improve the content of all essential amino acids. This approach has been successful in the case of high-lysine barley and several corn cultivars.

Table 15.6. Chemical composition of cereals (average values)

	Wheat	Rye	Corn	Barley	Oats	Rice	Millet
	weight %						
Moisture	13.2	13.7	12.5	11.7	13.0	13.1	12.1
Protein (N × 6.25)	11.7	9.5	9.2	10.6	12.6	7.4	10.6
Lipids	2.2	1.7	3.8	2.1	7.1	2.4[a]	4.05
Available carbohydrates	59.6	60.7	64.2	63.3	55.7	74.1	68.8
Fiber	13.3	13.2	9.7	9.8	9.7	2.2	3.8
Minerals	1.5	1.9	1.30	2.25	2.85	1.2	1.6
	mg/kg						
Thiamine	5.5	4.4	4.6	5.7	7.0	3.4	4.6
Niacin	63.6	15.0	26.6	64.5	17.8	54.1	48.4
Riboflavin	1.3	1.8	1.3	2.2	1.8	0.55	1.5
Pantothenic acid	13.6	7.7	5.9	7.3	14.5	7.0	12.5

[a] Polished rice: 0.8%.

Table 15.7. Fractions of various cereals separated by milling (average weight-%)

Cereal variety	Husk	Bran	Germ	Endosperm
Wheat	0	15.0	2.0	83.0
Corn	0	7.2	11.0	81.8
Oats	20	8.0	2.0	70.0
Rice	20	8.0	2.0	70.0
Millet	0	7.9	9.8	82.3

15.2.1.2 A Review of the Osborne Fractions of Cereals

In 1907 *Osborne* separated wheat proteins, on the basis of their solubility, into four fractions. Sequential extraction of a flour sample yielded: water-soluble albumins, salt-soluble (e. g., 0.4 mol/l NaCl) globulins, and 70% aqueous ethanol-soluble prolamins. The glutelins remained in the flour residue. They can be separated into two sub-fractions. For this purpose, all the proteins remaining in the residue are first dissolved in 50% aqueous 1-propanol at 60 °C with reduction of the disulfide bonds, e. g., with dithioerythritol. The high-molecular (HMW) subunits (cf. 15.2.1.3.1) precipitate out on increasing the propanol concentration to 60%, while the low-molecular (LMW) subunits (cf. 15.2.1.3.3) remain in solution.

Further separation of the *Osborne* fractions and subfractions into the components is possible analytically with electrophoretic methods (cf. Fig. 15.3, 15.4) and analytically and preparatively with RP-HPLC (cf. Figs. 15.5–15.8).

Table 15.8. Chemical composition of anatomical parts of a wheat kernel (average weight-% on dry weight basis)

	Ash	Crude protein (N × 6.25)	Lipids	Crude fiber[a]	Cellulose	Pentosans	Starch
Longitudinal cells	1.3	3.9	1.0	27.7	32.1	50.1	–
Cross- and tube cells	10.6	10.7	0.5	20.7	22.9	38.9	–
Fruit and seed coatings	3.4	6.9	0.8	23.9	27.0	46.6	–
Aleurone cells[b]	10.9	31.7	9.1	6.6	5.3	28.3	–
Germ[b]	5.8	34.0	27.6	2.4	–	–	–
Starchy endosperm	0.6	12.6	1.6	0.3	0.3	3.3	80.4

[a] Crude fiber includes parts of cellulose and pentosans.
[b] Data for carbohydrates are incomplete.

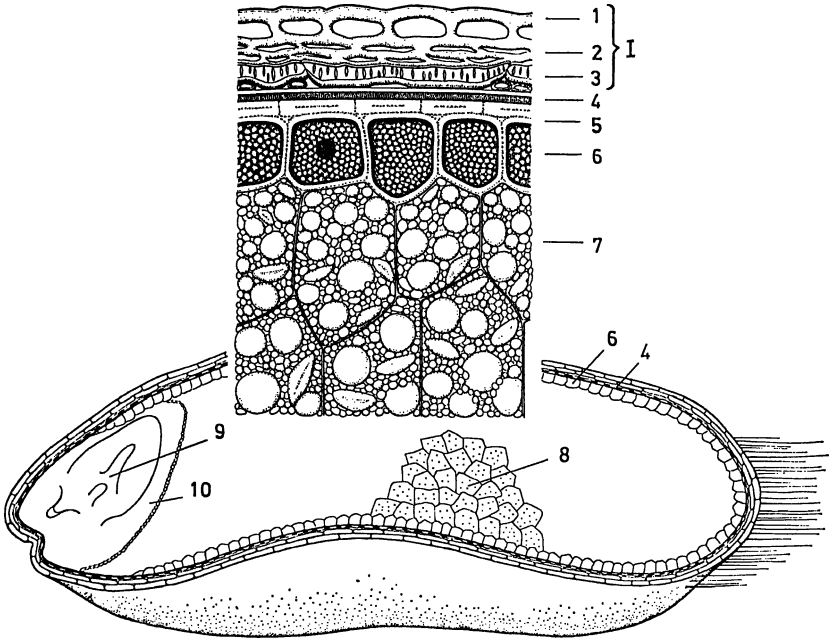


Fig. 15.2. Longitudinal section of a wheat grain. *I* Pericarp, *1* epidermis (epicarp), *2* hypodermis, *3* tube cells, *4* seed coat (testa), *5* nucellar tissue, *6* aleurone layer, *7* outer starchy endosperm cells, *8* inner starchy endosperm cells, *9* germ and *10* scutellum

Table 15.9. Mineral and vitamin distribution as % in kernel fractions of wheat

Fraction	Minerals	Thiamine	Riboflavin	Niacin	Pyridoxal phosphate	Pantothenic acid
Fruit coat	7	1	5	4	12	9
Germ	12	64	26	2	21	7
Aleurone layer	61	32	37	82	61	41
Starchy endosperm	20	3	32	12	6	43

In the literature, *Osborne* fractions derived from different cereals are often designated by special names (cf. review Table 15.11). The various designations may result in confusion and incorrect conclusions with regard to protein homogeneity. Therefore, it is better to preferentially use the general designations of the *Osborne* fractions and specify the protein source, e. g., wheat glutelin instead of glutenin.

Albumins and globulins are derived mostly from cytoplasmic residues and other subcellular fractions which are part of the kernel. Thus, enzymes are present in the first two *Osborne* fractions. Prolamins and glutelins, on the other hand, are storage proteins.

Cereals contain variable levels of *Osborne* fractions (Table 15.12). Wheat has the highest content of prolamin, corn has the second highest. The albumin fraction is the highest in rye and the lowest in corn. The content of albumin in oats is comparable to that in rye. Oats and rice have a higher content of glutelin than wheat, while rye, millet and corn have a much lower glutelin content. The amino acid composition of only the prolamins (Table 15.13) can be correlated to the botanical genealogy of cereals as shown in Fig. 15.1. In general, the amino acid composition is similar for wheat, of rye and barley. The prolamin composition of oats is intermediate between *Triticeae* and the other cereals. The amount of glutamic acid in

Table 15.10. Amino acid composition of the total proteins (mole-%)[a] of flours from various cereals

Amino acid	Wheat	Rye	Barley	Oats	Rice	Millet	Corn
Asx	4.2	6.9	4.9	8.1	8.8	7.7	5.9
Thr	3.2	4.0	3.8	3.9	4.1	4.5	3.7
Ser	6.6	6.4	6.0	6.6	6.8	6.6	6.4
Glx	31.1	23.6	24.8	19.5	15.4	17.1	17.7
Pro	12.6	12.2	14.3	6.2	5.2	7.5	10.8
Gly	6.1	7.0	6.0	8.2	7.8	5.7	4.9
Ala	4.3	6.0	5.1	6.7	8.1	11.2	11.2
Cys	1.8	1.6	1.5	2.6	1.6	1.2	1.6
Val	4.9	5.5	6.1	6.2	6.7	6.7	5.0
Met	1.4	1.3	1.6	1.7	2.6	2.9	1.8
Ile	3.8	3.6	3.7	4.0	4.2	3.9	3.6
Leu	6.8	6.6	6.8	7.6	8.1	9.6	14.1
Tyr	2.3	2.2	2.7	2.8	3.8	2.7	3.1
Phe	3.8	3.9	4.3	4.4	4.1	4.0	4.0
His	1.8	1.9	1.8	2.0	2.2	2.1	2.2
Lys	1.8	3.1	2.6	3.3	3.3	2.5	1.4
Arg	2.8	3.7	3.3	5.4	6.4	3.1	2.4
Trp	0.7	0.5	0.7	0.8	0.8	1.0	0.2
Amide group	31.0	24.4	26.1	19.2	15.7	22.8	19.8

[a] Mol amino acid per 100 mol amino acids.

Table 15.11. Designations of *Osborne*-fractions

Fraction	Wheat	Rye	Oats	Barley	Corn	Rice	Millet
Albumins	Leukosin						
Globulins	Edestin		Avenalin				
Prolamins	Gliadin	Secalin	Avenin	Hordein	Zein	Oryzin	Cafirin
Glutelins	Glutenin	Secalinin		Hordenin	Zeanin	Oryzenin	

Table 15.12. Protein distribution (%)[a] in *Osborne*-fractions[b]

Fraction	Wheat	Rye	Barley	Oats	Rice	Millet	Corn
Albumins	14.7	44.4	12.1	20.2	10.8	18.2	4.0
Globulins	7.0	10.2	8.4	11.9	9.7	6.1	2.8
Prolamins	32.6	20.9	25.0	14.0	2.2	33.9	47.9
Glutelins[c]	45.7	24.5	54.5	53.9	77.3	41.8	45.3

[a] Calculated from amino acid analyses.
[b] Ash content of the flours (% based on dry weight), wheat (0.55), rye (0.97), barley (0.96), oats (1.87), rice (1.0), millet (1.10), and corn (0.33).
[c] Protein residue after extraction of prolamins.

oat prolamins is similar to that of the *Triticeae*, whereas amounts of proline and leucine in oat prolamins are lower and higher, respectively, than those found in the *Triticeae*; this is also the case in comparison with rice, millet and corn. The amino acid compositions of rice, millet and corn are not related to the *Pooideae.*

The *Triticeae*, in which the prolamin amino acid compositions are closely related, can also cause *Celiac* disease (cf. 15.1.6). In comparison to other

Table 15.13. Amino acid composition (mole %) of the *Osborne* fractions of various cereals

Amino acid	Albumins						
	Wheat	Rye	Barley	Oats	Rice	Millet	Corn
Asx	9.7	8.8	10.2	10.2	9.9	11.0	16.7
Thr	3.8	4.0	4.7	4.4	4.6	5.0	4.4
Ser	6.2	6.2	6.4	8.9	6.5	6.3	6.2
Glx	20.9	22.1	13.8	12.4	14.2	12.1	12.4
Pro	9.3	12.0	7.4	6.1	4.6	5.1	8.6
Gly	6.9	6.6	9.7	12.6	9.8	10.0	9.7
Ala	6.9	6.5	8.2	7.6	9.4	10.5	10.0
Cys	3.2	2.3	3.8	6.8	1.9	1.4	1.8
Val	6.0	5.2	6.3	4.7	6.3	6.4	4.8
Met	1.6	1.3	2.0	1.2	1.7	2.0	1.1
Ile	3.3	3.4	3.3	2.7	3.7	3.3	3.0
Leu	6.4	6.3	5.9	5.5	6.9	6.5	5.1
Tyr	2.8	2.4	3.4	3.2	3.1	3.0	3.8
Phe	3.1	3.9	2.6	2.7	3.2	3.1	2.0
His	1.8	1.7	1.7	1.6	2.3	2.3	2.1
Lys	3.0	2.9	4.3	4.5	5.0	5.6	3.9
Arg	4.0	3.6	4.5	3.7	6.1	5.7	3.9
Trp	1.1	0.8	1.8	1.2	0.8	0.7	0.5
Amide groups	21.3	23.4	14.0	14.4	11.9	13.4	20.4

Amino acid	Globulins						
	Wheat	Rye	Barley	Oats	Rice	Millet	Corn
Asx	7.7	6.8	8.6	7.9	6.5	7.8	9.1
Thr	4.6	4.6	4.8	4.3	2.9	4.5	5.2
Ser	6.6	6.9	6.5	6.9	7.0	8.1	7.5
Glx	15.2	17.0	12.9	16.0	14.6	12.1	10.7
Pro	6.9	7.8	6.8	5.3	5.6	5.2	5.6
Gly	8.3	8.7	9.5	9.4	10.2	9.3	10.3
Ala	7.5	7.6	8.3	7.4	8.0	9.7	10.7
Cys	3.6	2.1	3.0	2.4	4.1	3.5	3.2
Val	6.8	6.3	6.8	6.5	6.1	6.3	6.2
Met	2.0	1.5	1.4	1.3	4.4	0.9	1.5
Ile	3.8	3.9	3.1	4.1	2.6	3.6	4.1
Leu	7.3	6.9	7.5	7.0	6.2	6.8	6.5
Tyr	2.9	2.3	2.7	2.7	3.7	3.0	2.6
Phe	3.1	3.6	3.3	4.0	2.8	3.3	3.2
His	2.4	2.5	2.2	2.4	2.2	2.9	2.3
Lys	4.0	4.3	4.7	4.4	2.4	4.0	4.6
Arg	6.4	6.5	7.0	7.3	9.8	8.2	6.0
Trp	0.9	0.7	0.9	0.7	0.9	0.8	0.7
Amide groups	13.9	14.6	9.6	14.5	10.4	11.3	11.2

Table 15.13. (continued)

Amino acid	Prolamins						
	Wheat	Rye	Barley	Oats	Rice	Millet	Corn
Asx	2.7	2.4	1.7	2.3	7.3	6.8	4.9
Thr	2.3	2.6	2.1	2.3	2.9	3.8	3.1
Ser	5.9	6.6	4.6	3.8	7.5	6.4	6.9
Glx	37.1	35.4	35.3	34.1	19.6	21.8	19.4
Pro	16.6	18.4	23.0	10.2	5.1	7.8	10.2
Gly	2.9	4.5	2.2	2.7	5.8	1.5	2.6
Ala	2.8	3.0	2.3	5.5	9.1	13.5	13.6
Cys	2.2	2.2	1.9	3.3	0.8	1.1	1.0
Val	4.2	4.4	3.9	7.7	6.9	6.4	4.0
Met	1.1	1.0	0.9	2.1	0.5	1.7	1.1
Ile	4.1	3.0	3.6	3.3	4.6	5.2	3.9
Leu	6.9	5.8	6.1	10.6	11.8	13.4	18.5
Tyr	2.0	1.7	2.3	1.7	6.1	2.1	3.6
Phe	4.6	4.5	5.8	5.3	4.8	4.9	4.9
His	1.7	1.2	1.2	1.1	1.5	1.3	1.1
Lys	0.8	1.0	0.5	1.0	0.5	0.0	0.0
Arg	1.7	1.9	2.0	2.7	4.7	0.8	1.2
Trp	0.4	0.4	0.6	0.3	0.5	1.5	0.0
Amide groups	37.5	34.7	34.9	31.6	23.3	28.6	23.0

Amino acid	Glutelins[a]						
	Wheat	Rye	Barley	Oats	Rice	Millet	Corn
Asx	3.7	7.1	4.9	9.3	9.5	7.6	5.5
Thr	3.6	4.7	4.2	4.2	4.2	5.1	4.2
Ser	7.3	6.9	6.7	6.6	6.7	5.9	6.1
Glx	30.1	19.7	24.2	19.0	15.5	16.8	16.0
Pro	11.9	9.4	14.2	5.5	5.1	8.4	11.1
Gly	7.9	9.2	6.4	7.9	7.4	6.9	6.9
Ala	4.4	7.3	5.6	6.5	7.9	10.1	9.4
Cys	1.4	0.8	0.5	1.2	1.2	1.7	1.8
Val	4.8	5.9	7.2	6.2	7.0	6.6	6.1
Met	1.3	1.6	1.3	1.3	2.4	1.6	2.8
Ile	3.5	3.7	4.0	4.6	4.5	4.1	3.4
Leu	6.9	7.4	7.5	7.8	8.4	9.1	10.9
Tyr	2.4	2.3	1.7	2.8	3.6	2.9	2.9
Phe	3.6	3.8	4.0	4.8	4.3	3.7	3.3
His	1.8	2.0	2.0	2.4	2.1	2.3	3.3
Lys	2.1	4.0	2.8	3.2	3.3	3.1	2.4
Arg	2.7	3.8	2.5	6.0	6.1	3.5	3.2
Trp	0.6	0.4	0.3	0.7	0.8	0.6	0.3
Amide groups	31.0	21.3	23.6	20.2	16.6	17.0	16.4

[a] Protein residue after extraction of prolamins.

cereals, *Triticeae* prolamins contain significantly higher levels of glutamic acid and proline. This suggests that the difference in prolamin composition, induced by these amino acids, may be responsible for *Celiac* disease.

15.2.1.3 Protein Components of Wheat Gluten

Wheat protein fractionation by the *Osborne* method provides prolamins and glutelins in a ratio of 1:1. Both fractions, in hydrated form, have different effects on the rheological characteristics of dough: prolamins are responsible, preferentially, for viscosity, and glutelins for dough strength and elasticity.

The genes for the gluten proteins occur at nine different complex loci in the wheat genome. The high molecular weight glutenin subunits are coded by the loci Glu-A1, Glu-B1 and Glu-D1, which are carried on the long arms of the chromosomes 1A, 1B and 1D. The low molecular weight glutenin subunits, the ω-gliadins and the γ-gliadins are coded by the loci Gli-A1, Gli-B1 and Gli-D1, which occur on the short arms of the chromosomes 1A, 1B and 1D. The α-gliadins are coded by the loci Gli-A2, Gli-B2 and Gli-D2 on the short arms of the group G chromosomes. It is presumed that the variation seen in different varieties is due to the presence of allelic genes at each of the nine storage protein loci. The relative importance of different alleles for gluten quality seems to be Glu-1 > Gli-1 > Gli-2.

A fractionation of gluten proteins is possible by two-dimensional electrophoresis. Figure 15.3 provides a schematic overview of the position of the most important protein groups in a two-dimensional electropherogram. The pattern of glutenins of two wheat cultivars are shown in Fig. 15.4.

Gluten proteins can be separated into their components on an analytical and micropreparative scale by using RP-HPLC. In general, this separation starts with the *Osborne* fractions or subfractions.

In this way, the *prolamines* of wheat can be separated into ω-, α-, γ-gliadins (Fig. 15.5), different varieties of wheat giving different patterns, e. g., the cultivars Clement and Maris Huntsman

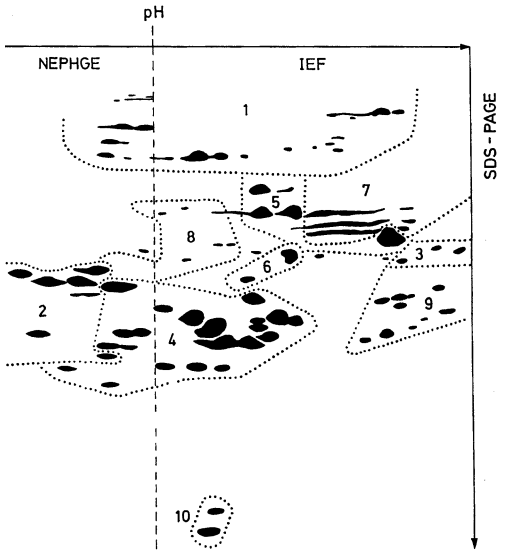


Fig. 15.3. Wheat endosperm proteins (cultivar "*Chinese Spring*"). Simplified schematic representation of a two-dimensional electrophoretic separation.
1st. Dimension: isoelectric focussing (IEF) and non-equilibrium pH gradient electrophoresis (NEPHGE). The electropherograms obtained by both methods are put together at the broken line in such a way that a continuous pH gradient is formed.
2nd. Dimension: polyacrylamide gel electrophoresis in the presence of sodium dodecyl sulfate and mercaptoethanol (SDS-PAGE).
The following protein fractions can be recognized: high-molecular glutenin subunits (1); basic (2) and acidic (3) low-molecular glutenin subunits; γ- (4) and ω-gliadins (5); subunits of the triplet band (6, 10); high-molecular albumins (7); globulins (8) and nonreserve proteins (9). (according to *Payne* et al., 1985)

known to produce sticky dough have a characteristically high ω-gliadin content.

The prolamin patterns of other cereals (Fig. 15.6) differ greatly from that of wheat. In *rye*, the hydrophilic ω-secalins are followed by the hydrophobic γ-secalins. And unlike wheat (α-gliadins), the area of moderate hydrophobicity is not occupied. In *barley*, a hydrophilic fraction is missing: the C-hordeins eluted in the middle area are followed by the hydrophobic B-hordeins. The chromatogram of *oats* is characterized by two hydrophobic fractions that are close to each other. The *low-molecular subunits of wheat glutelins* also give a chromatogram rich in components

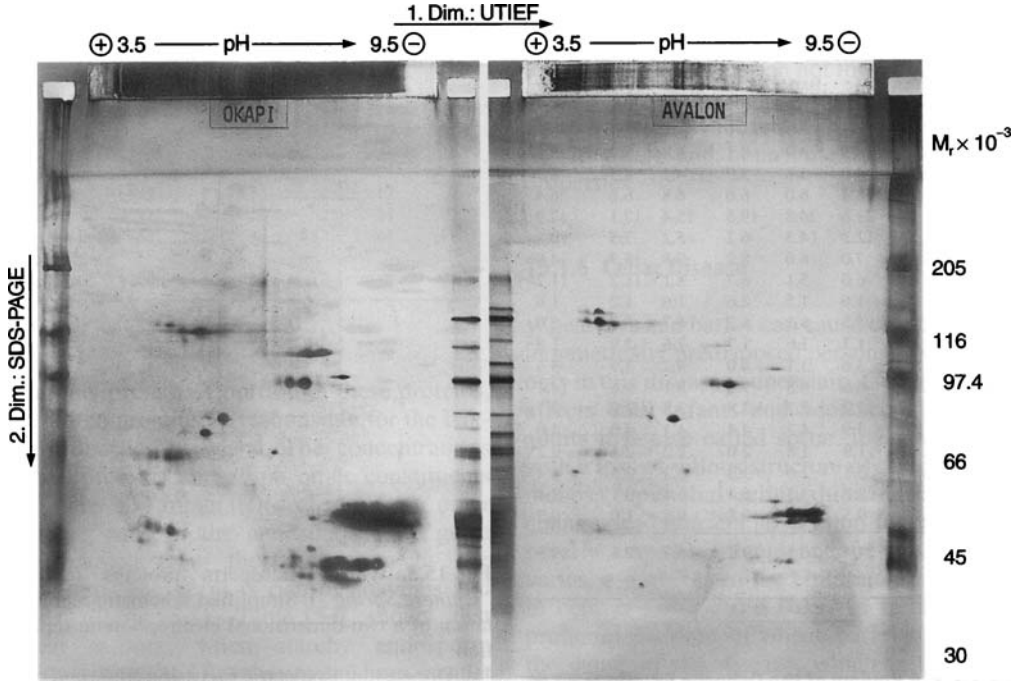


Fig. 15.4. Two-dimensional electrophoretic separation of glutenins[a] of the wheat cultivars *Okapi* (B4) and *Avalon* (A6)[b]. (according to *Krause* et al., 1988)
1st. Dimension: isoelectric focussing in ultrathin (0.25 mm) layer (UTIEF), pH 3.5–9.5; 8 mol/l urea.
2nd. Dimension: polyacrylamide gel electrophoresis in the presence of sodium dodecyl sulfate and mercaptoethanol (SDS-PAGE).
[a] Residue after extraction of defatted flour with water, salt solution, and aqueous ethanol.
[b] The baking quality class is given in brackets after the variety (bread volume yield for A6: average to high, for B4: low to average)

(Fig. 15.7). This chromatogram also contains the ω5-, ω1,2-, and γ-gliadins, which are not separated during pre-fractionation because of varying solubilities (cf. 15.2.1.2).

The *high-molecular subunits of wheat glutelins* show a protein pattern typical of the cultivar (Fig. 15.8).

Based on the data available on the structure of gluten proteins, three main groups can be formed which consist of several subunits. A *high-molecular group* with the HMW subunits of glutenins, a *group of intermediate molecular weights* with the ω5- and ω1,2-gliadins, and a *low-molecular group* with the α- and γ-gliadins as well as the LMW subunits of the glutenins. The properties of the protein groups mentioned are summarized in Table 15.14 and the amino acid composition is given in Table 15.15.

15.2.1.3.1 High-Molecular Group (HMW Subunits of Glutenin)

As shown in Table 15.15, the HMW subunits of glutenin are the only gluten proteins in which Gly (ca. 19%), and not Pro (ca. 12%), takes second place in the order of amino acids after Glx (ca. 36%). Furthermore, the proteins are characterized by the highest content of Tyr (ca. 6%) and Thr (ca. 3.5%) and the lowest content of Phe (ca. 0.3%) and Ile (ca. 0.8%). In the N-terminal amino acid sequence presented in Table 15.16, the sequence EGEAS-RQLQC is valid for all known HMW subunits and varies only in position 6 (E, K, G). From the total sequences known until now, it can be deduced that the HMW subunits consist of three segments (A–C in Table 15.17). The N- and C-terminal segments

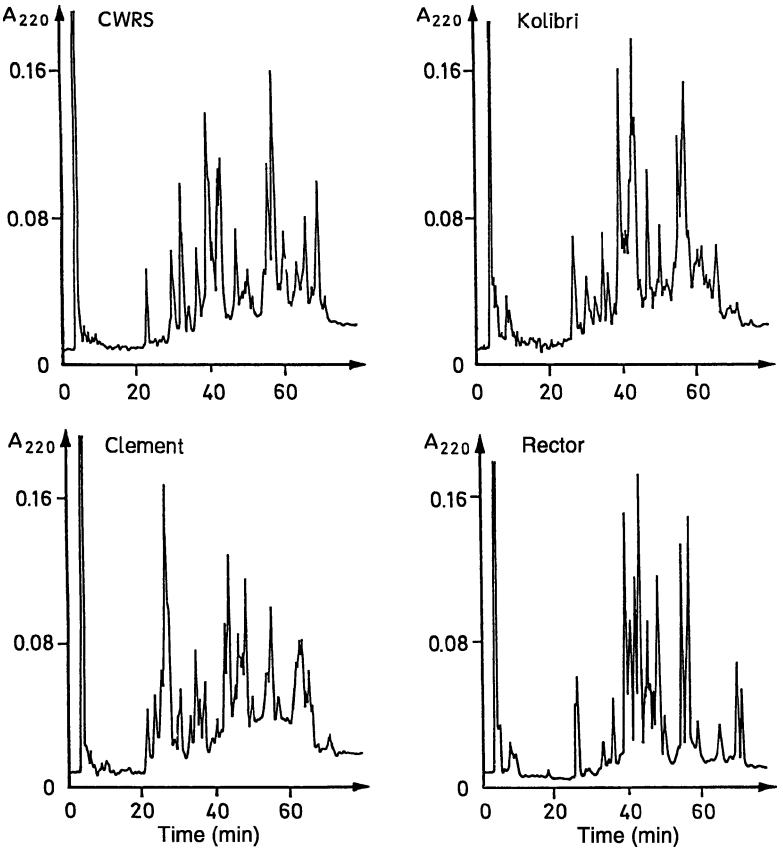


Fig. 15.5. RP-HPLC of the gliadin fractions of various wheat cultivars[a] on Synchro Pac C_{18} (50 °C, aqueous 2-propanol/trifluoroacetic acid/acetonitrile; 22–34 min: ω-gliadins, 33–51 min: α-gliadins, 52–72 min: γ-gliadins; according to *Wieser* et al., 1987)
[a] CWRS (Canadian Western Red Spring) is a mark of origin.

contain no recurring sequences and are characterized by the occurrence of Cys and amino acids with charged side chains. The middle segment consists of recurring sequences with the peptide unit QQPGQG as the backbone and insertions with the sequences YYPTSP, QQG, and QPG. It largely determines the unusual amino acid composition (high Gly and Tyr content). The individual HMW subunits differ mainly in the substitution of individual amino acid residues and in the number and arrangement of recurring peptide units.

The relative molecular masses (M_r) calculated from the known total sequences are 67,000–88,000, while the molecular masses derived from SDS-PAGE are 35–40% higher (Table 15.14).

Based on typical differences in the N-terminals and middle sequence segments, the HMW subunits can be assigned to two subgroups (x-type, M_r = 83,000−88,000; y-type, M_r = 67,000−74,000) (Tables 15.14 and 15.17). These proteins result from the fact that two genes are localized on each of the chromosomes of group 1 (1A, 1B, 1C; cf. 15.1.2). These genes code for the HMW subunits of type x and type y, e. g., ID contains the genes 1Dx and 1Dy. However, not all the genes are expressed in wheat cultivars. The allele pairs 1Dx2 and 1Dy12 as well as 1Dx5 and 1Dy10 are common. The pairs 1Bx6 and 1By8 as well as 1Bx7 and 1By9 are also frequently found. The occurrence of the corresponding HMW subunits 2, 5, 6–10,

Table 15.14. Classification and properties of gluten proteins

	HMW		MMW				
	HMW Subunits		ω-Gliadins		LMW		
Group	x-Type	y-Type	ω5	ω1,2	α-Gliadins	γ-Gliadins	LMW Subunits
$Mr \times 10^{-3}$ (SDS-PAGE)[a]	104–124	90–102	66–79	55–65	32	38–42	36–44
$Mr \times 10^{-3}$ (sequence)[b]	83–88	67–74	44–55[c]	34–44[c]	28–35	31–35	32–39
Number of amino acid residues	770–827	627–684	n.a.	n.a.	262–298	272–308	281–333
Content of gluten proteins	4–9%	3–4%	3–6%	4–7%	28–33%	23–31%	19–25%
Number of cysteine residues	4	7	0	0	6	8	8
μmol Cys/g flour	0.3	0.3	0	0	6.0	6.7	5.0

[a] Result of electrophoresis.
[b] Calculated from the amino acid sequence.
[c] Determined with MALDI-TOF mass spectrometry.
n.a.: not analyzed.

Table 15.15. Amino acid composition[a] of protein groups of wheat gluten (cultivar Rektor)

	HMW subunits of glutenin	ω5-Gliadins	ω1,2-Gliadins	LMW subunits of glutenin	α-Gliadins	γ-Gliadins
Asx	0.7–0.9	0.3–0.5	0.5–1.3	0.7–1.5	2.7–3.3	1.9–4.0
Thr	3.2–3.8	0.4–0.6	0.8–2.3	1.8–2.9	1.5–2.3	1.6–2.4
Ser	6.4–8.4	2.6–3.3	5.8–6.3	7.7–9.5	5.3–6.6	4.9–6.8
Glx	35.9–37.0	55.4–56.0	42.5–44.9	38.0–41.9	35.8–40.4	34.2–39.1
Pro	11.2–12.8	19.7–19.8	24.8–27.4	14.0–16.2	15.0–16.6	15.8–18.4
Gly	18.2–19.8	0.6–0.8	0.9–2.1	2.3–3.2	1.9–3.2	2.0–3.0
Ala	2.9–3.5	0.2–0.3	0.3–1.3	1.7–2.3	2.6–4.1	2.8–3.5
Cys	0.6–1.3	0.0	0.0	1.9–2.6	1.9–2.2	2.2–2.8
Val	1.6–2.7	0.3	0.6–1.4	3.8–5.3	4.2–4.9	4.4–5.4
Met	0.1–0.3	0.0	0.0–0.3	1.2–1.6	0.4–0.9	1.2–1.6
He	0.7–1.1	4.3–4.7	1.9–3.5	3.6–4.4	3.6–4.6	4.0–4.6
Leu	3.1–4.3	2.7–3.3	3.9–5.3	5.3–7.5	6.5–8.7	6.4–7.3
Tyr	5.1–6.4	0.6–0.7	0.8–1.5	0.9–1.9	2.3–3.2	0.6–1.4
Phe	0.2–0.5	9.0–9.5	7.6–8.1	3.8–5.5	2.9–3.9	4.7–5.6
His	0.8–1.9	1.3–1.4	0.6–1.1	1.3–1.8	1.4–2.8	1.1–1.5
Lys	0.7–1.1	0.4–0.5	0.3–0.6	0.2–0.6	0.2–0.6	0.4–0.9
Arg	1.6–2.1	0.5–0.6	0.5–1.4	1.5–2.1	1.7–2.9	1.2–2.9

[a] mol % (without Trp).

and 12 in a series of wheat cultivars is shown in Figs. 15.8 and 15.9. The amino acid sequences of the subunits 1Dx5 and 1By9 are shown in Table 15.17.

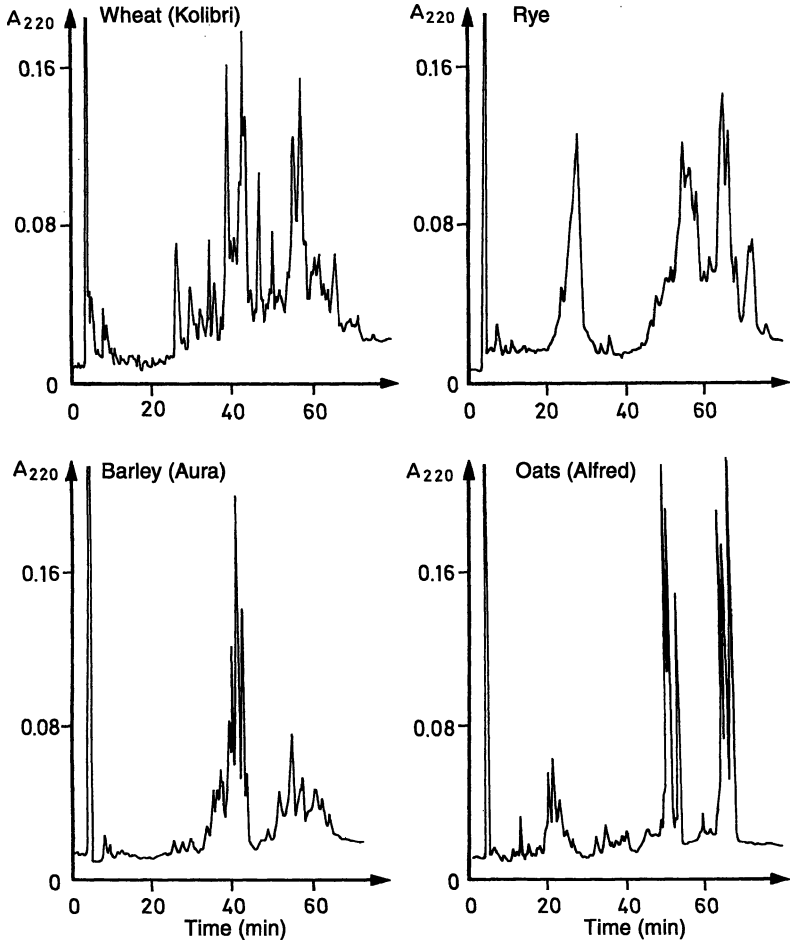


Fig. 15.6. RP-HPLC of the prolamin fractions of different varieties of cereal (conditions as in Fig. 15.5. *Wheat* 26–30 min: ω-gliadins, 32–50 min: α-gliadins, 54–71 min: α-gliadins. *Rye* 21–37 min: γ-secalins, 45–77 min: γ-secalins. *Barley* 32–44 min: C-hordeins, 46–66 min: B-hordeins. *Oats* 49–55 min/62–69 min: avenins; according to *Wieser*, *Belitz* et al., 1989)

15.2.1.3.2 Intermediate Molecular Weight Group (ω5-Gliadins, ω1,2-Gliadins)

This group of ω-gliadins is characterized by high values of Glx, Pro, and Phe (Table 15.15). The proportion of most of the other amino acids is less than in the other groups and the sulfur-containing amino acids Cys and Met are either absent or present only in traces. Total sequences have not yet been published, but some information is available on partial sequences. The ω-gliadins can be divided into two subgroups, the ω5-type and the ω1,2-type. This nomenclature is based on the varying mobility on acidic PAGE.

The *ω5-gliadins* are characterized by an extremely high content of Glx (ca. 56%) and a relatively high content of Phe (ca. 9%). Although the content of Pro (ca. 20%) is lower than in the ω1,2-type, it is clearly higher than in the other groups. These three amino acids account for about 85% of the total protein. ω5-Gliadins are free of sulfur-containing amino acids and the content of the remaining amino acids is comparatively low. It is noticeable that only this protein type has more Ile (ca. 4.5%) than Leu (ca. 3%).

The N-terminal sequences consist of the sequence SRLLSPRGKELHT and are typical of this type

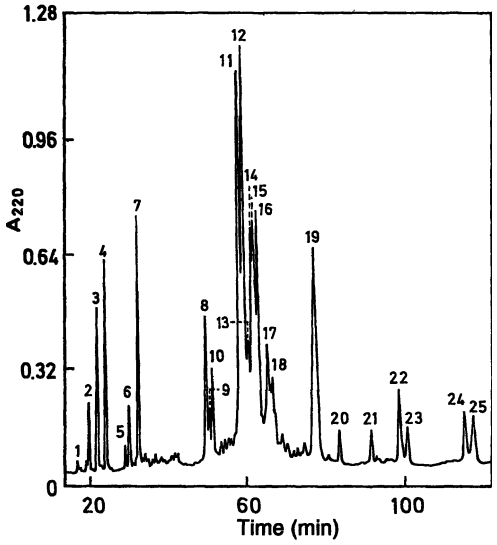


Fig. 15.7. RP-HPLC of low-molecular (LMW) subunits of wheat glutelin of the cultivar Rektor on Nucleosil C_{18} (60 °C, aqueous 2-propanol/trifluoroacetic acid/acetonitrile. After the prolamins, the protein fraction was extracted from the residue with 70% aqueous ethanol/0.5% dithioerythritol at pH 7.6 and 4 °C; peaks 2–4, 5–7: ω5-, ω1,2-gliadins. Peaks 8–17: LMW subunits, peaks 20–25: γ-gliadins or related proteins, according to *Wieser* et al., 1990)

Table 15.16. N-terminal sequences of the protein groups of wheat gluten

	Position 5 10
HMW subunits of glutenin	E G E A S R Q L Q C E G K
ω5-Gliadins	S R L L S P R G K E Q
ω1,2-Gliadins	– – – – – – – – – K E L Q S A R Q L N P S N K E
LMW-s[a]:	S H I P G L E R P S C
LMW-m[a]:	M E T S H I P G L E C
α-Gliadins	V R V P V P Q L Q P F P
γ-Gliadins	N M Q V D P S G Q V I S A

[a] The LMW type is named after the first amino acid in the sequence, serine (s) or methionine (m).

of protein. Recurring sequences with the peptide unit PQQQF evidently start from position 14. This represents a clear difference to the ω1,2-type, which explains the typical differences in the amino acid composition of the two subgroups.

The ω5-gliadins have a higher mobility than the ω1,2-gliadins in acidic PAGE and a lower mobility in SDS-PAGE, M_r being between 44,000 and 55,000 (Table 15.14).

In comparison with the ω5-gliadins, ω1,2-gliadins have lower values for Glx (ca. 43%), Phe (ca. 7.5%) and Ile (ca. 3%) (Table 15.14). Most of the other values are higher, especially the content of Pro (ca. 26%), which is the highest within the gluten groups of proteins. In the case of the N-terminal sequences, two basic variants apparently exist a: ARQLNPSNKELQS; b: KELQS, which with varying length are homologous and lead into a recurring sequence. The variant a was found more frequently in ω2-gliadins and the variant b more frequently in ω1-gliadins. The N-terminal sequence of the ω5-gliadins corresponds to that of variant a in 6 positions. The immediately following recurring sequence consists of the peptide unit PQQPY, while the dominating recurring peptide unit in this protein type seems to be the sequence PQQPFPQQ.

In acidic PAGE, ω1,2-gliadins have the lowest mobility. The molecular masses are in the range $M_r = 34{,}000-44{,}000$.

15.2.1.3.3 Low-Molecular Group (α-Gliadins, γ-Gliadins, LMW Subunits of Glutenin)

The quantitatively predominant low-molecular protein group in gluten (Table 15.14) has the best balanced amino acid composition. Most of the values lie between those of the high and intermediate molecular groups. Only the content of Cys, Val, Met, and Leu is higher (Table 15.15).

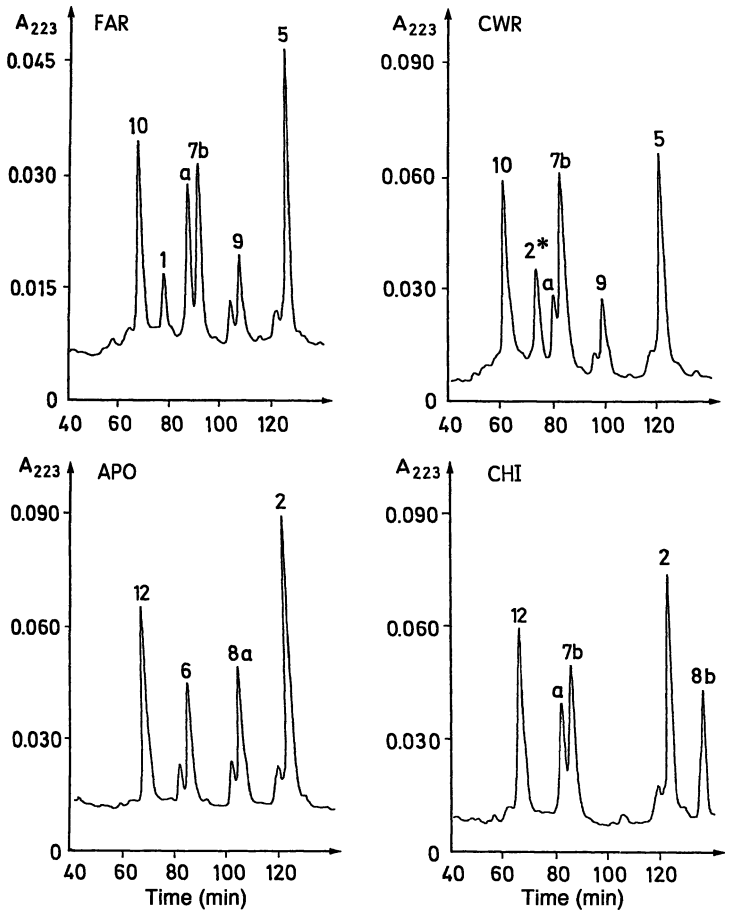


Fig. 15.8. RP-HPLC of the high-molecular (HMW) subunits of the glutelins of different varieties of wheat on Nucleosil C_8 (60 °C, urea/trifluoroacetic acid/acetonitrile/dithioerythritol; numbering of the peaks: 1–7 (x-type), 8–12 (y-type)); (FAR: Farmer, CWR: Canadian Western Red Spring, APO: Apollo, CHI: Chinese spring; according to *Seilmeier* et al., 1991)

A large number of partial and total sequences are found in the literature. With one exception (A-gliadin), the total sequences have all been derived from the corresponding nucleic acids. Based on present data, the low-molecular gluten proteins can be assigned to three subgroups (α-gliadins, γ-gliadins, LMW subunits of glutenin). As shown in Table 15.18 with three examples, the total sequences consist of up to seven differently structured segments: the N- and C-terminal sequence, segment 1–V. The individual proteins differ in the N- and C-terminal sequences, in the recurring sequences (segment I) and in the Gln-rich sequences (segment IV). On the other hand, they exhibit long homologous sequence segments that are low in Pro. These segments are characterized by the frequent occurrence of amino acids with charged side chains. In addition, with a few exceptions, they contain all the sulfurous amino acids. The M_r of this group of proteins lies in the range of 28,000–39,000 (Table 15.14).

As shown in Table 15.15, the amino acid composition of the α-gliadins differs on the whole only slightly from that of the γ-gliadins and LMW subunits of glutenin. In the case of individual amino acids, however, significant differences are exhibited. The content of Tyr (ca. 3%) is considerably

Table 15.17. Sequence comparison of the HMW subunits of glutenin

*a) x-Typ (HMW-subunit IDx5)**

N-terminal sequence		1	E G E A S E Q L Q **C** E R E L Q E L Q E R E L K A **C** Q Q V M D Q Q L R D I S P E **C**				
		41	H P V V V S P V A G Q Y E Q Q I V V P P K G G S F Y P G E T T P P Q Q L Q Q R I				
	A[a]	81	F W G I P A L L K R				
Recurring sequences		91	Y Y P S V T C P	Q–Q V S	448		Q Q P G Q G Q Q G
		103	Y Y P G Q A S P	Q–R P G Q G	457		Q Q P G Q G Q Q G
	B	117		Q–Q P G Q G Q Q G	466		Q Q P G Q G Q P G
		126	Y Y P– –T S P	Q–Q P G Q W	475	Y Y P T S P	Q Q S G Q G
		138		Q–Q P E Q G Q P R	487		Q Q P G Q W
		147	Y Y P– –T S P	Q–Q S G Q L	493		Q Q P G Q G Q P G
		159		Q–Q P A Q G	502	Y Y P T S P	L Q P G Q G Q P G
		165		Q–Q P G Q G Q Q G	517	Y D P T S P	Q Q P G Q G
		174		Q–Q P G Q G Q P G	529		Q Q P G Q L
		183	Y Y P– –T S S	Q L Q P G Q L	535		Q Q P A Q G Q Q G
		196		Q–Q P A Q G Q Q G	544		Q Q L A Q G Q Q G
		205		Q–Q P G Q A Q Q G	553		Q Q P A Q V Q Q G
		214		Q–Q P G Q G	562		Q R P A Q G Q Q G
		220		Q–Q P G Q G Q Q G	571		Q Q P G Q G Q Q G
		229		Q–Q P G Q G	580		Q Q L G Q G Q Q G
		235		Q–Q P G Q G Q Q G	589		Q Q P G Q G Q Q G
		244		Q–Q L G Q G Q Q G	598		Q Q P A Q G Q Q G
		253	Y Y P– –T S L	Q–Q S G Q G Q P G	607		Q Q P G Q G Q Q G
		268	Y Y P– –T S L	Q–Q L G Q G Q S G	616		Q Q P G Q G Q Q G
		283	Y Y P– –T S P	Q–Q P G Q G	625		Q Q P G Q G
		295		Q–Q P G Q L	631		Q Q P G Q G Q P W
		301		Q–Q P A Q G	640	Y Y P T S P	Q E S G Q G
		307		Q–Q P G Q G Q Q G	652		Q Q P G Q W
		316		Q–Q P G Q G Q Q G	658		Q Q P G Q G Q P G
		325		Q–Q P G Q G	667	Y Y L T S P	L Q L G Q G Q Q G
		331		Q–Q P G Q G Q P G	682	Y Y P T S L	Q Q P G Q G
		340	Y Y P– –T S	P Q-Q S G Q G Q P G	694		Q Q P G Q W
		355	Y Y P– –T S S	Q–Q P T Q S	700		Q Q S G Q G Q H W
		367		Q–Q P G Q G Q Q G	709	Y Y P T S P	Q L S G Q G
		376		Q–Q V G Q G Q Q A	721		Q R P G Q W
		385		Q–Q P G Q G	727		L Q P G Q G Q Q G
		391		Q–Q P G Q G Q P G	736	Y Y P T S P	Q Q P G Q G
		400	Y Y P– –T S P	Q–Q S G Q G Q P G	748		Q Q L G Q W
		415	Y Y L– –T S P	Q–Q S G Q G	754		L Q P G Q G Q Q G
		427		Q–Q P G Q L	763	Y Y P T S L	Q Q T G Q G
		433		Q–Q S A Q G Q K G	775		Q Q S G Q G Q Q G
		442		Q–Q P G Q G	784	Y Y	
C-terminal sequence		786	S S Y H V S V E H Q A A S L K V A K A Q Q L A A Q L P A M **C** R L E G G D A L				
	C	824	S A S Q				

Table 15.17. (continued)

*b) y-Type (HMW subunit 1 By 9)**

N-terminal sequence		1	EGEASRQLQ**C**ERELQESSLEA**C**RQVVDQQLAGRLPWSTGL				
		41	QMR**CC**QLRDVSAK**C**RPVAVSQVVRQYEQTVVPPKGGSFY				
	A[a]	81	PGETTPLQQLQQVIFWGTSSQTVQG				
Recurring sequence		106	YYPSVSSPQQGP	408		QQTRQG	
		118	YYPGQASP	QQPGQG	414	QQLEQG	
	B	132		QQPGKW	420		QQPGQG
		138		QELGQGQQG	426	QQTRQG	
		147	YYP– –TSL	HQSGQGQQG	432	QQLEQG	
		162	YYP– –SSL	QQPGQG	438	QQPGQGQQG	
		174		QQIGQGQQG	447	YYPTSP	QQSGQG
		183	YYP– –TSL	QQPGQG	459		QQPGQS
		195		QQIGQGQQG	465		QQPGQGQQG
		204	YYP– –TSP	QHPGOR	474	YYSSSL	QQPGQGLQG
		216		QQPGQG	489	HYPASL	QQPGQG
		222		QQIGQG	501		HPGQR
		228		QQLGQG	506		QQPGQG
		234		RQIGQG	512		QQPEQG
		240		QQSGQGQQG	518		QQPGQGQQG
		249	YYP– –TSP	QQLGQG	527	YYPTSP	QQPGQG
		261		QQPGQW	539		KQLGQGQQG
		267		QQSGQGQQG	548	YPTSPQ	QPGQG
		276	YYP– –TSQ	QQPGQGQQG	560		QQPGQGQQG
		291	QYP– –ASQ	QQPGQGQQG	569	H**C**PTSP	QQTGQA
		306	QYP– –ASQ	QQPGQGQQG	581		QQPGQG
		321	QYP– –ASQ	QQPGQGQQG	587		QQIGQV
		336	HYL– –ASQ	QQPGQGQQR	593		QQPGQGQQG
		351	HYP– –ASL	QQPGQGQQG	602	YYPISL	QQSGQG
		366	HYT– –ASL	QQPGQGQQG	614		QQSGQG
		381	HYP– –ASL	QQVGQG	620		QQSGQG
		393		QQIGQLGQR	626		HQLGQG
		402		QQPGQG	632		QQSGQEQQG
					641	YD	
C-terminal sequence		643	NPYHVNTEQQTASPKVAKVQQPATQLPIM**C**RMEGGDAL				
	C	681	SASQ				

[a] The capital letters mark sequence segments (cf. Fig. 15.12).

The numbers give the positions that the amino acids at the beginning of the line occupy in the total sequence. The segments of recurring sequences are arranged according to the best possible homology. (–:space to maximize homology) Cysteine residues (**C**) are marked in bold type.

* The numbering of the HMW subunits (5 and 9) corresponds to Figs. 15.8 and 15.9.

Table 15.18. Sequence comparison[a] of an α-gliadin (clone 1235), γ-gliadin (clone genesA), and a LMW subunit (clone LMWG-1D1)

N-terminal sequences	α-	1	V R V P V P Q L Q P Q N P S Q Q Q P Q E Q V P L M Q Q Q Q Q F P G				
	γ-	1	N M Q V D P F G Q V Q W P – Q Q Q P V L L				
	L M W	1	R **C** I P G L E R P W				
Recurring sequences 1[b]			α–Gliadin		γ-Gliadin		LMW
		34	Q Q E Q – F P – P Q Q P Y P			11	Q Q Q P L P P
		46	H Q Q P – F P – S Q Q P Y P	21	P Q Q P F S Q	18	Q Q T – F P
		58	Q P Q P – F P – P Q L P Y P	28	Q P Q Q T F P Q	23	Q Q P L F S
		70	Q T Q P – F P – P Q Q P Y P	36	P Q Q T F P H	29	Q Q Q Q Q Q L – F P
		82	Q P Q P Q Y P Q P Q Q P I S	43	Q P Q Q Q F P Q	38	Q Q P S F S
				51	P Q Q P Q Q Q F L Q	44	Q Q Q P P F W
				61	P Q Q P F P Q	51	Q Q Q P P F S
				68	Q P Q Q P Y P Q	58	Q Q Q P I L P
				76	Q P Q Q P F P Q	65	Q Q P P F S
				84	T Q Q P Q Q L F P Q	71	Q Q Q Q L V L P
				94	S Q Q P Q Q P Y P Q	79	Q Q P P F S
				104	Q P Q Q P F P Q	84	Q Q Q Q P V L P
				112	T Q Q P Q Q Q F P Q	93	P Q Q S P – F P
				122	S Q Q P Q – P F P Q	100	Q Q Q Q Q H
				131	P Q Q P Q Q S F P Q	106	Q Q L V
				141	Q Q P S	110	Q Q Q – I – P
Poly-Gln sequences (II)	α-	96	Q Q Q A Q Q Q Q Q Q Q				
Sequences low in Pro III	α-	108	T L Q Q I L Q Q Q L I P **C** R D V V L Q Q H N I A H A S S Q V L- - - - -Q Q S S Y				
	γ-	145	F I Q P S L Q Q Q L N P **C** K N L L L Q Q **C** R P V S L V S S L W – S M I W P Q S A **C**				
	L M W	115	V V Q P S I L Q Q L N P **C** K V F L Q Q Q **C** S P V A M P Q R L A R S Q M L Q Q S S **C**				
	α-		Q Q L Q Q L **C C** Q Q L F Q I P E Q S R **C** Q A I H N V V H A I I L				
	γ-		Q V M R Q Q **C C** Q Q L A Q I P Q Q L Q **C** A A I H S V V H S I S M				
	L M W		H V M Q Q Q **C C** Q Q L P Q I P Q Q S R Y E A I R A I I Y S I I L				
Sequences high in Gln IV	α-	176	H H H Q Q Q Q Q P S S Q V S Y Q Q P Q E Q Y P S G Q V S F Q S S Q Q N				
	γ-	216	Q E Q Q Q Q Q Q Q Q Q Q Q Q Q Q G M R I L L P L Y Q Q Q Q V G Q G T L				
	L M W	188	Q E Q Q Q V Q G S I Q S Q Q Q Q P Q Q L G Q C V S Q P Q Q Q S Q Q Q L G Q Q P Q Q Q Q				
Sequences low in Pro V	α-	212	P Q A Q G S V Q P Q Q L P Q F Q E I R N L A L Q T L P A M **C** N V Y I P P Y **C** S T T I A P F G				
	γ-	253	V Q G Q G I I Q P Q Q P A Q L E A I R S L V L Q T L P T M **C** N V Y V P P E **C** S I I K A P F A				
	LMW	231	L A Q G T F L Q P H Q I A Q L E V M T S I A L R I L P T M **C** S V N V P L Y R T T T S V P F G				
C-terminal sequences	α-	258	I F G T N				
	γ-	299	S I V T G I G G Q				
	L M W	277	V G T G V G A Y				

[a] The segments of the recurring and low-proline sequences are arranged according to the best possible homology (–: space to maximize homology). Cysteine residues (**C**) are in bold type.

[b] Roman numerals: division into sequence segments (cf. Fig. 15.10)

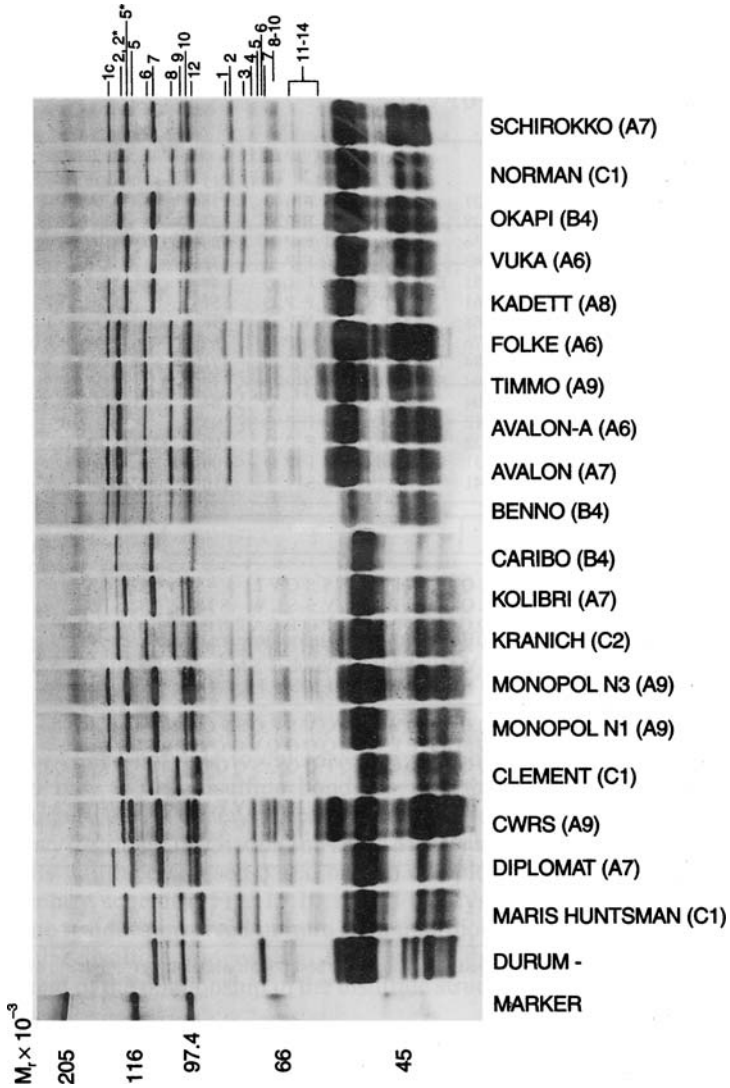


Fig. 15.9. Electrophoretic separation of the glutenins[a,b] of various wheat cultivars[c] on polyacrylamide gel in the presence of sodium dodecyl sulfate and mercaptoethanol (SDS-PAGE) (according to *Krause* et al., 1988)

[a] Residue after the extraction of defatted flour with water, salt solution, and aqueous ethanol.

[b] The numbering of the HMW subunits of glutenin differs from that in the original publication, Payne et al., 1981b: Band 1–7: (x-type), 8–12 (y-type).

[c] After each variety, the baking quality class is given in brackets (bread volume yield very high: A9, high to very high: A8, high: A7, average to high: A6, average: B5, low to average: B4, low: B3, very low to low: C2, very low: Cl).

higher and the content of Met (ca. 0.7%) and Phe (ca. 3.4%) is lower.

The N-terminal sequences determined directly by *Edman* degradation correspond to those derived from the nucleic acids. Apart from a few variations, the individual amino acid residues VRVPVPQLQPQN have been found for these N-terminal sequences (Table 15.16). The recurring sequences consist of the peptide unit QPQPFPPQQPYP, which usually occurs

five times and varies in individual amino acids (Table 15.18). The balanced Tyr/Phe ratio of the α-gliadins is based on this domain. Deviating from the γ-gliadins and the LMW subunits of glutenin, α-gliadin contains a poly-Gln sequence between the recurring and low-Pro sequence segments.

In comparison with the α-gliadins, the γ-*gliadins* exhibit higher values for Phe (ca. 5%) and Met (ca. 1.4%) and lower values for Tyr (ca. 1%) (Table 15.15).

The most common N-terminal sequence that is directly determined or derived from the nucleic acids is NMQVDPSGQV. Individual positions are modified, e. g., position 2 with I (Table 15.16). The recurring sequences consist of the peptide units PQQPFPQ, in which Q, TQQ, LQQ or PQQ can be inserted. There are up to 15 repetitions of such peptide units which can vary in individual residues (Table 15.18). The absence of Tyr in the recurring sequence segments shifts the Tyr/Phe ratio to ca. 1.5 (Table 15.15).

The *LMW subunits of glutenin* differ from the α- and γ-gliadins by having higher values for Ser (ca. 9%) and lower values for Ala (ca. 2%) and Asx (ca. 1%). The values for the other amino acids coincide (Table 15.15).

The N-terminal sequences of the LMW subunits were found to be SHIPGL or SCISGL (s-type) and METSCI or METSHI (m-type). The known total sequences show that the LMW subunits of glutenin have typical N-terminal, C-terminal, Gln-rich and recurring sequence segments (Table 15.18). The remaining sequence segments correspond largely to those of α- and γ-gliadins. The recurring peptide units usually consist of the sequence Q_nPPFS with $n = 2-10$. These units are repeated up to 20 times and the hydrophobic tripeptide PPF is partly varied (e. g., by PVL, PLP). In comparison with the α- and γ-gliadins, the high Ser content in the total composition is due to the recurring sequences.

15.2.1.4 Structure of Wheat Gluten

15.2.1.4.1 Disulfide Bonds

α-Gliadin and γ-gliadin are mainly monomeric proteins which, consequently, contain only intramolecular disulfide bonds. In comparison, the glutenins are protein aggregates of HMW and LMW subunits with molar masses from ca. 200,000 to a few million, which are stabilized by intermolecular disulfide bonds, hydrophobic interactions and other forces.

It has been possible to elucidate the position and type of the disulfide bonds so that the structure of the gluten proteins is discernible. First, α-gliadin, γ-gliadin and the LMW subunits will be discussed based on two complementary schemes. Figure 15.10 shows the cysteine residues involved in intra- and intermolecular disulfide bridges. Figure 15.11 shows the extent of the relationship in the disulfide structures.

In Fig. 15.10 and Fig. 15.12, the cysteine residues (C) at the N-terminal of the sequence are marked with the first letters of the alphabet and those at the C-terminal with the last letters of the alphabet. Homologous cysteine residues have the same letters. In α- and γ-gliadins, disulfide bonds are found in segments III–V; in LMW, also in segment I (Fig. 15.10). In γ-gliadin, four intramolecular disulfide bridges are concentrated in a relatively small sequence section so that a compact structural element is formed from the three small rings A, B, C and one large ring D (Fig. 15.11a). The disulfide structure of α-gliadin is related to that of γ-gliadin. Since the disulfide bond C^d/C^e is lacking (Fig. 15.10), the small rings A and B open to give a larger ring AB (Fig. 15.11b). LMW subunits do contain the small rings A and B, but since the disulfide bond C^w/C^z is lacking (Fig. 15.10), ring D expands to give ring CD (Fig. 15.11c).

For steric reasons, the cysteine residues C^{b*} and C^x in the LMW subunits cannot form intramolecular disulfide bonds, but are available for intermolecular disulfide bridges, preferably with other LMW and HMW subunits (Fig. 15.10).

HMW subunits of the x-type contain four and those of the y-type contain seven cysteine residues (Table 15.17). Except for the residue C^y in the y-type, all the residues are in the segments A and C (Fig. 15.12). In the x-type, the residues C^a and C^b form an intramolecular disulfide bridge (Fig. 15.12) and C^d and C^z are available for intermolecular bonding. The y-type contains five cysteine residues in segment A and one in each of the segments B and C (Fig. 15.12). Until now, intermolecular disulfide bonds to other

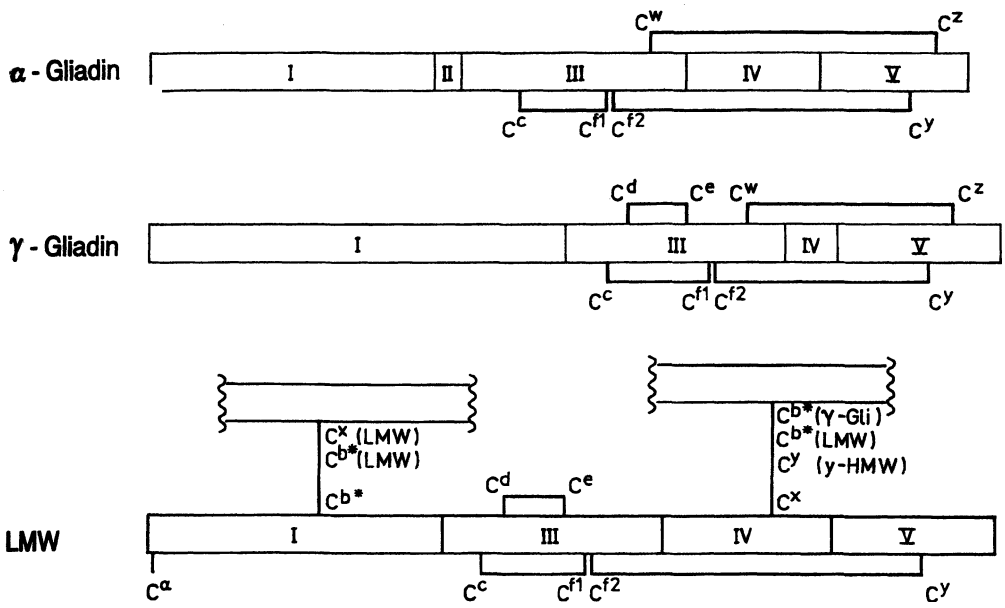


Fig. 15.10. Schematic representation of the disulfide structures of α-gliadins, γ-gliadins and LMW subunits (according to *Köhler* et al., 1993). Segments I–V (cf. Table 15.18)

HMW subsunits of the y-type as well as to LMW subunits could be detected (Fig. 15.12).

It is noticeable that small amounts of α-, γ- and ω-gliadins are not extractable from flour with aqueous alcohol, but remain with the glutenins. It is assumed that these proteins contain an odd number of cysteine residues due to point mutations, one residue being available for intermolecular disulfide bonding. In fact, it has been observed that LMW subunits are linked to γ-gliadins which have 9 instead of 8 cysteine residues, via a bridge from C^x to C^{b*} (Fig. 15.10).

15.2.1.4.2 Contribution of Gluten Proteins to the Baking Quality

Investigations of the structure and amount of gluten proteins in wheat cultivars with varying dough and baking properties allow an estimation of the contributions of individual gluten proteins to quality. An important feature is the suitability for forming, as far a possible, high molecular protein aggregates. The x-type of the HMW subunits appears to be especially predestined for this because, e. g., it can form linear polymers via the cysteine residues C^d and C^z (Fig. 15.12). This is expressed in the close relationship (correlation coefficient $r > 0.8$) between its amount and the strength of the dough (Fig. 15.13).

The considerably lower coefficient in the case of y-type ($r < 0.3$; Fig. 15.13) indicates that cross linkage via C^{c1} and C^{c2} or of C^y with LMW subunits (Fig. 15.12) does not have an especially positive effect on the consistency of the dough.

Apart from the HMW subunits of the x-type, the LMW subunits also make a positive contribution to the strength of dough and gluten ($r = 0.58-0.85$). It is to be assumed that the tendency of C^{b*} and C^x to polymerize is responsible for this effect (Fig. 15.10). However, about twice the amount of LMW subunits in flour is required for the same effect. The reason for this could be that the bonds of C^{b*} and C^x are not firmly directed but variable. Thus, C^x also binds to γ-gliadin with an odd number of cysteine residues (cf. 15.2.1.4.1) which would lead to chain breakage in the polymerization of gluten proteins, which possibly occurs during dough making.

Monomeric gliadins (cysteine-free ω-gliadins, α- and γ-gliadins with an even number of cysteine residues) are regarded as "solvent" or

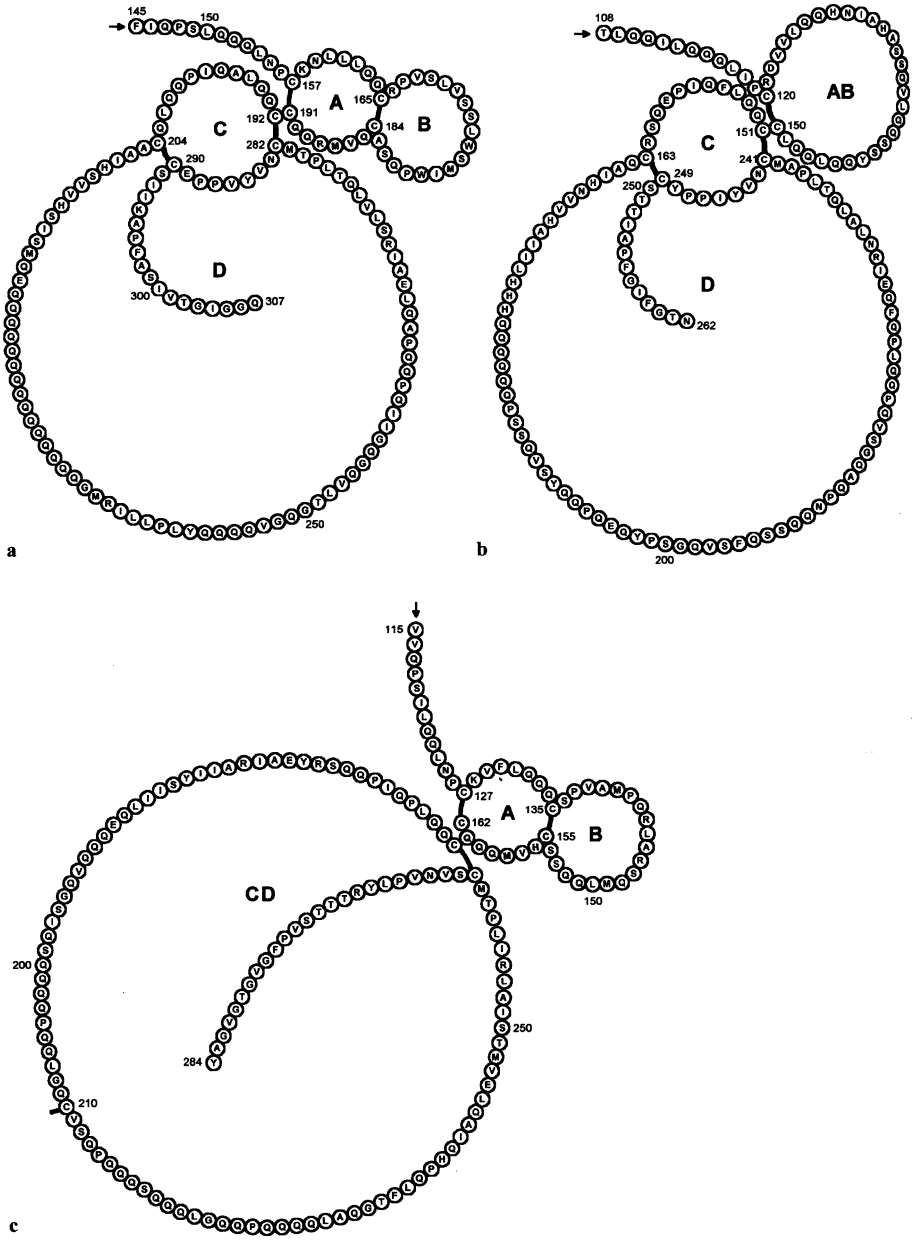


Fig. 15.11. Schematic two-dimensional structures of the C-terminal segments of γ-gliadin **(a)**, α-gliadin **(b)** and LMW subunits **(c)** (according to *Müller* and *Wieser*, 1997)

"lubricant" for aggregated glutenins and made responsible for the viscosity of dough and gluten. Accordingly, it is not the absolute amount of gliadins that is correlated with the rheological properties of dough and gluten, but their quantitative ratio to the glutenins (Fig. 15.14). The homologous arrangement of the intramolecular disulfide bonds of α- and γ-gliadins is reflected in their similar contributions to the rheological properties of dough and gluten.

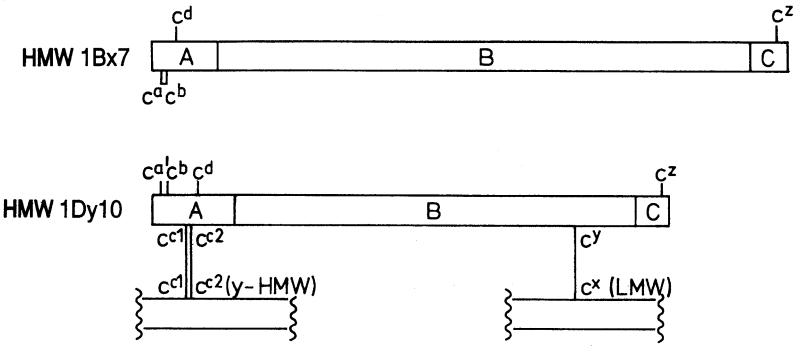


Fig. 15.12. Schematic representation of the disulfide structures of HMW subunits of the x-type and y-type (according to *Köhler* et al., 1993). Segments A–C (cf. Table 15.17). Nomenclature of the cysteine residues as in Fig. 15.10.

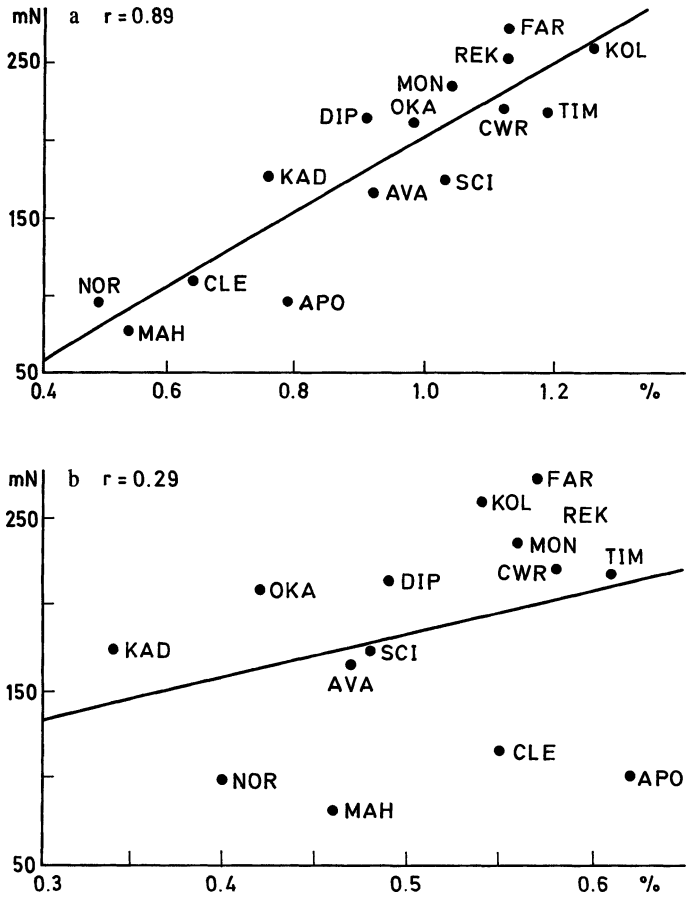


Fig. 15.13. Correlation between the maximal resistance to stretching of dough from various wheat cultivars in a micro-scale extension test and the concentration of HMW subunits (% based on flour) of x- **(a)** and y-type **(b)**. (According to *Wieser* et al., 1992)

In summary, in the dough preparation and gluten formation phase, the competing processes of chain formation and termination are substantial factors for the properties of dough and significantly depend on the type of disulfide bonds. For high dough and gluten strength, a sufficient

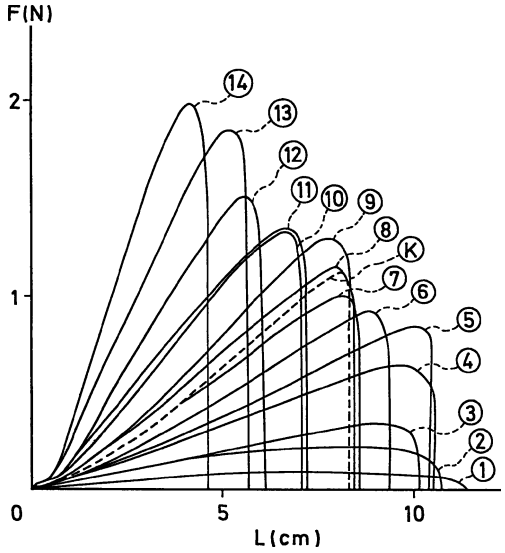


Fig. 15.14. Tensile tests of glutens with varying content of gliadin (gluten K from retail wheat flour was extracted with 70% aqueous ethanol. The extracted gliadin and the remaining glutenin were freeze dried, remixed in different proportions, and then hydrated. Gliadin content of the glutens: K) 33.9%, 1) 55.9%, 14) 22.6%; the gliadin contents of the other samples are in between, according to *Kim* et al., 1988)

amount of polymerizable gluten proteins (HMW subunits of the x-type, LMW subunits) is required with the lowest possible amounts of terminators (low molecular thiol compounds, gliadins with an odd number of cysteine residues, possibly also HMW subunits of the y-type).

15.2.1.5 Puroindolins

The wheat endosperm contains two basic, cysteine-rich proteins, puroindolin a and b (PIN-a and -b). The name is derived from the presence of tryprophan-rich segments in the amino aicd sequences: Trp-Arg-Trp-Trp-Lys-Trp-Trp-Lys in PIN-a and Trp-Pro-Thr-Trp-Trp-Lys in PIN-b. PIN-a consists of a peptide chain with 115 residues (M_r 12,479) and five disulfide bridges. The peptide chains of PIN-a and PIN-b are homologous to an extent of 60%. It has been shown that the puroindolins are identical to the basic friabilins which have been discovered on the surface of starch granules. PIN-a and -b are positively charged and bind negatively charged phospholipids with a high affinity. PIN-a also forms stable complexes with glycolipids while PIN-b is less suitable. It is assumed that the indolyl residues of the tryptophan-rich segments are involved in the stabilization of the complexes, hydrogen bridges being formed between the indole-NH and the OH-groups of the glycolipids. Thus, the higher stability of PIN-a compared with PIN-b complexes is based on the longer tryprophan-rich segment.

Foams of PIN-a and, to a smaller extent, of PIN-b are stabilized especially in the presence of polar wheat lipids. In this respect, PIN-a is clearly superior to egg white proteins as shown by the following comparison. After a drip off time of 5 min, a foam density of 0.028 was obtained with 0.3 mg of PIN-a/ml, while 1.25 mg/ml of egg white proteins were required for this purpose.

For the baking process, it is expected that the puroindolins protect the foam-like texture of the dough from destabilization by lipids.

15.2.2 Enzymes

Of the enzymes present in cereal kernels, those which play a role in processing or are involved in the reactions which are decisive for the quality of a cereal product will be described.

15.2.2.1 Amylases

α- and β-amylases (for their reactions, see 4.4.5.1) are present in all cereals. Wheat and rye amylases are of particular interest; their optimum activities are desirable in dough making in the presence of yeast (cf. 15.4.1.4.8). In mature kernels, α-amylase activity is minimal, while it increases abruptly during sprouting or germination. Unlike the situation with wheat, dormancy in rye is not very pronounced. Unfavorable harvest conditions (high moisture and temperature) favor premature germination ("*sprouting*"), not visible externally. During this time, α-amylase activity rises, resulting in extensive starch degradation during the baking process. Bread faults appear, as mentioned under 15.4.1.2.

Table 15.19. Amylases in wheat

Properties	α-Amylase I	α-Amylase II	β-Amylase
pH optimum	3.6–5.75	5.5–5.7	5.4–6.2
Molar mass	37,000[a]	21,000[a]	64,200[b]
Isoelectric point	4.65–5.11	6.05–6.20	4.1–4.9

[a] gel chromatography, [b] ultracentrifugation.

Two α-amylases, α-AI and α-AII, have been isolated from wheat by affinity chromatography and chromatofocussing. These two enzymes produce a series of multiple forms on SDS-PAGE electrophoresis. The ratio of the concentrations of the two α-amylases depends on the stage of development. After flowering, α-AI appears first in the outer layers of the kernel, then decreases with increasing ripeness. Low activities of α-AII are detectable even before dormancy, but they greatly increase during germination. The two α-amylases differ in their pH optimum, molar mass, and isoelectric point (Table 15.19). α-AII is more temperature resistant.

The pH optimum of α-amylase in germinating rye lies in a range similar to that of α-AII of wheat. Therefore, α-amylase is partially inhibited by the decrease in pH in sour dough (cf. 15.4.2.2).

The properties of wheat β-amylase are shown in Table 15.19.

15.2.2.2 Proteinases

Acid endopeptidases with pH optima of 4–5 occur in wheat, rye and barley. Their substrate specificity has been determined. The possibility that the wheat proteinases are involved in cleavage of gluten bonds, thereby affecting softening or mellowing of gluten during baking, is still disputed.

15.2.2.3 Lipases

These enzymes occur in various concentrations in all cereals. Carboxylester hydrolase, readily isolated from wheat germ, is not considered a lipase but an esterase (cf. 3.7.1.1). The activity in dormant seeds is low, but increases greatly on germination and can be detected with great sensitivity with a fluorochrome substrate, e. g., fluorescein dibutyrate. Therefore, this forms the basis of a method for the quick detection of "sprouting" in wheat and rye.

In addition to the esterase, a wheat lipase occurs enriched in the bran. A rise in free fatty acids observable during flour storage also involves lipases from metabolism of microorganisms present in flour.

In comparison to other cereals, oats contain a significant level of lipase. Its high activity is released once the oat kernel is disintegrated, crushed or squeezed. Linoleic acid is released from the acyl lipids that are present. It is then converted into hydroxy fatty acids by lipoxygenase and hydroperoxidase enzymes, giving rise to off-flavors (Fig. 15.11). All these enzymes are inactivated by heat treatment and thus quality deterioration can be avoided (cf. 15.3.2.2.2).

It should be taken into account in lipid extraction that the phospholipase D activities are relatively high in ripe cereals and this enzyme transfers the phosphatidyl residue of phospholipids to alcohols, which are used to extract lipids (cf. 3.7.1.2.1). The enzyme is inactivated during extraction with boiling water-saturated butanol. A phospholipase that hydrolyzes both acyl residues in the lecithin molecule ("phospholipase B") has been found in germinating cereal. It influences the foam stability in beer (cf. 20.1.7.9).

In the production and storage of egg dough products, phopholipases B and D can lower the phospholipid content.

15.2.2.4 Phytase

Cereals contain about 1% of phytate [myoinositol (1,2,3,4,5,6) hexakisphosphate], which binds about 70% of the phosphorus in the grain. Since it occurs mainly in the aleurone layer, the content of phytate in flour depends on the extent of grinding (Table 15.20). A part of it is hydrolyzed in stages to myo-inositol during dough making.

The phytases originate in cereals (Table 15.21), but are also synthesized by microorganisms, e. g., yeast. Therefore, if the baking process

Table 15.20. Phytate content in wheat flour

Degree of grinding	Phytate (mg/kg)[a]
70%	53
85%	451
92%	759

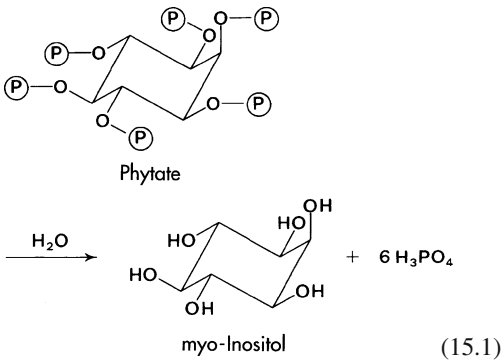
[a] Based on solids.

Table 15.21. Phytase activity and phytate content in cereals

Type of cereal	Phytase activity[a]	Phytate content[b]
Wheat	180	12.4
Triticale	650	12.9
Rye	2800	11.8
Barley	350	11.9
Oats	48	11.3
Corn	9	9.2

[a] Activity: units/g cereal.
[b] Content: mg/g cereal.

takes 1 hour, 85–90% of the phytate is degraded in white bread made of flour with 1.2 g of phytate/kg. In rye whole grain bread (10 g of phytate/kg), 25–35% is degraded and 40–50% if the baking process is extended to 4 hours.



(15.1)

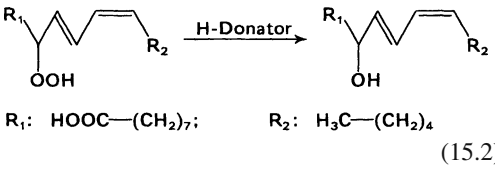
Partial hydolysis of phytate to myo-inositoltetrakis- and -triphosphate is desirable from a nutritional physiological point of view. In comparison with phytate, these less phosphorylated myo-inositols do not form such stable complexes with cations. Consequently, the absorption of zinc, iron, calcium and magnesium ions is not impeded. On the other hand, they still possess the positive nutritive properties of phytate.

15.2.2.5 Lipoxygenases

Cereals contain lipoxygenases (cf. 3.7.2.2) which, with the exception of the enzyme from rye, oxidize linoleic acid preferentially to 9-hydroperoxy acids. The rye lipoxygenase forms mainly the 13-hydroperoxide isomer. Though the enzyme from wheat belongs to the specifically reacting LOX (cf. Table 3.33) and thus cooxidizes carotenoids at a slow rate, it can still bring about a loss of yellow color in pasta products. This is the reason for the inactivation of wheat lipoxygenase during the preparation of pasta products (cf. 15.5).

The involvement of endogenous lipoxygenase in the baking of wheat flour is not clear. However, by addition of lipoxygenase-active soy flour, a significant improvement of the flour quality is achieved (cf. 15.4.1.4.3).

As shown in Fig. 15.11, oats contain a lipoxygenase with lipoperoxidase activity. This activity reduces the hydroperoxides initially formed, in the presence of phenolic compounds as H-donors, to the corresponding hydroxy acids:



(15.2)

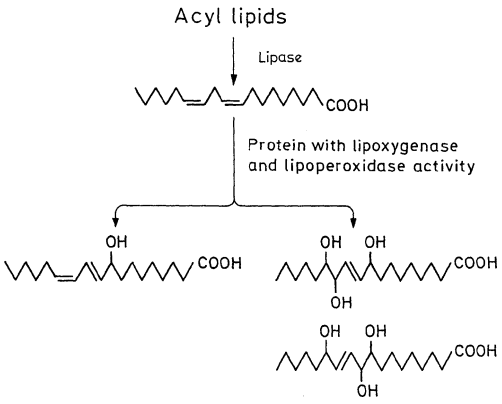


Fig. 15.15. Formation of bitter tasting compounds in oats (taste threshold values cf. 3.7.2.4.1)

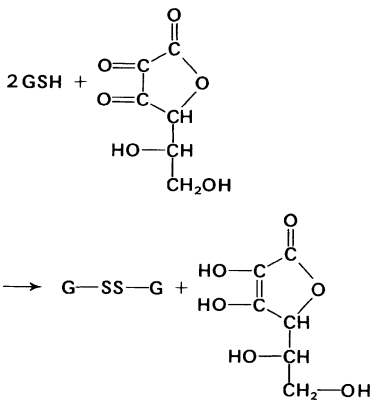
15.2.2.6 Peroxidase, Catalase

Both enzymes are widely distributed among cereals. The pH-activity curves of the enzymes from wheat show that at the normal pH values of a dough, about 6.3, catalase still has 40–50% and peroxidase less than 10% of its activity at the pH optimum (peroxidase pH 4.5; catalase pH 7.5). Therefore, it is unlikely that the oxidative cross-linkage of pentosans (Fig. 15.19), which is catalyzed by peroxidase, plays an essential role in dough.

As heme catalysts they accelerate the nonenzymatic oxidation of ascorbic acid to the dehydro form. The involvement of both enzymes in the action of ascorbic acid as an improver will be discussed (cf. 15.4.1.4.1).

15.2.2.7 Glutathione Dehydrogenase

This enzyme catalyzes the oxidation of glutathione (GSH) in the presence of dehydroascorbic acid as an H-acceptor:



(15.3)

It has been purified from wheat flour in which its activity is relatively high (Table 15.22). The enzyme is specific for the H-donor (Table 15.23) because it oxidizes only GSH, and with a much lower velocity also γ-glutamyl cysteine, but neither cysteinyl glycine nor cysteine, which also occur in wheat flour (Table 15.24). The specificity for the H-acceptor is not so pronounced. As shown in Table 15.23, all four diastereomeric forms of dehydroascorbic acid are converted, but with different velocities. The substrate specificity corresponds to the varying activity of the diastereomeric dehydroascorbic acids in flour improvement (cf. 15.4.1.4.1).

Table 15.22. Activity of glutathione dehydrogenase (GSH-DH) in wheat flour

Wheat cultivar	GSH-DH[a]
Kranich	17.3
Kolibri	13.2
Benno	15.4
Mephisto	16.1
Diplomat	13.2
Jubilar	16.1
Caribo	12.5

[a] Activity at pH 6.5 (25 °C): μmol of L-*threo*-ascorbic acid per minute and g of flour.

15.2.2.8 Polyphenoloxidases

In cereals, polyphenoloxidases preferably occur in the outer layers of the kernels. Wheat enzymes that exhibited cresol activity only (cf. 2.3.3.2) and were known as tyrosinases have been separated from polyphenoloxidases by chromatography and preparative gel electrophoresis.

Polyphenoloxidases can cause browning in whole-meal flours.

15.2.2.9 Ascorbic Acid Oxidase

An ascorbic acid oxidase (AO) occurs in wheat flour (Table 15.25), which oxidizes L-*threo*- and D-*erythro*-ascorbic acid at comparable rates. In addition, a substance has been found in flour extracts which oxidizes L-*threo*-ascorbic acid at pH 10 at a maximal rate. In comparison with AO, this activity does not decrease on incubation with proteases nor is it inhibited by the addition of the AO inhibitors KCN and NaF. It obviously catalyzes a nonenzymatic oxidation of ascorbic acid.

15.2.2.10 Arabinoxylan Hydrolases

In aqueous extracts of wheat flour, arabinoxylan hydrolases have been detected with the synthetic

Table 15.23. Substrate specificity of glutathione dehydrogenase (GSH-DH) from wheat

Substrate	Relative activity (%)	Kinetic constants	
		V_M (nkat/ml)	K_M(mmol/l)
H-Donor			
Glutathione (GSH)	100	362[a]	1.8
Cysteine	0	0	n.a.
Cysteinyl glycine (Cys-Gly)	0	1.3[b]	n.a.
γ-Glutamyl cysteine (Glu-Cys)	n.a.	37[a]	5.5
H-Acceptor[c]			
Dehydroascorbic acid (DHAsc)[d]			
L-*threo*	100	275[e]	0.14
L-*erythro*	67	n.a.	n.a.
D-*erythro*	60	305	1.2
D-*threo*	16	n.a.	n.a.

[a] Concentration of L-*threo*-DHA: 0.5 mol/l.
[b] Reaction system: L-*threo*-DHA 0.5 mmol/l, Cys-Gly 34 mmol/l.
[c] Reaction system: H-acceptor 0.29 mmol/l, GSH 0.5 mmol/l.
[d] Structures of the corresponding ascorbic acid diastereomers, cf. 15.4.1.4.1.
[e] Concentration of GSH: 3 mmol/l.
n.a.: not analyzed.

Table 15.24. Occurrence of low-molecular thiols in wheat flour[a]

Thiol	Concentration (nmol/g flour)
Glutathione (GSH)	100
Glu-Cys	17
Cys-Gly	5
Cysteine	13

[a] Origin: DNS (ash 0.78%).

Table 15.25. Activity of ascorbic acid oxidase (AO) in wheat flour

Wheat cultivar	AO[a]
Domino	60
Otane	40
Norseman	39
Amethyst	30
Sapphire	21
Brock	18

[a] Activity at pH 6.2 (25 °C): nmol L-*threo*-ascorbic acid per minute and g of flour.

substrates p-nitrophenyl-β-D-xylopyranoside and p-nitrophenyl-α-L-arabinofuranoside. A water soluble arabinoxylan gave arabinose and xylose on incubation as the main products and xylobiose and xylotetraose as the side products. The results show that low activities of arabinofuranosidase, xylosidase and endo-xylanase are found in wheat flour.

15.2.3 Other Nitrogen Compounds

Wheat contains glutathione and cysteine in the free state as thiol compounds (GSH, CSH), in the oxidized forms (GSSG, CSSC) and in the protein-bound forms (GSSP and CSSP) (Table 15.26). Reduction of GSSP and CSSP releases GSH and CSH respectively, e. g., with dithioerythritol.
It has been shown that glutathione is predominantly localized in the germ and in the aleurone layer. Therefore its concentration in flour increases as the extraction grade increases (Table 15.27).
During dough making, GSH reacts very quickly undergoing disulfide interchange with the flour proteins PSSP:

$$GSH + PSSP \rightleftharpoons PSSG + PSH \qquad (15.4)$$

If high-molecular gluten proteins are cleaved, the viscosity of the dough drops. Rheological meas-

Table 15.26. Reduced (GSH), oxidized (GSSG) and protein-bound glutathione (PSSG), total glutathione (GSS) as well as cysteine (CSH) and CSS[a]

Wheat cultivar	Ash (wt. %)	Concentration (nmol/g flour)					
		GSH	GSSG	PSSG	GSS	CSH	CSS
DNS	0.78	100	n.a.	n.a.	279	13	159
Maris Huntsman	0.68	81	n.a.	n.a.	232	9	145
Kanzler	0.62	35	n.a.	n.a.	180	8	118
Fresco[b]	n.a.	31	24	131	210	n.a.	n.a.
Norman[b]	n.a.	74	15	73	177	n.a.	n.a.
Mercia[b]	n.a.	74	27	102	230	n.a.	n.a.
Haven[b]	n.a.	18	20	89	147	n.a.	n.a.

[a] CSS consists of free cysteine, cystine and cysteine, which is linked with wheat proteins only via disulfide bridges but not via peptide bonds.
[b] Degree of grinding 64–68%.
n.a.: not analyzed.

Table 15.27. Glutathione concentration as a function of the degree of grinding

Wheat cultivar	Ash (w/w%)	Glutathione[a]	
		GSH	Total[b]
CWRS[c]	0.54	16	172
	0.71	35	348
	1.44	60	575
DNS[c]	0.59	41	175
	0.78	110	345
	1.57	215	657
Maris	0.55	20	185
Huntsman	0.68	94	273
	1.73	210	435

[a] Calculated as GSH in nmol/g based on the dry weight.
[b] Sum of GSH, GSSG, and GSSP.
[c] Marks of origin: Canadian Western Red Spring (CWRS), Dark Northern Spring (DNS).

urements of flour/water dough show the effect of GSH (Fig. 15.16). At 124 nmol/g, the concentration of GSH in the sample of flour is relatively high. The strength of the dough decreases with the addition of 100 nmol/g GSH. GSSG is also active but not as much as GSH (Fig. 15.16) because it first has to be reduced to GSH, e. g., by proteins with free SH groups (PSH, cf. Formula 15.5), before it can depolymerize aggregated gluten proteins as shown in Formula 15.4.

$$\mathrm{GSSG} + \mathrm{PSH} \rightleftharpoons \mathrm{GSSP} + \mathrm{GSH} \qquad (15.5)$$

Cysteine is also rheologically active and cystine after disulfide exchange, e. g., with PSH. To identify the disulfide bonds in gluten proteins, which are cleaved by endogenous GSH by disulfide exchange, flour was kneaded with added [^{35}S]-GSH. The use of high specific radioactivity allowed the additive to be kept very low in comparison to the GSH present in flour. The disulfide bonds labelled by [^{35}S]-GSH are cleaved by the endogenous GSH according to the reaction given

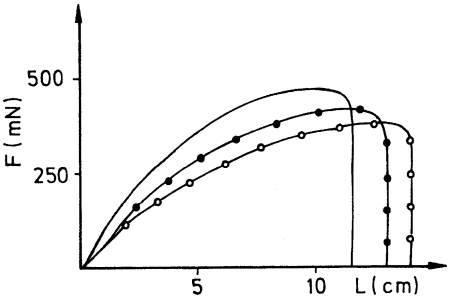


Fig. 15.16. Influence of reduced (GSH) and oxidized glutathione (GSSG) on the rheological properties of wheat dough (according to *Hahn* and *Grosch*, 1998). Tensile tests with dough made of 10 g of DNS flour (0.76% ash, 15.5% protein, 124 nmol/g GSH), water, 2% NaCl and the following additives (nnol/l flour): GSH (100; ○–○), GSSG (50; ●–●), control without additive (—). F: force, L: distance

in Formula 15.4. It was found that GSH reacts very specifically in dough making because the intermolecular disulfide bridges involving C^{b*} and C^{x} in LMW (Fig. 15.10) are reduced to an extent of 47% in each case. Intramolecular disulfide bonds are hardly attacked. Since only one cleavage of intermolecular disulfide bonds can weaken the gluten and the dough, the strong rheological effect of GSH is understandable. The specificity of GSH is very remarkable since per g of flour, 50–100 nmol of GSH are faced with about 9000 nmol/g PSSP, which contain intermolecular disulfide bonds only to an extent of 10%.

15.2.4 Carbohydrates

15.2.4.1 Starch

The major carbohydrate storage form of cereals, starch (cf. Table 15.6) occurs only in the endosperm cells. The size and form of the starch granules are specific for different cereals. The polysaccharide molecules in starch granules are radially organized. Due to the presence of alternating amorphous (mainly amylose) and semicrystalline layers (amylopectin), differences in indices of refraction can be observed under a microscope.

Starch granules swell when heated in water suspension. At the end of swelling, they lose their form; i. e. they gelatinize. The temperature range in which these changes occur and also the extent of swelling at a given temperature are characteristic (cf. 4.4.4.14.1) and may be used for starch source identification. Starch absorbs ca. 45% of water in the baking process.

Cereal starches consist of about 25% amylose and 75% amylopectin (cf. Table 4.20). The chemical structures of these polysaccharides are presented in 4.4.4.14.3 and 4.4.4.14.4. Starch granules in some cultivars, for instance waxy corns, contain only amylopectin, while some cultivars

Table 15.28. Lipids in various cereal starches

	Wheat	Corn[a] (maize)	Amylomaize[a]	Waxy maize[a]
	(% or mg/100 g)[b]			
Nonpolar lipids	6%	60%	73%	88%
Sterol esters	2	3	9	7
Triacylglycerols	15	5	16	12
Diacylglycerols	7	3	16	6
Monoacylglycerols	8	12	13	5
Free fatty acids	27	380	650	105
Glycolipids	5%	1%	5%	6%
Sterol glycosides	3	7	13	3
Monogalactosyldiacylglycerols	4			1
Monogalactosylmonoacylglycerols	10		18	
Digalactosyldiacylglycerols	11			2
Digalactosylmonoglycerols	24		17	3
Phospholipids	89%	39%	22%	6%
Lyso-phosphatidyl ethanolamines	104	17	16	1
Lyso-phosphatidyl glycerols	23	6	7	trace
Lyso-phosphatidyl cholines	783	226	183	8
Lyso-phosphatidyl serines	26	8	6	trace
Lyso-phosphatidyl inositols				
Total lipids	1,047	667	964	153

[a] Amylose content in starch amounts to 23% (corn), 70% (amylomaize) and 5% (waxy maize cultivars).
[b] Results for lipid classes are expressed as % of total lipids present in starch, and for individual lipid compounds as mg/100 g starch dry matter.

are rich in amylose (cf. Table 4.20). Waxy corn starch swells considerably on heating, while granules with amylose swell only slightly (cf. Table 4.20 and Fig. 4.31).
Lipids (Table 15.28) and proteins (about 0.5%) are among the heterogeneous constituents of starch granules. Lipids are enclosed within the amylose helices. In wheat starch, they consist predominantly of lysolecithins (Table 15.28). They are extractable from partially gelatinized starch by using hot water-saturated butanol. During extraction, the lipid in the amylose helix is replaced by butanol.
The lipids complexed within the starch granules retard swelling and increase their gelatinization temperatures; thus they influence the baking behavior of cereals and the properties of the baked products.

15.2.4.2 Polysaccharides Other than Starch

Cereals also contain polysaccharides other than starch. In endosperm cells their content is much less than that of starch (cf. Table 15.29). They include pentosans, cellulose, β-glucans and glucofructans. These polysaccharides are primarily constituents of cell walls, and are more abundant in the outer portions than the inner portions of the kernel. Therefore, their content in flour increases as the degree of fineness increases (cf. rye as an example in Table 15.36).
From a nutritional and physiological viewpoint, soluble and insoluble polysaccharides other than starch and lignin (cf. 18.1.2.5.1) are also called dietary fiber. The most important fiber sources are cereals and legumes, while their content in fruits and vegetables is relatively low.

Table 15.29. Distribution of carbohydrates in wheat (%)

	Endosperm	Germ	Bran
Pentosans and hemicelluloses	2.4	15.3	43.1
Cellulose	0.3	16.8	35.2
Starch	95.8	31.5	14.1
Sugars	1.5	36.4	7.6

15.2.4.2.1 Pentosans

The pentosan content of cereals varies. Rye flour is exceptionally rich (6–8%) in comparison to wheat flour (1.5–2.5%). A portion of pentosans, 25–33% in wheat and 15–25% in rye, is water-soluble.
Unlike the water-soluble proteins of cereals, the soluble pentosans are able to absorb 15–20 times more water and thus can form highly viscous solutions. This soluble fraction consists mainly (ca. 85%) of a linear arabinoxylan and a soluble highly branched arabinogalactan peptide. A chain of D-xylopyranose units is typical of the structure of arabinoxylan (Ws-AX), which is extractable with water. The OH groups in the 2- and 3-position of this chain are glycosidically linked to L-arabinofuranose (e. g. 3-position in Fig. 15.17). The arabinose residues can be cleaved by mild acid hydrolysis or treatment with an α-L-arabinofuranosidase, giving water-insoluble xylan. Although a part of the arabinoxylan is insoluble in water (Wi-AX) as a result of cross-linking of the chains, it can become soluble by means of alkaline or enzymatic hydrolysis. The backbone of the arabinogalactan peptide is made of $\beta(1 \rightarrow 3)$ and $\beta(1 \rightarrow 6)$ linked galactopyranose units. It is α-glycosidically bound and contains, in addition, arabinofuranose residues. The bonding to the peptide is achieved via 4-transhydroxyproline.
The Ws-AX cause up to 25% of the water binding in dough. They increase the viscosity and, consequently, the stability of the gas bubbles. In contrast, the action of Wi-AX is considered to be unfavourable. They form physical barriers against the gluten and destabilize the gas bubbles.

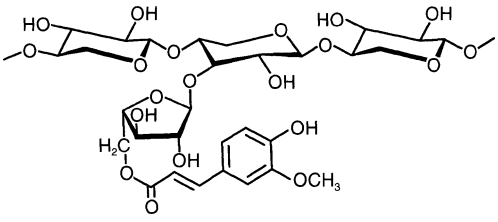


Fig. 15.17. A section of the structure of a water soluble arabinoxylan from wheat. A xylose in the $(1 \rightarrow 4)$-β-xylan section is linked in position 3 with a 5-O-*trans*-feruloyl-α-L-arabinofuranose

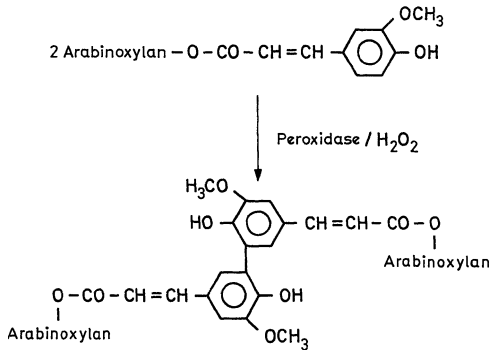


Fig. 15.18. Oxidative crosslinking of cereal pentosans

Accordingly, the baking result is positively influenced by endoxylanases which preferentially hydrolyze Wi-AX. Since inhibitors are present in wheat which inhibit the activity of added endoxylanases, attempts are being made with the help of molecular engineering techniques to produce microbial enzymes which do not react with these inhibitors.

The insoluble portion of pentosans from rye swells extensively in water. This portion is responsible for the rheological properties of dough and the baking behaviour of rye, and increases the crumb juiciness and chewability of baked products. An optimum starch-pentosan ratio is 16:1 (by weight) for rye flour.

Pentosan solutions gel when treated with hydrogen peroxide/peroxidase. This is due to the presence of low levels of ferulic acid (ca. 0.2%). An enzymic phenol oxidation occurs (cf. Fig. 15.18), which causes polymerization. This results in build-up of a network which, along with the low content of branched arabinofuranose, is responsible for the lack of solubility of most pentosans.

15.2.4.2.2 β-Glucan

The β-glucan content of cereals varies: barley 3–7%, oats 3.5–4.9%, wheat and rye kernels only 0.5–2%. These are linear polysaccharides with D-glucopyranose units joined by β-1,3 and β-1,4 linkages. Polysaccharides of the β-glucan type are also called lichenins. At 38 °C, 38–69% of the β-glucans of barley dissolve in 2 hours and 65–90% of the β-glucans of oats. β-Glucans are slimy mucous substances which provide a high viscosity to water solutions. In beer production from barley β-glucans can interfere in wort filtration.

15.2.4.2.3 Glucofructans

Wheat flour contains 1% water-soluble, nonreducing oligosaccharides of molecular weight up to 2 kdal. They consist of D-glucose and D-fructose. Glucofructan, which predominates in durum wheats, probably has the following structure:

$$\begin{array}{l}\text{ß-D-Fru}_f\,(2\rightarrow6)\text{ß-D-Fru}_f\,(2\rightarrow6)\text{ß-D-Fru}_f\,(2\rightarrow1)\alpha\text{-D-Glc}_p \\ \qquad\qquad\qquad\quad 1 \\ \qquad\qquad\qquad\quad \uparrow \\ \qquad\qquad\qquad\quad 2 \\ \qquad\qquad\qquad\quad \text{ß-D-Fru}_f\end{array} \qquad (15.6)$$

15.2.4.2.4 Cellulose

Cellulose is a minor constituent of the carbohydrate fraction obtained from starchy endosperm cells (cf. Table 15.29).

15.2.4.3 Sugars

Mono-, di- and trisaccharides, as well as other low molecular weight degradation products of starch, occur in wheat and other cereals in relatively low concentrations (Table 15.30). When starch degradation occurs during dough making, their levels increase (cf. 15.4.2.5). Mono-, di- and trisaccharides are of importance for dough leavening in the presence of yeast (cf. 15.4.1.6.1).

15.2.5 Lipids

Cereal kernels contain relatively low levels of lipids; nevertheless, differences occur among cer-

Table 15.30. Mono- and oligosaccharides in wheat flour

Compound	(%)
Raffinose	0.05–0.17
Glucodifructose	0.20–0.30
Maltose	0.05–0.10
Saccharose	0.10–0.40
Glucose	0.01–0.09
Fructose	0.02–0.08
Oligosaccharides[a]	1.2–1.3

[a] Fraction soluble in 80% ethanol.

eals (cf. Table 15.6). The endosperm cells of oats contain a higher level of lipids (6–8%) than wheat (1.6%). For this reason, the overall lipid content of oats is higher than in wheat and in other cereals.

The lipids are preferentially stored in the germ which, in the case of corn and wheat, serves as a source for oil production (cf. 14.3.2.2.4). Lipids are stored to a smaller extent in the aleurone layer. Cereal lipids do not differ significantly in their fatty acid composition (Table 15.31). Linoleic acid always predominates. Close attention has been given to wheat lipids since they greatly influence baking quality and they have therefore been studied thoroughly.

A wheat kernel weighs 30–42 mg and contains 0.92–1.24 µg of lipid. The germ and the aleurone cells are rich in triglycerides, which are present as spherosomes, while phospholipids and glycolipids predominate in the endosperm.

Wheat flour contains 1.5–2.5% lipids, depending on milling extraction rate. Part of this lipid is nonstarch lipid. This portion is extracted with a polar solvent, water-saturated butanol, at room temperature. Nonstarch lipid comprises about 75% of the total lipid of flour (Fig. 15.19). The residual lipids (25%) are bound to starch (cf. 15.2.4.1).

Nonstarch- and starch-bound lipids in wheat differ in their composition (cf. Table 15.28 and Table 15.32). In nonstarch-bound lipids the major constituents are the triacylglycerides and digalactosyl diacylglycerides, while in starch-bound lipids, the major constituents are lysophosphatides in which the acyl residue is located primarily in position 1. A decrease in amylose content is accompanied by a decrease in the lipid content (Table 15.28). The ratios of nonstarch-bound lipid classes are dependent on the flour extraction grade. An increase in extraction grade increases the triacylglyceride content, since more of the germ is transferred into the flour.

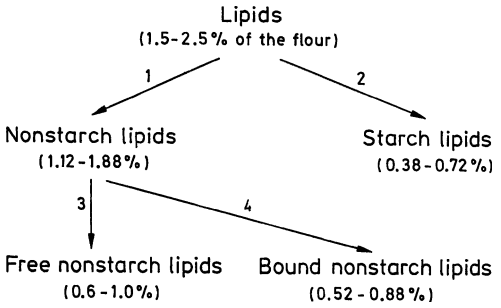


Fig. 15.19. Differentiation of wheat flour lipids by their solubility. *1* Flour extraction with water-saturated butanol (WSB) at room temperature, *2* with WSB at 90–100 °C, *3* with petroleum-ether, and subsequently, *4* with WSB

The rheological dough properties are affected by nonstarch-bound lipids which are separated into free and bound lipids when extracted with solvents of different polarity. The free lipid fraction contains 90% of the total nonpolar lipids and 20% of the total polar lipids listed in Table 15.32. By kneading the flour into dough, the glycolipids become completely bound to gluten, while other lipids are only 70–80% bound. The extent of binding of triacylglycerides depends on dough handling. Intensive oxygen aeration and, particularly, addition of lipoxygenase (cf. 15.4.1.4.3) increase the fraction of free lipids.

The increased binding of lipids in the transition of flour to dough, which is expressed in their decreasing extractability, is explained by the following hypothesis.

Table 15.31. Average fatty acid composition of acyl lipids of cereals (weight-%)

	14:0	16:0	16:1	18:0	18:1	18:2	18:3
Wheat		20	1.5	1.5	14	55	4
Rye		18	<3	1	25	46	4
Corn		17.7		1.2	29.9	50.0	1.2
Oats	0.6	18.9		1.6	36.4	40.5	1.9
Barley	2	22	<1	<2	11	57	5
Millet		14.3	1.0	2.1	31.0	49.0	2.7
Rice	1	<28	6	2	35	39	3

Table 15.32. Nonstarch lipids in wheat flour

	mg/100g[a]
Nonpolar lipids (59%)	
Sterol lipids	43
Triacylglycerols (TG)	909
Diacylglycerols (DG)	67
Monoacylglycerols (MG)	53
Free fatty acids (FFA)	64
Glycolipids (26%)	
Sterol glycosides	18
Monogalactosyldiacylglycerols (MGDG)	115
Monogalactosylmonoacylglycerols (MGMG)	17
Digalactosyldiacylglycerols (DGDG)	322
Digalactosylmonoacylglycerols (DGMG)	52
[3pt] *Phospholipids* (15%)	
N-Acyl-phosphatidyl ethanolamines	95
N-Acyl-lyso-phosphatidyl ethanolamines	33
Phosphatidyl ethanolamines	
Phosphatidyl glycerols	19
Phosphatidyl cholines	96
Phosphatidyl serines	
Phosphatidyl inositols	9
Lyso-phosphatidyl glycerols	5
Lyso-phosphatidyl cholines	29

[a] Based on dry matter.

The neutral lipids are present in flour in the form of spherosomes and their membranes are formed by a part of the phospholipids. The spherosomes can be extracted with nonpolar solvents. The other phospholipids and all the glycolipids form inverse hexagonal phases (cf. 8.15.2.2), which are only partly extractable. During dough making, the water added results in the conversion of the inverse hexagonal to a laminar phase, which in turn stabilizes a microemulsion of the neutral lipids. The microemulsion vesicles are enclosed by the network of gluten proteins and, consequently, difficult to extract. If the dough is suspended in water, the lipids appear in the aqueous phase that separates on ultracentrifugation only when the framework of gluten proteins has been destroyed by reduction, e. g., with dithiothreitol.

Other hypotheses which explain the decreasing extractability of free lipids by selective binding, e. g., of glycolipids to starch and gluten, have not been confirmed.

The gas-holding capacity of doughs and, after passing through a minimum, the baking volume (Fig. 15.20) are positively influenced by polar lipids. Two effects are assumed in explanation. The polar lipids get concentrated in the boundary layer gas/liquid and stabilize the gas bubbles against coalescence. In addition, the lipid vesicles seal the pores which are formed in the protein films on kneading. On the other hand, the nonpolar lipids generally negatively influence the backing result with most varieties of wheat (Fig. 15.20).

Carotenoids and tocopherols belong to the minor components of the cereal lipid fraction. Wheat flour has a carotenoid content averaging 5.7 mg/kg. In durum wheats, which have a more intense yellow color, the carotenoids are 7.3 mg/kg of flour.

The major carotenoid, lutein (cf. 3.8.4.1.2), is present in free or esterified form (either mono or diester) with the fatty acids listed in Table 15.31). The following carotenoid pigments are also present: β-carotene, β-*apo*-carotenal, cryptoxanthin, zeaxanthin and antheraxanthin (for structures see 3.8.4.1). Carotenoid content of corn, depending on the cultivar, is 0.6–57.9 mg/kg, with lutein and zeaxanthin being the major constituents.

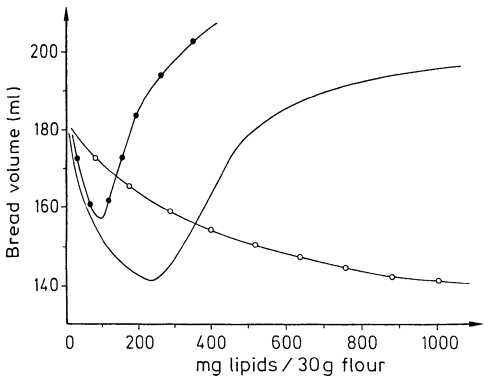


Fig. 15.20. The effect of free nonstarch lipids on the baking quality of defatted wheat flour (according to *Morrison*, 1976). — Lipids (total), —○—○— nonpolar lipids, –●–●– polar lipids

Table 15.33. Tocopherol content of parts of the wheat kernel

Part of kernel	Tocopherols in mg/kg			
	α-T	β-T	α-T-3	β-T-3
Germ	256	114	n.d.	n.d.
Aleurone layer	0.5	n.d.	10	69
Endosperm	0.07	0.10	0.45	13.5

n.d., not detectable.

The composition of the tocopherols of wheat (Table 15.33) shows that the proportions of germ and aleurone lipids in nonstarch lipids can be determined by using β-T and β-T-3 as markers. Values of ca. 25% have been found, but they can fluctuate greatly depending on the milling process and extraction grade.

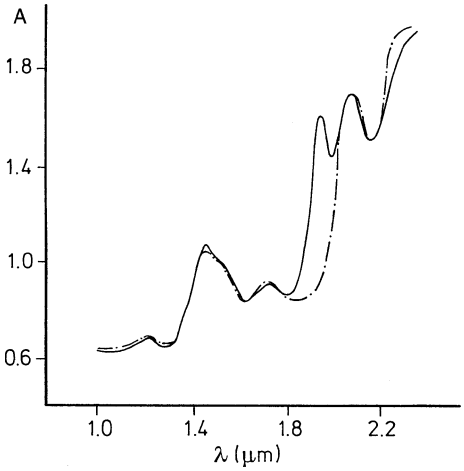


Fig. 15.21. Absorption of ground wheat in the near IR region. Sample dried (–·–·–) and with 9 w/w % water (——)

15.3 Cereals – Milling

15.3.1 Wheat and Rye

Quality control of the raw materials and milling products usually includes the determination of water, protein, and minerals. The absorption bands of food in the near infrared region (0.8–2.6 μm) are suitable for a quick basic analysis (water, protein, fat, carbohydrates etc.).

The overtones of CH, OH, and NH valence vibrations appear in the near IR region. Therefore, foods give a large number of absorption bands that can be assigned to definite components and have intensities that correlate with the amounts of the constituents. As an example, Fig. 15.21 shows the absorption of wheat in the near IR region. The sample containing water absorbs at 1.94 μm in addition. Therefore, after subtraction of the absorption of dried wheat and after calibration, the water content can be determined. Other consituents which can be determined in food by near-infrared (NIR) spectrophotometry are listed in Table 15.34.

In the development of methods for these materials, the measurement of IR reflection was at first given the most attention because it is technically easier to perform. Since reproducible results can be obtained only if the surface and granulation of the samples are constant, sources of error arise here. In the meantime, however, technical improvements allow food, e. g., cereal kernels, to be irradiated in the range of 0.8–1.1 μm. Thus, the water and protein content in unground samples can also be determined by measuring the transmission. In food technology, measurements in the near IR region are widely used for the quick quality control of raw materials (Table 15.34).

Table 15.34. Examples of quantitative analysis of foods by near-infrared (NIR) spectrophotometry

Component	Food
Water	Meat, cereals, control of fruit and vegetable drying processes, chocolate, coffee
Protein	Meat, cereals, milk and milk products
Fat	Meat, cereals, milk and milk products, oil seeds
Minerals	Cereals, meat
Starch	Cereals
Pentosans	Wheat
β-Glucans	Barley
Lysine	Wheat, barley

15.3.1.1 Storage

Cereals can be stored without loss of quality for 2 to 3 years, provided that the kernel moisture content, which is 20–24% after threshing, is reduced to at least 14%. The low moisture content prevents microbial spoilage, especially by mycotoxin-forming organisms, and it also lowers kernel respiration, i. e., metabolism.

The water is slowly removed from grains by ripple-type dryers in a stream of hot air or burned gas at 60–80 °C (to the extent of 4% per passage) to avoid damage to kernels by uncontrolled shrinkage. Grains with high moisture content can be stored for short periods of time in the cold without quality deterioration. Stored grains are fumigated for pest control. Aluminum and magnesium phosphides are introduced. At 20 °C and 75% relative humidity, they decompose into gaseous PH_3. HCN or ethylene oxide fumigants are also used.

Wheat and rye are suitable for the production of bakery products, especially bread, and are called bread cereals. Other cereals serve only as additives for bakery products and are mainly used in other ways, e. g., for porridge and pancakes.

15.3.1.2 Milling

The aim of milling is to obtain preferentially a flour in which the constituents of the endosperm cells predominate. The outer part of the kernel, including the germ and aleurone layer (cf. Fig. 15.2) is removed. Such a requirement is not easy to accomplish since the kernel's groove and the unequal sizes of aleurone cells in cereals do not facilitate simple dehulling. Therefore, the grain has to be carefully broken, the particles sorted and separated by size and, only then, further disintegrated.

In a preliminary step to milling, the grain is cleaned of impurities such as weed seeds, straw, soil particles, spoiled decayed grains, dust, etc. This cleaning step is based on the cereal's kernel size and specific gravity. Washing with water is rarely done, since it promotes the growth of microorganisms.

The next step is grain wetting or steeping in water for 3–24 h, since an increased moisture content to 15–17% facilitates the separation of starchy endosperm cells from germ and hull. An alternative procedure is wheat conditioning at elevated temperatures up to 65 °C; it is faster than steeping and also favorably affects the baking quality. The kernels are disintegrated stepwise. Each passage through rollers involves particle size reduction by pressure and shear forces, followed by flour separation according to particle size using sieves in the form of flat sifters (Fig. 15.22). Rollers are matched to the product needed. Their size, surface flutes, rotation velocity, gap between pairs of rollers rotating in opposite directions at dissimilar speeds – all can be selected or adjusted. Wheat and rye are milled differently because of structural differences in the kernels. The wheat kernel is rather brittle; the rye kernel is gluey or sticky. Therefore, rye is less suitable for coarse grist milling than wheal. The wheat milling process can be adjusted so that the first passages provide the grist and the following ones provide the flour.

The germ of the rye kernel, because of its loose attachment, falls off readily during the cleaning

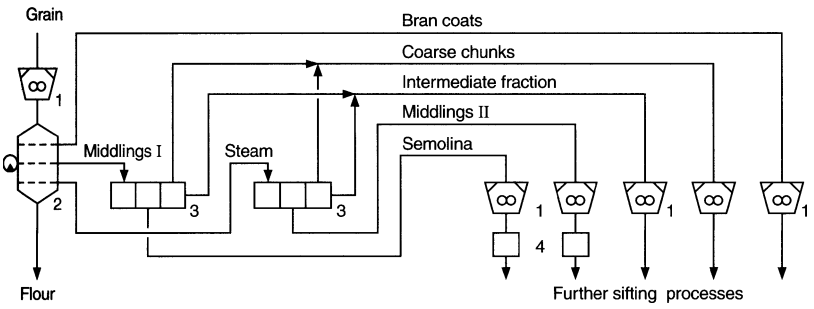


Fig. 15.22. Milling of cereal (*1*: roller mill, *2*: sifters, *3* and *4*: purifiers)

step, while the wheat germ is removed only on sifters. The hull and a substantian part of the aleurone layer is removed in the form of bran.

A portion (ca. 5–8%) of the starch granules is mechanically damaged during milling. The extent depends both on the type and intensity of milling and on the hardness of the kernel. The harder the structure of the kernel, the greater the damage. Since the rate of water absorption during dough making and the enzymatic degradation of starch increase with increasing damage, they are important for the baking process and desirable to a limited extent. To measure starch damage, the amylose extractable with a sodium sulfate solution is determined. Alternatively, the amount of starch degradable without gelatinization, e. g., at 30 °C by a- and/or β-amylase is determined. The starch damage expected during the milling process can also be estimated by determining the hardness of the kernel, e. g., by NIR reflectance spectrophotometry (cf. Table 15.34).

15.3.1.3 Milling Products

A miller distinguishes the end-products of milling on the basis of particle size or diameter, e. g., >500 µm for grist; 200–500 µm for semolina from durum or farina from bread wheats; 120–200 µm for "*dunst*"; and 14–120 µm for flour. The larger flour particles can be felt between the fingers (*graspable flour*), as opposed to smooth or polished flours in which the average particle size is 40–50 µm.

Differently milled flours vary considerably in baking quality. Flours obtained also differ greatly from cultivar to cultivar. This is especially the case with wheat cultivars (cf. 15.4.1.1). In addition, quality depends on whether the milled flour comes from the inner or outer parts of the endosperm. Therefore, milled flour is controlled in the plant for its baking properties and blended or mixed to yield a commercial product based on present market standards (see also below). The characteristics of a few milling products and their applications are listed in Table 15.35.

The chemical composition of the flour depends on the milling extraction rate, e. g., flour weight obtained from 100 parts by weight of grain. Examples are given in Table 15.36. Increasing the rate of flour extraction decreases the pro-

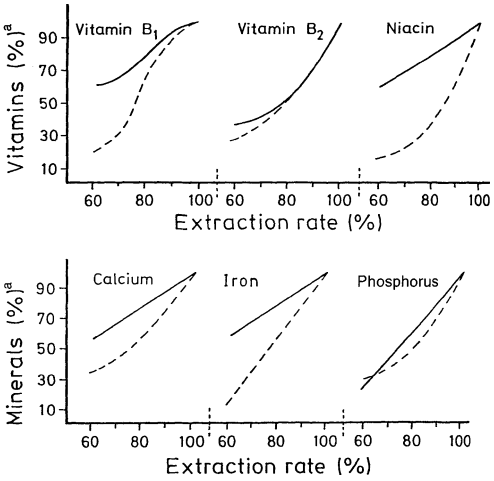


Fig. 15.23. Content of B vitamins and minerals in flour as affected by milling extraction rate (according to Lebensmittellexikon, 1979). —— rye, - - - wheat
[a] Calculated as percent of the total content present in grain.

Table 15.35. Wheat and rye milling products

All purpose flour	Commercially available (retail market) flour for household preparations of baked products.
Special flour	It is used for special baked products, e. g., strong gluten wheat flour for toast bread, wheat flour with weak gluten for baked goods of loose tender or crispy structure as pastry etc.
Compounded (ready to use) flour	Special flour that contains other ingredients such as milk or egg powder, sugar etc., required by formulation of a selected baked product.
Groats (grist)	Coarsely ground dehulled cereal (devoid of germ and seed hull).
Whole grain groats	Ground from whole kernel (including germ).

Table 15.36. Average composition of wheat and rye flours[a]

A. Wheat flour

	Type				
	405	550	812	1050	1700[b]
	Flour extraction rate[c]				
	40–56%	64–71%	76–79%	82–85%	100%
Starch	82.3	81.8	78.1	77.8	69.2
Protein (N × 5.8)	11.7	12.3	13.0	12.9	12.7
Lipids	1.0	1.2	1.5	2.0	2.3
Dietary fiber[d]	4.7	5.0	5.6	6.0	13.4
Minerals (ash)	0.41	0.55	0.81	1.05	1.7

B. Rye flour

	Type				
	815	997	1150	1370	1740
	Flour extraction rate[c]				
	69–72%	75–78%	79–83%	84–87%	90–95%
Starch	74.8	73.5	71.3	71.1	68.6
Protein (N × 5.8)	7.2	8.03	9.6	9.6	11.7
Lipids	n.a.	1.3	1.5	1.7	1.8
Dietary fiber[d]	7.6	10.1	9.3	10.5	16.2
Minerals (ash)	0.82	1.0	1.15	1.37	1.74

[a] Weight-% per dry matter of wheat and rye flours. Flour average moisture content is 13 weight-%.
[b] Whole wheat flour.
[c] Approximate data.
[d] Indigestible carbohydrates (water soluble and insoluble), lignin. n.a.: not analyzed.

portion of starch and increases the amount of kernel-coating constituents such as minerals, vitamins and crude fiber (cf. Tables 15.8 and 15.9). Comparing products of the same extraction rate, rye flour contains higher proportions of both minerals and vitamins than wheat flour (Fig. 15.23). It should be pointed out that in the case of some B-vitamins, such as niacin, this difference is well-balanced by the higher concentrations in wheat in comparison to rye kernels (cf. Table 15.6). Consequently the concentrations of such vitamins are similar in rye and wheat flour.

Bread flours are standardized on the basis of their ash content in Europe and, particularly, Germany. The type of flour = ash content (weight %) × 1000 corresponds to the extraction grade. Examples are provided in Table 15.36 for wheat and rye flours and their chemical composition is detailed. Protein and starch contents are also related to flour particle size (cf. Table 15.37). Because of the variable particle sizes and densities of protein and starch, a flour sample can be separated by air classification into a fraction enriched in protein and starch. These are the so-called special purpose flours.

Table 15.37. Protein content of wheat flours as affected by flour particle size

Particle size (μm)	As portion of flour (weight %)	Protein content (weight %)
0–13	4	19
13–17	8	14
17–22	18	7
22–28	18	5
28–35	9	7
>35	43	11.5

The commercial product semolina ("*griess*") is made from endosperm cells of hard durum wheats. Semolina keeps its integrity during cooking and is used mostly for pasta production. Since semolina is a milled flour of low extraction rate, it contains few minerals and vitamins.

Table 15.38. Vitamin content of raw, white and parboiled rice

	B-vitamins (mg/kg)		
	Thiamine	Riboflavin	Niacin
Raw rice	3.4	0.55	54.1
White rice	0.5	0.19	16.4
Parboiled rice	2.5	0.38	32.2

15.3.2 Other Cereals

15.3.2.1 Corn

Corn endosperm, with the germ removed, is ground to grist for corn porridge (*Polenta*) and into corn flour for flat cakes (*tortillas*). Corn flakes are made from cooked and sweetened corn slurry, by drying, flaking and toasting. Similar products are made from millet, rice and oats.

15.3.2.2 Hull Cereals

Dehulling of rice, oats and barley requires special processes (cf. 15.1.4).

15.3.2.2.1 Rice

Rice milling involves the following processing steps: rough rice (paddy rice) → hull removal → brown rice → polishing to remove the bran coats (fruit and seed coats), the silvery cuticle, the germ and the aleurone layer → rubbing-off or rice polishing to obtain the end-product, white rice. Undamaged rice (45–55%), broken kernels or flour (20–35%) and a husk/hull fraction (20–24%) are obtained.

Polished white rice is made from this cleaned rice by additional treatment of the kernels with talc (a magnesium silicate) and 50% glucose solution. This imparts a glossy, transparent coating to the kernels.

White rice, in comparison to rough or brown rice, is low in vitamin content (cf. Table 15.38) and in minerals. A nutritionally improved product may be obtained by a parboiling process, orginally developed to facilitate seed coat removal. About 25% of the world's rice harvest is treated by the following process: raw rice → steeping in hot water, steaming in autoclaves, followed by drying and polishing → parboiled rice.

This treatment causes the following changes: the starch gelatinizes, but partly retrogrades again during drying. Enzymes are inactivated by the heat, causing inhibition of the enzymatic hydrolysis of lipids during storage of rice. The oil droplets (cf. 3.3.1.5) are broken and lipids partly migrate from the endosperm to the outer layers of the rice kernels. Since antioxidants are simultaneously destroyed, parboiled rice is more susceptible to lipid peroxidation. In contrast, minerals and vitamins diffuse from the outer layers to the inner endosperm and remain there after the separation of the aleurone layer (Table 15.38). The changes in starch mentioned above result in reduced cooking time.

Unlike in Europe and USA, some rice varieties popular in Asia develop a popcorn-like aroma on cooking. This is due to the formation of 2-acetyl-1-pyrroline, which is present in concentrations of 550–750 µg/kg in aromatic varieties of rice (cooked) and <8 µg/kg in lowaroma varieties.

15.3.2.2.2 Oats

Oat flakes are produced by the following processing steps: the kernels (12–16% water content) are steamed and then the moisture content is decreased to 7–10% in 2–3 h by heating at 90–100 °C. The hull (fruit and seed coats) is removed, i. e., the kernel is polished. This is followed by repeated steaming, squeezing between drum rollers, and drying of the moist flakes till the water content is 10–11%. The yield is 55–65%. This hydrothermic process also inactivates the oat enzymes involved in offflavor development. (E,E,Z)-2,4,6-Nonadienal produces the cereal-like, sweet aroma of oat flakes. It has

an extremely low odor threshold and is formed from linolenic acid.

15.3.2.2.3 Barley

Removal of hull (fruit and seed coatings) yields groats which, after grinding, provide marketable products of large or fine particle size.

15.4 Baked Products

Baked products (for a review, see Table 15.39) are made from milled wheat, rye and, to a lesser extent, other cereals by the addition of water, salt, a leavening agent and other ingredients (shortening, milk, sugar, eggs, etc.). The following operations are involved:

- Selection and preparation of the raw materials
- Dough making and handling
- Baking
- Measures for quality preservation

15.4.1 Raw Materials

Among the ingredients involved in a formulation, only flour and those additives which affect dough rheological and/or baking properties will be covered. Flour improvers and dough leavening agents will be emphasized.

Characterization of the raw materials and additives is, in practice, made by assessing the dough rheological properties and by baking tests. Basic research endeavors to understand the nature of flour constituents and the reactions which affect their behavior in dough handling and baking.

Table 15.39. Classification of baked products

Bread including small baked products (rolls, buns)	Made entirely or mostly from cereal flours; moisture content on average 15%. Addition of sugar, milk and/or shortenings amounts to less than 10%. Small baked products differ from bread only by their size, form and weight.
Fine baked goods, including long term or extended shelf life products such as biscuits, crackers, cookies etc.	Made of cereal flours with at least 10% shortening and/or sugar, as well as other added ingredients. In baked goods for long shelf life the moisture content is greatly reduced.

15.4.1.1 Wheat Flour

A flour of optimal baking properties is required and chosen to match the quality of the desired product (cf. Table 15.35). The baking quality of wheat is strongly influenced by the cultivar (cf. Table 15.41) and also by conditions of growth and cultivation (climate, location), and subsequently by flour storage conditions and duration. Prior quality control is of importance to assess the overall baking quality of wheat flour. Flour particle size and color are assessed by sensory analysis. Graspable flours (cf. 15.3.1.3) are made from hard gluten-rich cultivars. Water uptake is slow when compared to smooth flour, and they make dry doughs.

The color difference is important, and is assessed with a wetted flour sample on a black background (*Pekar*-test).

15.4.1.1.1 Chemical Assays

Flour *acidity* (ml of 0.1 mol/l NaOH/10 g, titrated in the presence of phenolphthalein) depends upon the extraction rate of the flour and ranges between 2.0 ml/g (flour type 450) and 5.5 ml/g (flour type 1800). Too low acidity often reflects poorly aged flour. Acidity above 7.0 suggests microbial spoilage.

The *gluten content*, which is the residue left after the dough is washed (10 g flour kneaded into a dough with 6 ml of 2% NaCl, then washed with tap water), provides an indication of flour quality. A very low gluten content (<20%) frequently results in dough deterioration when machine-handled and also in baking faults. A higher content of gluten will not guarantee good baking quality (see "Maris Huntsman"

Table 15.40. Concentration of SH- and SS-groups in flour of different wheat cultivars

Cultivar	SH	SS	SS/SH
	µmole	per g	flour
Kolibri	1.15	12.5	10.9
Caribo topfit	0.88	12.2	13.9
Strong Canadian wheats	0.95	13.4	14.1
Inland wheat I[a]	0.75	10.2	13.6
Inland II[a]	1.05	12.6	12.0
Canadian Western Red Spring Wheat (CWRS)	1.26	12.9	10.2

[a] Marketed flour blendings.

cultivar, Table 15.41). Gluten swelling power is assessed by a *sedimentation value* as recommended by *Zeleny.* In this test, flour is suspended in an aliquot of a mixture of lactic acid (3.8 g), isopropanol (200 ml) and water (800 ml). The higher the volume of the sedimented gluten and starch, the better should be the baking quality of the flour.

For a given wheat cultivar, grown under similar climatic and soil conditions, the baking volume correlates with the *protein content* of the flour (Fig. 15.24). A similar linear relationship is not readily attainable for flours from different cultivars, as evidenced by the very different slopes of the regression lines.

The parameters involved here are those described in Section 15.2.1.4 as responsible for the properties of gluten. These include type, amount, and degree of polymerization of the HMW and LMW subunits of glutenin as well as the ratio gliadin/glutenin.

On the whole, the structure of wheat gluten has been so far evaluated to be able to describe variety-specific differences in the technological properties.

Wheat cultivars differ in the content of their *thiol* and *disulfide groups* (Table 15.40). This implies that the stability of a dough may be strongly influenced by a SH/SS exchange between a low molecular weight SH-peptide and gluten proteins. This also implies that a positive correlation

Table 15.41. Baking quality data of some wheat flours

	Wheat cultivar[a]		
	Monopol	Nimbus	Maris Huntsman
Protein (% dry matter)[b]	13.2	11.6	11.8
Wet gluten (%)	35.1	24.7	34.3
Farinogram[c]			
Water absorption (%)	59.2	54.8	59.8
Dough development time (min)	5.0	1.0	2.0
Dough stability (min)	5.0	1.5	0.5
Mixing Tolerance Index[d] (FU)	30	80	130
Extensogram[e]			
Area (dough strength, cm^2)	143	75	17
Resistance of the dough to extension (EU)	700	680	110
Extensibility (mm)	170	92	100
Baking test			
Dough surface	somewhat wet to normal	normal	wet, gluey
Dough elasticity	normal	somewhat short	weak
Baking volume (ml)	738	630	510

[a] Wheat cultivars with breadmaking quality corresponding to very good ("Monopol"), average ("Nimbus") and poor ("Maris Huntsman").
[b] Factor N × 5.7.
[c] Explanation in Fig. 15.26; dough consistency: 500 FU.
[d] Measured after 10 min in Farinogram units (FU).
[e] Explanation in Fig. 15.29.

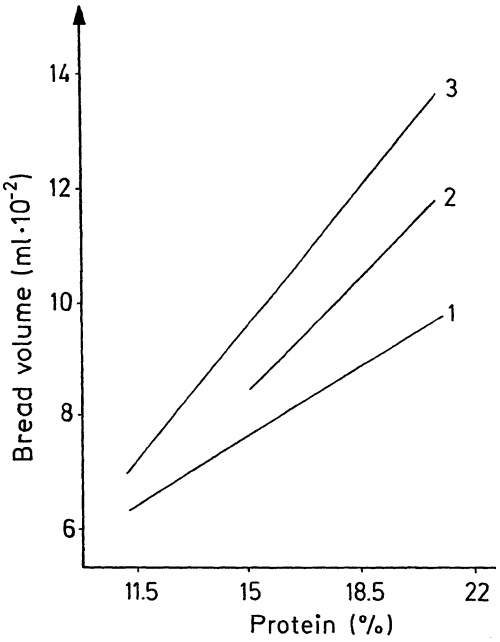


Fig. 15.24. Examples of relationship between protein content of flour and bread volume (according to *Pomeranz*, 1977). United States winter wheat cultivars: *1* Chiefkan, *2* Blackhull, *3* Nebred. The regression lines are based on numerous sample analyses

between the contents of SH- and SS-groups in flour, or their ratios, would be reflected in baking quality. However, low correlation coefficients of about 0.6 have been found. This corresponds to the observation (15.4.1.4.1) that the relationships are much more complex and cannot be grasped by means of an easily determinable characteristic quantity.

Of all enzymes in flour, quality control is aimed at the determination of amylase activity. The *Falling Number* test (*Hagberg* and *Perten*) serves this aim. A piston-type mixer falls through an aqueous flour paste. The falling time of the piston is measured for a given distance under standard conditions. The results are related, among other things, to starch granule stability in the presence of amylase enzymes. The *dextrin value* should be determined to assess amylase activity specifically. In a method developed by *Lemmerzahl*, the extent of standard dextrin hydrolysis in the presence of flour extract is measured. The fermentation power of a flour (cf. 15.4.1.6.1) involves determination of the *maltose value* (diastatic activity). This is a quantitative determination of reducing sugars prior to and after incubation of a flour suspension at 27 °C for 1 h. Flours with a maltose content of $<1.0\%$ are regarded as weak fermentation promoters; values above 2.5% are flours from sprouted kernels. They provide poor baking quality.

15.4.1.1.2 Physical Assays

The instruments widely used in practice for the determination of the rheological properties of dough can be divided into recording dough kneaders and tensile testers. Dough development is followed with a Brabender farinograph (Fig. 15.25), with which measurement is made of the volume of water absorbed by the flour in order to make a dough of predetermined consistency (normal consistency). A plot of dough consistency versus time is recorded, as shown in Fig. 15.26.

In addition to the water absorption, the shape of the farinogram is used to characterize a flour. Var-

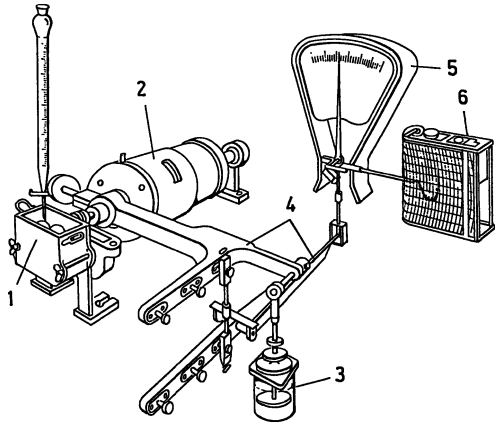


Fig. 15.25. Farinograph (according to *Rohrlich* and *Thomas*, 1967). The apparatus consists of a thermostated mixer or kneader *(1)*, its blades are driven by an electromotor *(2)*. The reaction torque acts through a lever system *(4)* of analytical balance precision on the indicator scale *(5)* simultaneously recorded on a strip chart recorder *(6)*. The movement of the lever system is damped by an oil dash pot *(3)*. The farinogram is a diagram of force versus time

ious indices have been defined (cf. Fig. 15.26); usually they refer to doughs with a maximum consistency of 500 FU.

Flours with strong gluten absorb more water and show longer dough development and stability times than do flours with weak gluten (Table 15.41). Corresponding results are obtained with the Swanson and Working mixographs.

A standardized piece of dough is stretched with the hook of a Brabender extensograph until the piece breaks (Fig. 15.27). As shown in Fig. 15.29, a graph of force (resistance to extension) versus stretching distance (extensibility) provides information about the stability of a dough, its gasholding capacity and fermentation tolerance. Of the examples given in Table 15.41, the "Monopol" cultivar obviously has strong gluten. The "Nimbus" cultivar has short gluten, as reflected by its low extensibility. The "Maris Huntsman" cultivar has a very weak gluten, as shown by the low resistance of its dough to extension and also by its low extensibility, and very small extension area.

Similar results are obtained with the Chopin extensograph or alveograph used widely in France. A piece of dough mounted on a perforated plate is blown into a ball. The pressure in the ball of dough is plotted against the time (cf. Fig. 15.28). In contrast to the Brabender extensograph, the dough is extended in two dimensions. As in the extensogram, the resistance of the dough to extension and its extensibility are obtained from the maximal height and width of the alveogram.

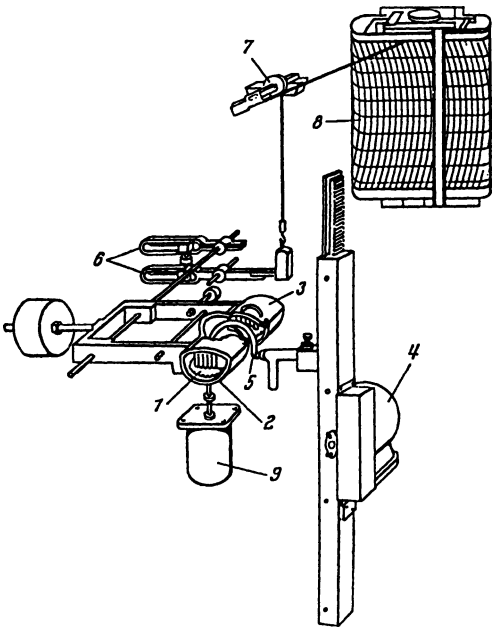


Fig. 15.27. Extensograph (according to *Rohrlich* and *Thomas*, 1967). The cylindrical piece of dough *(1)* is fixed by dough clamps *(3)* and placed on the balance fork *(2)*. The motor *(4)* of the stretching unit *(5)* is then started. The arm moves downward into the dough and extends it at constant speed. Simultaneously, the forces opposing the stretching action are transmitted through the lever system *(6)* to the balance system *(7)*. This is coupled to a recording arm of the strip chart recorder *(8)*. The fork of the balance system is coupled to an oil damper *(9)* to reduce the recoil

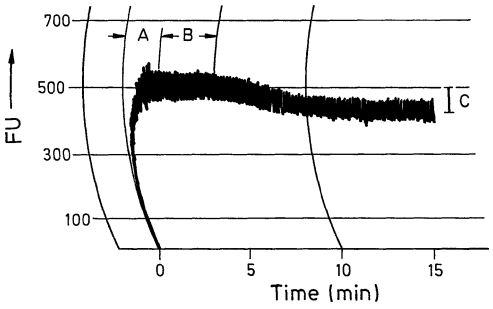


Fig. 15.26. Farinogram. The following data are pertinent for quality assessment of flour: *A* dough development time, *B* dough stability (dough consistency does not change), *C* decrease in dough consistency after a given time, here 12 min. FU: farinogram units

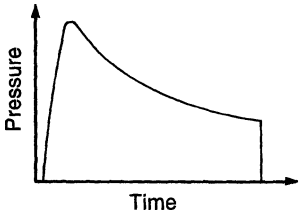


Fig. 15.28. Alveogram (cf. text)

15.4.1.1.3 Baking Tests

Direct information about the baking quality of a flour is obtained from baking tests under standardized conditions. Baking volume (cf. Ta-

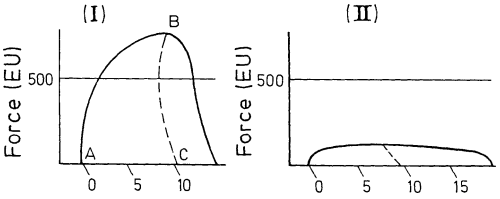


Fig. 15.29. Extensograms of a normal *(I)* and weak dough *(II)*. For quality assessment the following parameters are determined: resistance to extension, height of the curve at its peak (B–C) given in extensogram units (EU); extensibility, abscissa length between A–C in mm; extension area (A–B–C–A, cm^2) is related to energy input required to reach the maximum resistance; extensogram number (overall dough quality) is the ratio of extension resistance to extensibility

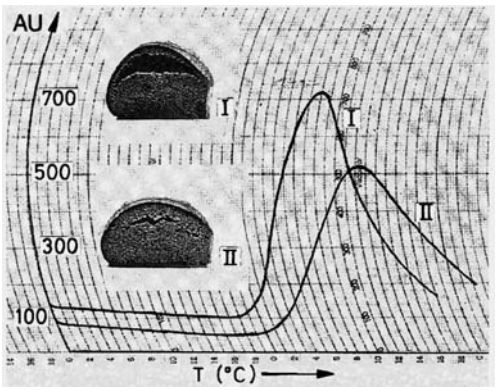


Fig. 15.30. Amylograms of two rye flours (according to *H. Stephan*, 1976)

	Gelatinization maximum (peak)	Gelatinization temperature	α-Amylase
Flour I	720 AU	67 °C	high
Flour II	520 AU	73.5 °C	low

AU: amylogram units.

ble 15.41), form, crumb structure and elasticity, and the taste of the baked product are evaluated. A baking test is performed with 1000 g flour for each product.

When the effects of expensive and not readily available flour constituents and/or additives are tested or a new cultivar is assessed, of which only several hundred kernels are available, a "*micro baking test*" is used, with 10 g flour for each baked product (cf. Fig. 15.35). If even less material is available, 2 g are sufficient. The sample is then kneaded in a mixograph and baked in a capsule.

15.4.1.2 Rye Flour

The Falling Number test (cf. 15.4.1.1.1) and an amylographic assay are the most important tests to assess the baking properties of rye flour. These tests depend to a great extent on gelatinization properties of starches and the presence of α-amylase. The higher the α-amylase activity, the lower the Falling Number.

An amylograph is a rotational torsion viscometer. It measures the viscosity change of an aqueous suspension of flour as a function of temperature. The recorded curve, called an amylogram (Fig. 15.30), shows that with increasing temperature there is an initial small fall followed by a steep rise in viscosity to a maximum value. The steep rise is due to intensive starch gelatinization. The viscosity value and temperature at maximum viscosity (i. e., the temperature reflecting the end of gelatinization) are then read.

In rye flour with balanced baking properties, an optimal relationship should exist between α-amylase activity and starch quality. The extent of enzymatic starch degradation influences the stabilty of the gas-cell membranes which are formed by gas released in the dough and which consolidate during baking into an elastic crumb structure. These membranes contain pentosans, proteins and intact starch granules in addition to gelatinized and partially hydrolyzed starch. High α-amylase activity in rye or a large difference between the temperatures needed for enzyme inactivation (close to 75 °C) and those required for termination of starch gelatinization will produce poor bread since too much starch will be degraded during breadmaking. The gas-cell membranes are liquefied to a great extent; so the gas can escape. This gas will then be trapped in a hollow space below the bread crust (I in Fig. 15.30). Low α-amylase activity, especially in conjunction with low starch gelatinization, leads to a firm and brittle crumb structure.

15.4.1.3 Storage

Rye flour acquires optimal baking properties after 1–2 weeks of storage after milling. Wheat flour requires 3–4 weeks. This storage period is the flour "maturation time". In wheat the time is needed for oxidative processes to occur and thus provide a stronger (shorter) gluten. In this time, the concentrations of endogenous glutathione (GSH, GSSG), which reduces the stability of gluten in dough making (cf. 15.2.3), and PSSG decrease, the rate depending on the wheat cultivar.

Flour with a moisture content of $<12\%$ may be stored at 20 °C and a relative humidity of $<70\%$ for more than 6 months without significant change in baking quality.

Flour fumigation with $Cl_2, ClO_2, NOCl, N_2O_4$ or NO, or treatment with dibenzoyl or acetone peroxide results in carotenoid destruction. The flour becomes bleached. Other reactions, not yet elucidated, are involved with $Cl_2, NOCl, ClO_2$ and acetone peroxide treatment since they provide simultaneous improvement in baking quality of flours which have weak gluten.

15.4.1.4 Influence of Additives/Minor Ingredients on Baking Properties of Wheat Flour

The baking properties of wheat flours differ widely (cf. Table 15.41). In small traditional plants, a baker can use his experience to compensate for changes in the quality of raw materials: flexibility in formulations, dough handling and baking – all these parameters can be adjusted in order to obtain the desired end-product.

In a large-scale automated bakery, economic production demands uniform raw materials with uniform properties. Additives are used when necessary to adjust the flour characteristics to match the baking process (for instance, shortened dough handling time with low energy input). Additives are also used to ensure that the end-product meets existing standards. Incorporation of ascorbic acid, alkali bromates or enzyme-active soy flour improves the quality of weak gluten flour – e. g., in bread or bun baking. In these cases the dough becomes drier and there are increases in dough resistance to extension, mixing tolerance and fermentation stability. In addition, baking volume will increase and the crumb structure will improve. Ascorbic acid and lipoxygenase require oxygen for their actions; hence their beneficial role is very dependent on the intensity of dough mixing, which traps oxygen from the air.

In contrast, opposite effects may be observed by adding cysteine or proteinases, the result being gluten softening. Biscuits are made from such mellowed, softened doughs, which are made with little energy input. Additives which affect the rheological quality of the dough and/or the quality of baked products include emulsifiers, shortenings, salt, milk, soy flour, α-amylase and proteinase preparations and starch syrups.

15.4.1.4.1 Ascorbic Acid

The improver effect of ascorbic acid (Asc) was recognized by *Jorgensen* as early as 1935. He found that small amounts (2–10 g Asc per 100 kg flour) caused an improvement in flour. The dough becomes stronger (Fig. 15.31) and drier and the bread volume increases in most cases. The oxidation product of Asc, dehydroascorbic acid (DHAsc) is also effective (Table 15.42), but its use would be uneconomical. In the example in Fig. 15.31, the addition of 40 mg/kg of Asc has a greater strengthening effect on dough than 20 mg/kg. A further increase in Asc to 80 or even 160 mg/kg no longer increases the effect. But in comparison with

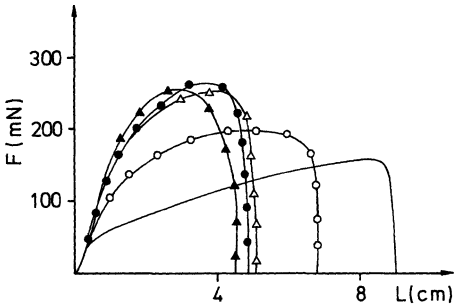


Fig. 15.31. Rheological properties of wheat dough as a function of different concentrations of added L-*threo*-ascorbic acid (Asc) (according to *Kieffer*, unpublished). Tensile tests with dough made of 10 g of flour of the variety Flair. Addition of Asc (mg/kg): 20 ○–○), 40 (●–●), 80 and 120 (▲–▲), 160 (Δ–Δ). Control without additive: —

oxidizing agents like bromate, no overdosage is observed.

In dough making, the Asc added to the flour oxidizes very rapidly to DHAsc (Fig. 15.32). Diastereomers of Asc are converted at the same rate. In contrast, the four diastereomers of Asc (stereochemistry in Fig. 15.33) as well as the corresponding DHAsc differ in their effect as flour improvers. As shown in Table 15.42, L-*threo*-Asc (vitamin C) has the highest dough strengthening effect. The two *erythro*-Asc have a weaker effect and D-*threo*-Asc is almost ineffective. Since these differences correspond with the substrate specificity of the GSH dehydrogenase found in flour (cf. 15.2.2.7), it is assumed that this enzyme is involved in flour improvement on the addition of Asc as shown in Fig. 15.34.

The atmospheric oxygen kneaded into the dough first oxidizes Asc to DHAsc (Reaction a in Fig. 15.34). The reaction is accelerated by ascorbic acid oxidase (cf. 15.2.2.9) and other factors. Subsequently (Reaction b), the GSH present in flour is oxidized to the disulfide. This reaction proceeds very rapidly because it

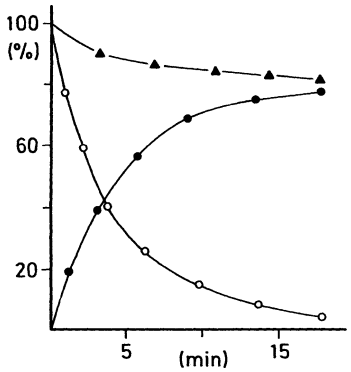


Fig. 15.32. Oxidation of ascorbic acid in dough making from wheat flour (according to *Nicolas* et al., 1980)
○—○ ascorbic acid, ●—● dehydroascorbic acid,
▲—▲ sum of ascorbic and dehydroascorbic acids

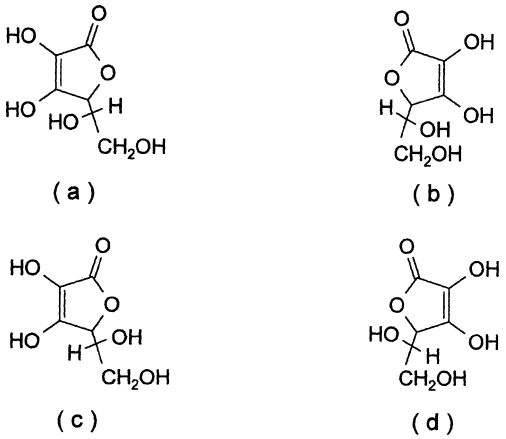


Fig. 15.33. Chemical structures of stereoisomeric ascorbic acids (Asc).
(a) L-*threo*-Asc (vitamin C), (b) D-*threo*-Asc,
(c) D-*erythro*-Asc (isoascorbic acid), (d) L-*erythro*-Asc

Table 15.42. Effect of additives on the rheological properties of wheat dough

Additive (0.15 µmol/g flour)	Resistance to extension (%)	Extensibility[a] (%)
Control (without additive)	100	100
Cysteine	63	106
Glutathione (reduced form)	56	105
L-*threo*-Ascorbic acid	147	58
D-*erythro*-Ascorbic acid	122	86
L-*erythro*-Ascorbic acid	118	93
D-*threo*-Ascorbic acid	94	88
L-*threo*-Dehydroascorbic acid	145	56

[a] Relative values.

$$\text{L-}threo\text{-Asc} + {}^{1}/_{2}\,O_2 \xrightarrow{\text{(AO)}} \text{L-}threo\text{-DHAsc} + H_2O \quad \text{(a)}$$

$$\text{L-}threo\text{-DHAsc} + 2\,GSH \xrightarrow{\text{(GSH-DH)}} \text{L-}threo\text{-Asc} + GSSG \quad \text{(b)}$$

$$GSSG + PSH \rightarrow PSSG + GSH \quad \text{(c)}$$

$$PSSP + GSH \rightarrow PSSG + PSH \quad \text{(d)}$$

$$CSSC + GSH \rightarrow CSH + GSSC \quad \text{(e)}$$

$$PSSP + CSH \rightarrow PSSC + PSH \quad \text{(f)}$$

$$CSSC + PSH \rightarrow PSSC + CSH \quad \text{(g)}$$

Fig. 15.34. Reactions involved in flour improvement by ascorbic acid (according to *Grosch* and *Wieser*, 1999)
Asc, ascorbic acid; DHAsc, dehydroascorbic acid; AO, ascorbic acid oxidase; GSH-DH, glutathione dehydrogenase; GSH, reduced glutathione; GSSG, oxidized glutathione; CSH, cysteine; CSSC, cystine; PSSP, gluten proteins

is catalyzed by enzyme GSH-DH (cf. 15.2.2.7) which requires DHAsc as a cofactor. Ascorbic acid is reformed which explains that relatively small amounts of Asc are sufficient for flour improvement. The GSSG formed in Reaction (b) can undergo an SH/SS exchange with gluten proteins (Reaction c), which has been shown to proceed especially rapidly on addition of Asc. Thus, GSH is incorporated into gluten proteins as a terminator of polymerization reactions via the intermediate GSSG. On the other hand, GSH formed in Reaction (c) is immediately oxidized. The reaction sequence (a→b→c) stops when all the GSH is present as GSSG or incorporated into gluten proteins. Consequently, GSH is largely withdrawn from the dough before it can depolymerize the gluten proteins by SH/SS interchange. If it is not withdrawn from the dough, Reactions (d)–(f) proceed without any interference. In comparison with Reaction (c), Reaction (d) can result in the softening of the dough because GSH very specifically cleaves intermolecular disulfide bonds of the gluten proteins (cf. 15.2.3).

The results summarized in Tables 15.43 and 15.44 show that free cysteine increases rapidly in dough making. This is explained by Reaction (e) in Fig. 15.34, which shows that GSH reacts with the cystine present in flour. Cysteine increases and can, in turn, depolymerize gluten proteins (Reaction f). If, however, L-*threo*-Asc is added to the dough, GSH is so rapidly oxidized (Reaction b) that the comparatively slow Reaction (e) is strongly inhibited and cysteine increases only slightly (Tables 15.43 and 15.44). Corresponding to the substrate specificity of GSH-DH (cf. 15.2.2.7), D-*erythro*-Asc is almost ineffective; cysteine increases and GSH decreases as in the experiment without an additive (Table 15.43). The reaction scheme shown in Fig. 15.34 also explains the baker's experience that the consistency of dough can be reduced by the addition of cysteine almost independently of the presence of L-*threo*-Asc. Reaction (f) is not prevented due to the substrate specificity of GSH-DH which is only directed at GSH. Reaction (g) is promoted by the addition of L-*threo*-Asc because the reduction of cystine (Reaction e) is inhibited by the trapping of GSH. Consequently, cystine can undergo SS/SH interchange with gluten proteins according to Reaction (g) so that PSSC increases, as demonstrated in model experiments.

The reaction scheme in Fig. 15.34 also explains the observation that Asc cannot be overdosed. The effect of Asc stops at the moment when all the GSH is bound as GSSP and GSSG. An increase in Asc has no further effect.

Table 15.43. Influence of L-*threo*- and D-*erythro*-ascorbic acid (Asc) on the concentration of cysteine (CSH) and glutathione in wheat dough

Sample[a]	Additive (30 mg/kg)	CSH (nmol/g)	GSH (nmol/g)
Flour	Without	13	100
Dough	Without	42	44
Dough	L-*threo*-Asc	28	20
Dough	D-*erythro*-Asc	41	39

[a] Production of the dough: DNS flour (0.78% ash, 10 g) and water (6.5 ml) are kneaded at 30 °C for 2 min; liquid nitrogen is poured over the dough which is then freeze dried; CSH and GSH are determined by isotopic dilution analysis.

Table 15.44. Changes in concentration of glutathione (GSH) and cysteine (CSH) in dough on addition of L-*threo*-ascorbic acid or bromate

Additive[a]	GSH (nmol/g)			CSH (nmol/g)		
	Kneading time (min) at 30 °C					
	3	9	9 + 20[b]	3	9	9 + 20[b]
Without	57	22	17	68	28	31
L-*threo*-Asc (30 mg/kg)	11	6	2	26	17	19
$KBrO_3$ (50 mg/kg)	40	20	11	52	26	27

[a] The DNS flour used contained 124 nmol/g GSH and 22 nmol/g cysteine.
[b] The dough was allowed to rest for 20 min.

15.4.1.4.2 Bromate, Azodicarbonamide

Addition of alkali bromates to flour also prevents excessive softening of gluten during dough making. The reaction involves oxidation of endogenous glutathione to its disulfide. Bromate reacts slower than ascorbic acid (Table 15.44). After a kneading time of 3 minutes, GSH decreases from 124 nmol/g to a concentration of 40 nmol/g and cysteine increases from 22 nmol/g to 52 nmol/g. These values are relatively close to the corresponding values in dough without additives. On the other hand, only 11 nmol/g of GSH remain and cysteine increases only slightly after the addition of Asc. The reactions of bromate in dough have not yet been elucidated. Model experiments indicate that it can link gluten proteins by the formation of intermolecular disulfide bonds. Then the oxidation of GSH would not be the decisive step in flour improvement. In comparison with Asc, bromate can be overdosed, which also shows that another mechanism must be involved here. During baking, bromates are completely reduced to bromides with no bromination of flour constituents.
Azodicarbonamide is of interest as a flour improver

$$H_2N{-}CO{-}N{=}N{-}CO{-}NH_2 \qquad (15.7)$$

since it improves not only the dough properties of weak gluten flour, but also lowers the energy input in dough mixing (cf. Fig. 15.40). Details of the reactions involved are unknown.

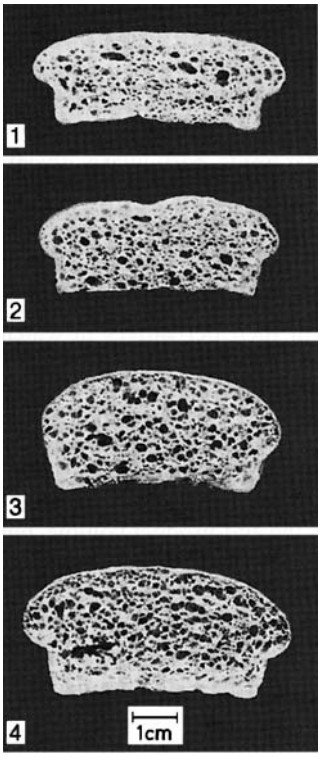


Fig. 15.35. Wheat flour quality improvement by the nonspecific lipoxygenase enzyme of soybean[a] (according to *Kieffer* and *Grosch*, 1979). Additions: **1** control (no addition, bread volume 31 ml), **2** extract of defatted soya meal in which lipoxygenase was thermally inactivated (31 ml), **3** extract of a defatted soya meal with 290 units of lipoxygenase[b] (35 ml), **4** purified type-II enzyme with 285 activity units (37 ml).
[a] Results in small-scale baking, 10 g flour cv. Clement.
[b] One enzyme unit = 1 µmole · min^{-1} oxygen uptake with linoleic acid as substrate

15.4.1.4.3 Lipoxygenase

The addition of a small amount of enzymeactive soy flour to a wheat dough increases the mixing tolerance, improves the rheological properties and may increase the bread volume. The effect on dough rheology is shown only with high-power mixing in the presence of air. The carotenoid pigments of wheat flour are bleached by the addition of enzyme-active soy flour. This is desirable in the production of white bread. The amount of enzyme-active soy flour is restricted to approximately 1% since higher levels may generate off-flavors.
It was demonstrated that nonspecific lipoxygenase (cf. 3.7.2.2) is responsible for the improver action (Fig. 15.35) and the bleaching effect caused by the enzyme-active soy flour. This enzyme, in contrast to endogenous wheat flour lipoxygenase, releases peroxy radicals which cooxidize carotenoids and other flour constituents.

15.4.1.4.4 Cysteine

Cysteine, in its hydrochloride form, softens gluten due to a SH/SS interchange with the glutenin fraction. The resistance to extension

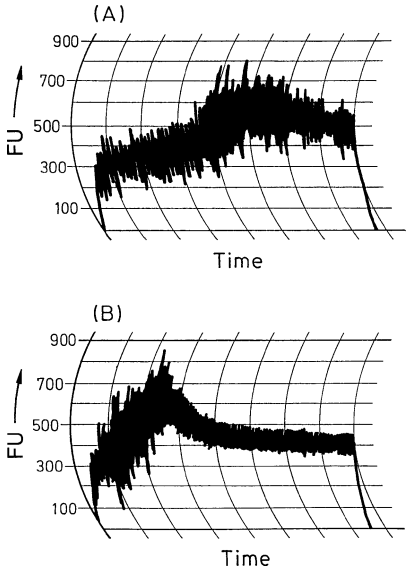


Fig. 15.36. Farinograms. Effect of L-cysteine hydrochloride on a flour with strong gluten (according to *Finney* et al., 1971). **A** control (no addition), **B** cysteine added (120 ppm)

of the dough decreases and the extensibility increases (cf. Table 15.42). Decreases in dough development time and dough stability, as shown in farinograms (Fig. 15.36), clearly reveal the addition of cysteine. Flours with strong gluten and with optimum levels of cysteine also show a favorable increase in baking volume since, prior to baking, the gas trapped within the dough can develop a more spongy dough. The action of sodium sulfite is similar to that of cysteine.

15.4.1.4.5 Proteinases (Peptidases)

Proteinase preparations of microbial or plant origin are used for dough softening (cf. 2.7.2.2.1). Their action involves protein hydrolysis, i. e., gluten-protein endo-hydrolysis. Their effect on dough rheology, therefore, depends on the nature of the enzymes and the activity of the preparations towards gluten proteins. This is shown in Fig. 15.37. Despite equal hydrolase activities with hemoglobin as a test substrate, a fungal proteinase degrades gluten to a lesser extent and consequently causes a smaller decrease in dough resistance to extension in comparison to

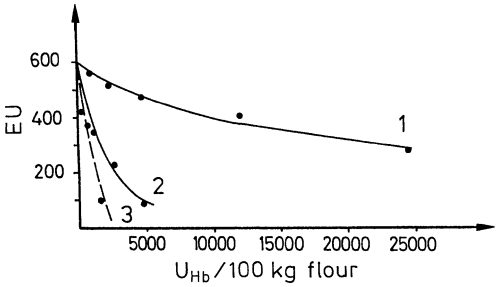


Fig. 15.37. The effect of a proteinase preparation on resistance to extension (in extensogram units) of a wheat flour dough (according to *Sproessler*, 1980). Proteinase preparation: *1* fungal, *2* papain, and *3* bacterial. U_{Hb} proteinase activity units determined with hemoglobin as a substrate

a bacterial enzyme preparation. Also, the latter is more effective than papain.

Fungal proteinases, because of their low enzyme activity and, therefore, high dosage tolerance, are suitable for optimization of flours containing strong gluten, used for bread and buns. However, bacterial enzymes are preferred in production of biscuits and wafers since they degrade gluten to a greater extent, providing accurate flat dough pieces with high form stability. Bacterial enzymes are also preferred for the desirable end product qualities of porosity and breaking strength.

Data are shown in Table 15.45 for white bread prepared with and without papain. There is a rise in the content of both free amino acids in the crumb and volatile carbonyl compounds in the crust when proteinase is used. As long as proteinases are active in a baking process, they release amino acids from flour proteins, which are then changed via *Strecker* degradation

Table 15.45. Effects of papain addition in white bread making (values in µmole/g dry matter)

Constituent		Without papain	With papain
Free amino acids	Dough	183	186
	Crumb	182	272
	Crust	10	15
Volatile carbonyl compounds	Crust	158	217

(cf. 4.2.4.4.7) into volatile carbonyl compounds in the crust. Bread aroma is enhanced, as is the crust color, by a build-up of melanoidin compounds from nonenzymatic browning reactions.

15.4.1.4.6 Salt

The taste of bread is rounded-off by the addition to dough of about 1.5% NaCl. As with other salts with small cations (e. g., sodium fumarate or phytate), the addition of NaCl increases dough stability. It is assumed that this is due to the ions masking the repulsion between one charged gluten protein molecule and another of like charge. This allows a sufficiently close approach of one molecule to another, thus hydrophobic and hydrophilic interactions can occur.

15.4.1.4.7 Emulsifiers, Shortenings

Flour baking quality is positively correlated to the content of polar lipids, particularly glycolipids (cf. 15.2.5). Further improvements in dough properties, baking results and end-product freshness or shelf life (cf. 15.4.4) are gained by adding emulsifiers to the dough, e. g., crude lecithin (cf. 3.4.1.1), mono- and diacylglycerides or their derivatives in which the OH-group(s) is esterified with acetic, tartaric, lactic, monoacetyl or diacetyl tartaric acid (cf. 3.3.2 and 8.15.3.1). The hypotheses presented in 15.2.5 are under discussion to explain this effect in the baking process.

Addition of triacylglycerides (shortenings) generally reduces the end-product volume, but there are exceptions depending on the wheat variety. As illustrated by flour I in Table 15.46, addition of 3 % shortening provides a substantial increase in baking volume. Emulsifiers are also added to the dough to delay the aging of the crumb (cf. 15.4.4).

Table 15.46. The effect of shortening on baking volume

Wheat flour	Baking volume (ml)[a]	
	Without shortening	With 3% shortening
I	64.5	81.0
II	73.3	71.8
III[b]	51.6	46.3

[a] Baking test performed on a small scale (10 g flour).
[b] Flour of poor baking quality.

15.4.1.4.8 α-Amylase

Flours contain very small amounts of sugars which are metabolizable by yeast (cf. Table 15.30). Addition of sucrose or starch syrup at 1–2% to dough is advisable to maintain favorable growth of yeast and therefore to provide CO_2 needed for dough leavening. Uniform leavening over an extended time improves the quality of many baked end-products; the crumb structure acquires finer and more uniform porosity, while the crust has greater elasticity.

Flours derived from wheat without sprouted grains have some β- but very little α-amylase activity (cf. 15.2.2.1). Thus, only a small amount of starch is degraded to fermentable maltose by handling dough. An insight into the extent of starch degradation is provided by the maltose value (cf. 15.4.1.1.1). Addition of α-amylase in the form of malt flour or as a microbial preparation increases the flour capacity to hydrolyze the starch.

The activity of α-amylase as well as the levels of maltose and glucose increase in the germination of cereals; hence, addition of flour from malted grains enhances the growth of yeast in dough. However, the addition of malt to flours with weak gluten may not be expedient because of the proteolytic activity of the malt. α-Amylase preparations free of proteolytic activity are available from microorganisms (cf. 2.7.2.2.2).

Examples in Table 15.47 illustrate the effects of α-amylse from various sources on baking quality. While malt and fungal amylases show similar effects, the heat-stable α-amylase from *Bacillus subtilis*, with its prolonged activity even in the oven, may be easily used to excess. Products formed by the activities of α- and β-amylases are also available as reactants for nonenzymatic browning reactions. This favorably affects the aroma and color of the crust. α-Amylases are added to flour not only to standardize the baking properties, but also to delay the aging of the crumb (cf. 15.4.4).

Table 15.47. The effect of α-amylase preparations on baking results

α-Amylase preparation		White bread		
Origin	Activity[a] (units)	Volume (ml)	Crumb	
			pores	structure
Without addition		2400	average	average
Wheat malt	140	2790	good	good
	560	3000	good	good
	1120	2860	average	good
Aspergillus oryzae	140	2750	very good	very good
	560	2900	good	good
	1120	2950	average	average
Bacillus subtilis	7	2600	good	good
	35	2600	good	average
	140	2640	poor	very poor

[a] α-Amylase units in 700 g flour.

15.4.1.4.9 Milk and Soy Products

Dairy products such as skim milk, buttermilk, whey and casein are added to flour in combination with the ingredients or additives mentioned so far. These dairy products are used in either powdered or liquid form as well as either whole or in the form of defatted powder. In such cases, the proteins added to the dough increase its water binding capacity and provide a juicy crumb.

15.4.1.5 Influence of Additives on Baking Properties of Rye Flour

Rye flour often requires an improved water binding capacity. For this purpose, 2–4% of pregelatinized flour is added. In addition, artificial acidification of the rye dough is practiced; hence both aspects will be covered.

15.4.1.5.1 Pregelatinized Flour

Pregelatinized flour is made from ground cereals such as wheat, rye, rice, millet, etc. by cooking and steaming in autoclaves followed by drying and repeated milling. Such pregelatinized flours are sometimes blended with guar flour or alginates.

15.4.1.5.2 Acids

Rye flour is used in bread baking with sour dough fermentation (cf. 15.4.2.2).
Artificial acidification can be achieved by the addition of lactic, acetic, tartaric or citric acid to rye dough or by adding acidic forms of sodium and calcium salts of ortho- and/or pyrophosphoric acids.
Other preparations for acidification, the so-called dry or instant acids, consist of pregelatinized flour blended with a sour dough concentrate or of cereal mash prefermented by lactic bacteria. The acid values (for definitions see 15.4.1.1.1) vary from 100–1000.

15.4.1.6 Dough Leavening Agents

Dough consisting only of flour and water gives a dense flat cake. Baked products with a porous crumb, such as bread, are obtained only after the dough is leavened. This is achieved for wheat dough by addition of yeast while, for fine baked products, baking powders are used. Rye dough

leavening is achieved by a sour dough formulation which includes lactic and acetic acid bacteria.

15.4.1.6.1 Yeast

A given amount (Table 15.48) of surface-fermenting yeast, *Saccharomyces cerevisiae*, is used. While normal yeasts preferentially degrade sucrose rather than maltose, special rapidly fermenting yeasts are used which metabolize both disaccharides at the same rate, shortening the fermentation time.
Yeasts differ in their growth temperature optima (24–26 °C) and their fermentation temperature optima (28–32 °C). The optimum pH for growth is 4.0–5.0. In addition to CO_2 and ethanol, which raise the dough, the yeast forms a variety of aroma compounds (cf. 5.3.2.1). Whether other compounds released by the growth of yeast would affect the dough rheology is unclear; there appears to be no effect of yeast proteinase and GSH.

15.4.1.6.2 Chemical Leavening Agents

The interaction of water, acid, heat and chemical leavening agents (baking powders) releases CO_2. The release of gas may occur in the dough prior to or during oven baking. The agents consist of a CO_2-generating source, as a rule sodium bicarbonate, and an acid carrier, usually disodium dihydrogendiphosphate, sometimes monocalcium phosphate $[Ca(H_2PO_4)_2]$. Glucono-δ-lactone or tartar (acidic potassium tartrate) are used as acid carrier for phosphate-free baking powder. The phosphate-free leavening mixtures produced on an industrial scale contain citric acid or its acidic sodium salt. In baking powder, the two reactive constituents are blended with a filler which consists of corn, rice, wheat or tapioca starch or sometimes dried wheat flour. The filler content in the powder is up to 30%. The role of the filler is to prevent premature release of CO_2. The market also offers baking powders flavored with vanillin or ethyl vanillin.
For every 500 g of flour, baking powder should develop 2.35–2.85 g CO_2, equivalent to about 1.25 liters.
In individual cases, $NaHCO_3$ alone is used for some flat shelf-stable cookies and ammonium hydrogencarbonate (NH_4HCO_3) for many others. Ginger and honey cookies are leavened by NH_4HCO_3, mostly together with potash (K_2CO_3). To a small extent, a 1:1 mixture of ammonium hydrogencarbonate and ammonium carbamate ($H_2NCOONH_4$) is used in some countries. Both decompose above 60 °C to NH_3,CO_2 and water.

Table 15.48. Amount of yeast used in bread and other baked products

Baked product	Yeast added[a] (%)
Rye bread	0.5–1.5
Rye mix bread	1.0–2.0
Wheat mix bread	1.5–2.5
Wheat bread	2.0–4.0
Breakfast rolls	4.0–6.0
Rusk (“Zwieback”)	6.0–10.0

[a] Based on flour content.

15.4.2 Dough Preparation

15.4.2.1 Addition of Yeast to Wheat Dough

15.4.2.1.1 Direct Addition

Flour, water, yeast, salt and other ingredients are directly mixed into the dough.

15.4.2.1.2 Indirect Addition

Yeast is propagated at 25–27 °C in a well-aerated liquid pre-ferment which contains flour, water and some sugar. After a given time, the liquid is blended with the bulk of flour and water and other ingredients and then made into a dough in a mixer.
For continuous indirect addition of yeast, special liquid starters (sponges) with a pH of 5.0–5.3 are also used with incubation at 38 °C to develop aroma. Such matured fermented sponge is then metered continuously into a kneader which handles the dough.

15.4.2.2 Sour Dough Making

In sour dough making (lowering the pH to 4.0–4.3) rye flour acquires the aroma and taste properties so typical of rye bread (cf. 15.1.5).

Yeast (*Saccharomyces cerevisae, Saccharomyces minor* and others), which are mainly responsible for dough leavening, and a complex bacterial flora in which lactic acid-forming organisms dominate (*Lactobacillus plantarum, Lactobac. San Francisco* and *Lactobacillus brevis*) are present in sour dough.

Sour dough is prepared by various procedures which differ considerably in the length of time required (Fig. 15.38). A three-stage procedure takes into account the optimum temperature and humidity needs of yeast and bacteria. Yeast prefer to grow at 26 °C, while the bacteria of interest grow best at 35 °C.

In setting up a three-stage process, initially an aqueous flour suspension is inoculated. This is the first "full sour" build-up stage (Fig. 15.38). After maturation, further amounts of flour and water are added and the process is continued with a "basic sour" stage at 35 °C and then, in a similar way, continued with an additional "full sour" third stage at 26 °C.

The incubation conditions given in Fig. 15.38 are only the essential outline. Temperature deviations influence the spectrum of fermentation products. At warmer temperatures (30–35 °C) lactic acid is preferentially formed (Fig. 15.39), while at cooler temperatures (20–25 °C) more acetic acid is produced. The desirable lactic acid: acetic acid ratio, called the "fermentation ratio", is close to 80:20. A ratio with a higher acetic acid concentration gives too sharp an acid taste. The portion of rye flour in the end-product determines the amount of rye sour (full sour) to be added to the dough in the preparation stage. Thus, for rye bread the sour dough to be added is 35–45%, while for a rye mix bread it is 40–60% (on the basis of rye flour).

In the short sour method the growth of yeast is negligible. Only a single sour stage, which lasts about 3 h, is involved, yeast is added and the dough is ready for use (Fig. 15.38). However, this short method requires a relatively high content of starter saved from a previous ripe sour. Additional time can be saved by using dough acidifiers (cf. 15.4.1.5.2 and Fig. 15.38). In short sour processes all the organic acids needed for the sour taste of the rye endproduct are present. However, there is a lack of aroma compounds and precursors from which odorants can be generated during baking. In a three-stage rye sour procedure, part of the flour proteins is hydrolyzed by proteinases of the microflora into free amino acids which then

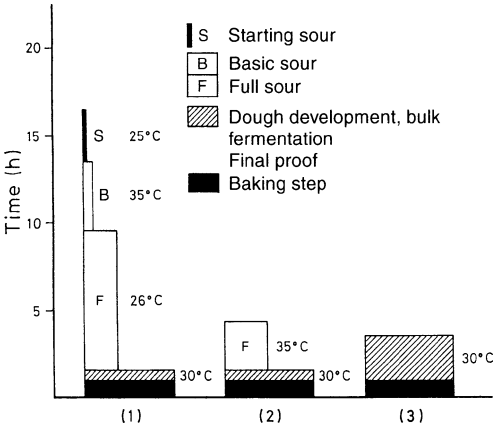


Fig. 15.38. Time requirement for various sour dough development methods (according to *Rothe*, 1974). *1* A three step process, *2* short sour, *3* dough souring agents used

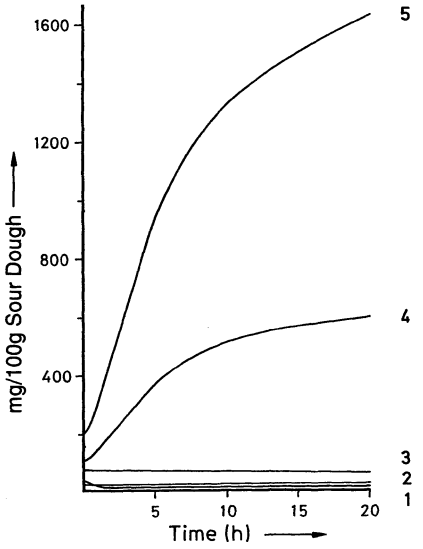


Fig. 15.39. Acid formation in sour dough versus time at 30 °C (according to *Rabe*, 1980). *1* Malate, *2* pyruvate, *3* citrate, *4* acetate, and *5* lactate

participate in *Maillard* reactions during baking, providing the more intense aroma.

15.4.2.3 Kneading

The kneading process is characterized by the following stages: mixing of the ingredients and seasonings; dough development and dough plastification.

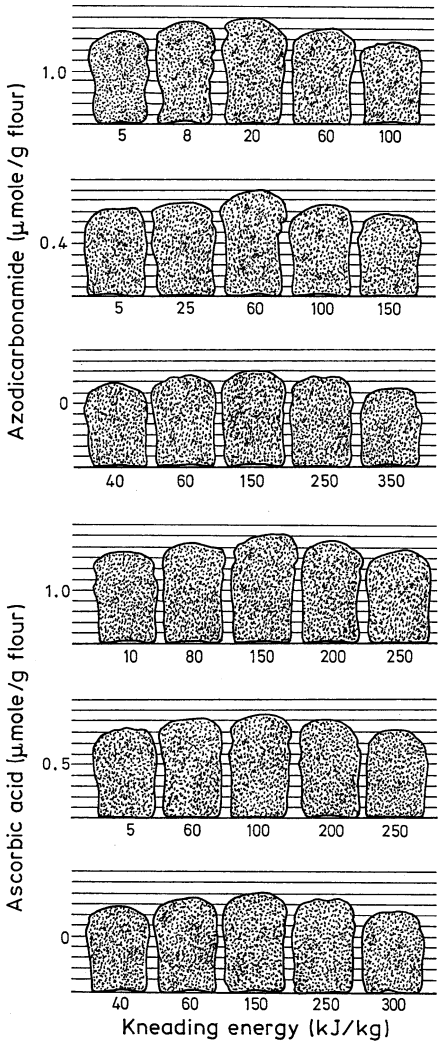


Fig. 15.40. Bread volume as affected by kneading energy input (according to *Frazier* et al., 1979)

The energy input into dough kneading, the dough properties and baking volumes are interrelated. For each dough the baking volume passes through an optimum which is dependent on kneading energy input (Fig. 15.40). This optimum shifts towards lower energy input with a flour of weak gluten content and towards higher energy input with flours of strong gluten content; and, as expected, the position of the optimum can be influenced by flour improvers. Increased additions, especially of azodicarbonamide, to the dough result in a successive drop in kneading energy input (Fig. 15.40).

As the kneading energy moves away from the optimum, the dough becomes wetter, it starts to stick to trough walls and its gasholding ability drops (cf. 15.4.2.5 and Fig. 15.44, *14* and *56*). Dough development of wheat flours requires close to double the kneading time of rye flours.

The machines used for kneading are grouped according to their performance based on kneading time: fast, intensive, and high power kneaders and mixers (Table 15.49). However, the groups are not sharply divided. As the kneading speed increases, the temperature of the dough rises (Table 15.49). Hence, cooling must be used during kneading to keep the temperature at 22–30 °C or, with high speed mixers, at 26–33 °C. The mixer, in a true sense, does not knead the dough, but rips or ruptures it. This could reduce the stability of the dough to such an extent that it could be baked only as panbread (in which case the pan walls support the dough) but not as bread made from selfsupporting dough.

Table 15.49. Examples for kneading conditions in white bread dough making

Dough mixer/ kneader	Speed (rpm)	Kneading time (min)	Dough heat[a] ΔT(°C)
Rapid kneader	60–75	20	2
Intensive kneader	120–180	10	5
High power kneader	450	3–5	
Mixer	1440	1	9
Mixer	2900	0.75	14

[a] Temperature rise during kneading time.

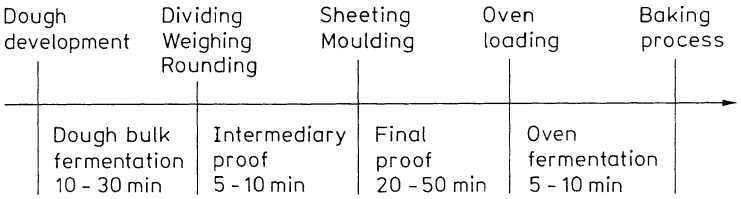


Fig. 15.41. Fermentation process for biologically leavened dough; temperature 26–32 °C (according to *Bueskens*, 1978)

15.4.2.4 Fermentation

Dough passes through several stages of fermentation in the presence of growing yeast, a biological leavening agent (Fig. 15.41). After initial fermentation, the dough is divided and scaled, then the dough pieces are rounded-off. A short fermentation is followed by sheeting and moulded dough fermentation. The dough acquires its enlarged final volume in the oven. The yeast produces CO_2 and ethanol which, as long as they do not dissolve in the aqueous phase of the dough, expand the air bubbles (10^2–10^5 /mm^3) that arise in the dough during kneading. The volume of a square white loaf increases 4 to 5 fold and more during initial, intermediate, and moulded dough fermentation and 5 to 7 fold during oven fermentation. The length of time of the fermentation varies. It depends on flour type (cf. Fig. 15.42), seasonings incorporated, the amount of yeast and oven temperature. The flour character determines the fermentation tolerance, i. e. the minimum or maximum time after which the fermentation has to be stopped and the dough loaded into the oven. Dough fermentation of a weak gluten flour is rapid, but its fermentation tolerance is low.

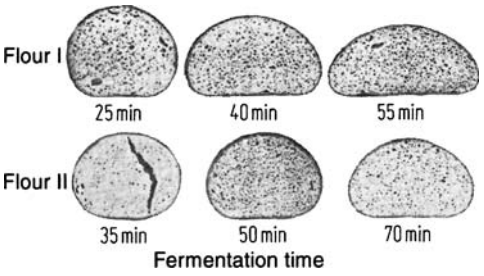


Fig. 15.42. The effect of fermentation time on baking results. (rye-mix bread with two flours which differ in baking quality; according to *Bueskens*, 1978)

The main dough fermentation step (cf. Fig. 15.41) can be substantially shortened by kneading the dough energetically and/or by incorporating fast-acting additives (for example, a mixture of bromates, ascorbic acid and cysteine) into the dough. This provides a favorable dough structure, able to accommodate large amounts of yeast. This is the basis for "no-time" dough making procedures, which provide a continuous flow of dough.
In continuously operated baking processes, the resting times required during the working of dough (intermediate and final fermentation) are realized in air conditioned fermentation rooms. The resting dough forms pass through these rooms with a defined speed.

15.4.2.5 Events Involved in Dough Making and Dough Strengthening

15.4.2.5.1 Dough Making

Bread dough is prepared by mixing water and flour (70:30 w/w). Water uptake, which depends on flour type, predetermines most of the subsequent reactions. A high water uptake favors the mobility of all the constituents involved in reactions, e. g., enzymatic degradation of starch into reducing sugars (Fig. 15.43).
Observation of wheat dough development by light or scanning electron microscopy reveals that a sequence of forceful changes occurs in the arrangement of the water-insoluble flour proteins.
When a light microscope is used to look at a wheat flour particle under water, practically no protein structure is discernible (Fig. 15.44, *1a*). If the particle is stretched in one direction by moving the slide cover glass against the microscope slide, numerous protein strands with inserted starch granules become visible. These strands are

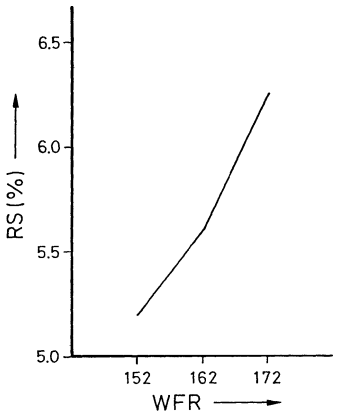


Fig. 15.43. The reducing sugar content in wheat bread crumb as affected by water content of dough (according to *Wassermann* and *Doerfner*, 1971).

$$\text{Water flour ratio (WFR)} = \frac{(\text{flour} + \text{water}) \times 100}{\text{flour}}$$

RS: Reducing sugar expressed as maltose

oriented in the direction of stretching (*1b, 1c*) and partially adhere to the glass at one end (*2*). If circular movements are made with the cover glass, the protein strands are two-dimensionally stressed and most of the starch is released (*3* and *4*). As a result of the stickiness of the protein, the strands can be easily aggregated to a ball by further rotary movements. Another way of representing the protein structure is to spread flour particles on the water surface (*5*). The protein strands which radially grow out of the flour particle during hydration are linked by protein films and, thus, bent. After appropriate fixation of these structures, the protein films can be selectively removed with 60% ethanol and the strands lose their taut structure (*8*). The ethanol-soluble gliadins and the strand-shaped insoluble glutenins possibly exist separately even in the grain. Under a scanning electron microscope at higher magnification, a flour particle, after the removal of starch with amylase, looks like a protein sponge (*6*) in which starch granules were inserted. One-dimensional stretching gives strands (*7*). Similar gluten structures are detected in dough as in flour particles, but the proteins form differently arranged aggregates, which are more resistant to tear, because of the strong mechanical treatment.

In ripe, dry grain, the gluten proteins are stored as particles in the endosperm cells. The diameter of these particles is 1–10 μm, depending on the wheat cultivar. In addition, these particles can still fuse together in the cell to form aggregates with a diameter of up to 50 μm. At the start of the kneading process, the particles and the aggregates are hydrated and they form net-like structures (*10*) as a result of their cohesive properties. The exceptional cohesiveness of the gluten proteins is due to their high glutamine content, which allows the formation of innumerable hydrogen bridges. Due to the mechanical processing in the kneader, the proteins are increasingly brought into close contact so that they aggregate to larger networks (*12*). Strong shear forces are present in the dough because of the low amount of free water. Thus, like in a ball mill, the proteins are mixed with other flour constituents and can react with them. With increasing kneading time, the interactions between the gluten proteins become stronger and stronger, making the structures denser and denser (*14*) until the kneading resistance reaches a maximum, which can be measured in a farinograph. As a result of the high content of starch (70% of the dough), which is homogenously distributed in the dough, the net-like structures are still very thin (Fig. 15.46a). These structures are partially broken down (*56*) again by overkneading, weakening the support function of the gluten. If the gluten is extended two-dimensionally to a thin membrane, it starts to perforate (*15*) and with increasing relaxation forms strands, which are as round as possible. The energetic state of these strands is lower than that of the membranes because of the low surface area.

The connected gluten framework formed in this way is responsible for the gas retention capacity of wheat dough. In fact, stands which are as thick as possible but easily extensible under the pressure of the fermentation gases are of advantage for the stability of the dough.

With the help of transmission electron microscopy, it can be shown at still higher magnification that the surface of unstretched protein strands has an irregular globular structure (*18*). As a result of the washing out of gliadin with a large excess of water, these strands should essentially consist of glutenin. On twodimensional stretching, the globular surface is flattened (*19*) and platelet-like forms appear (*20*) which are arranged parallel to the plane of stretching and are less than 10 nm in thickness. The globular surface structures are probably highly tangled, strand-shaped proteins which are unfolded due to

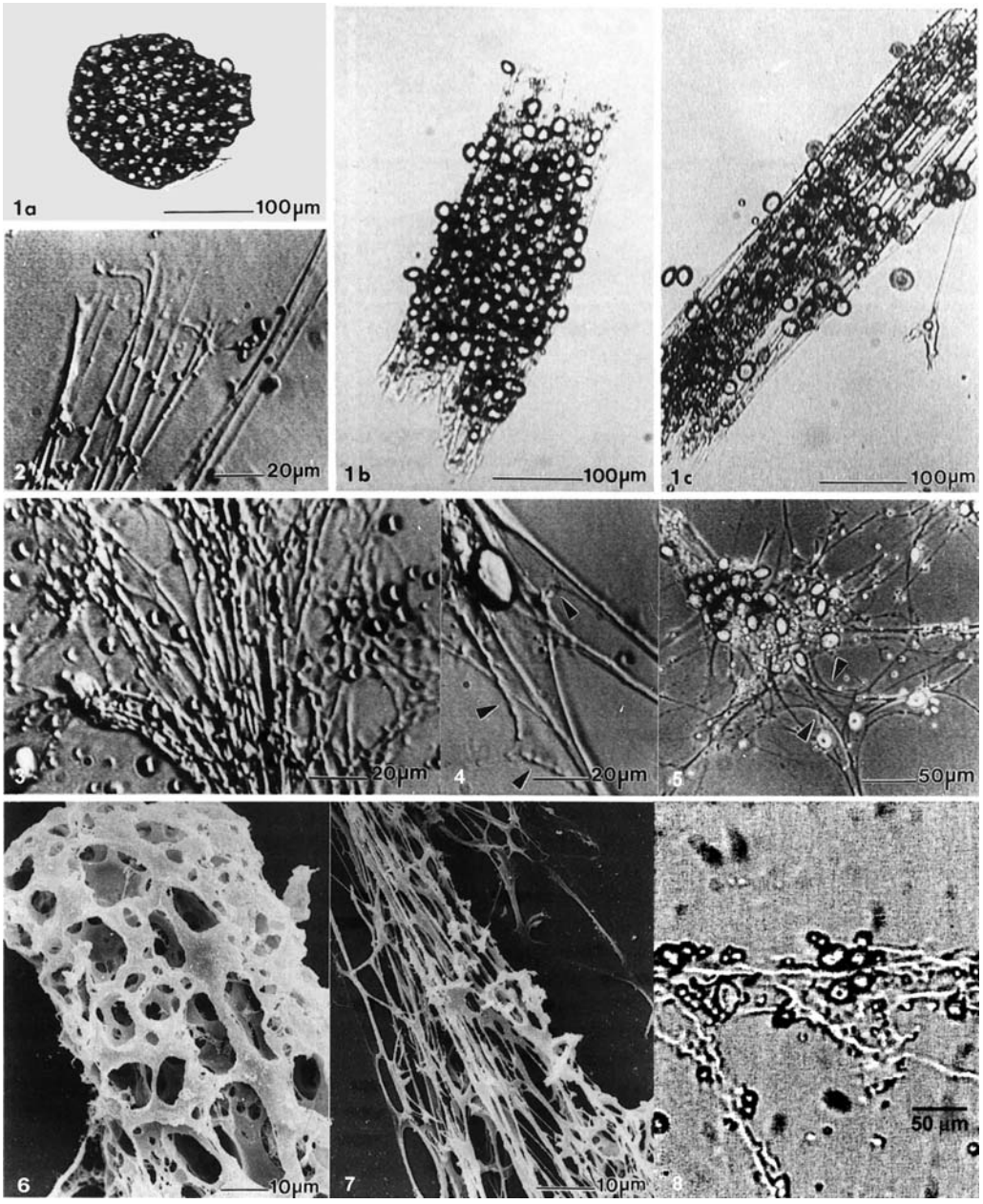


Fig. 15.44. *1–5 Light microscopy*. *1a*: Individual flour particles in water. *1b*: Flour particles, slightly extended by moving the cover glass. *1c*: Flour particles, highly extended; *2*: Extended protein strands with one end adhering to the glass. *3*: Network of protein strands after two-dimensional extension of a flour particle. *4*: Protein film (*arrows*) between bent protein strands. *5*: Flour particles stretched on the water surface. Protein films between bent protein strands (*arrows*). *6–17, 56–57 Scanning electron microscopy.* *6*: Flour particle unstretched, holes from enzymatically removed starch. *7*: Flour particle, extended (starch removed). *8*: Spread preparation (*5*) washed with 60% ethanol.

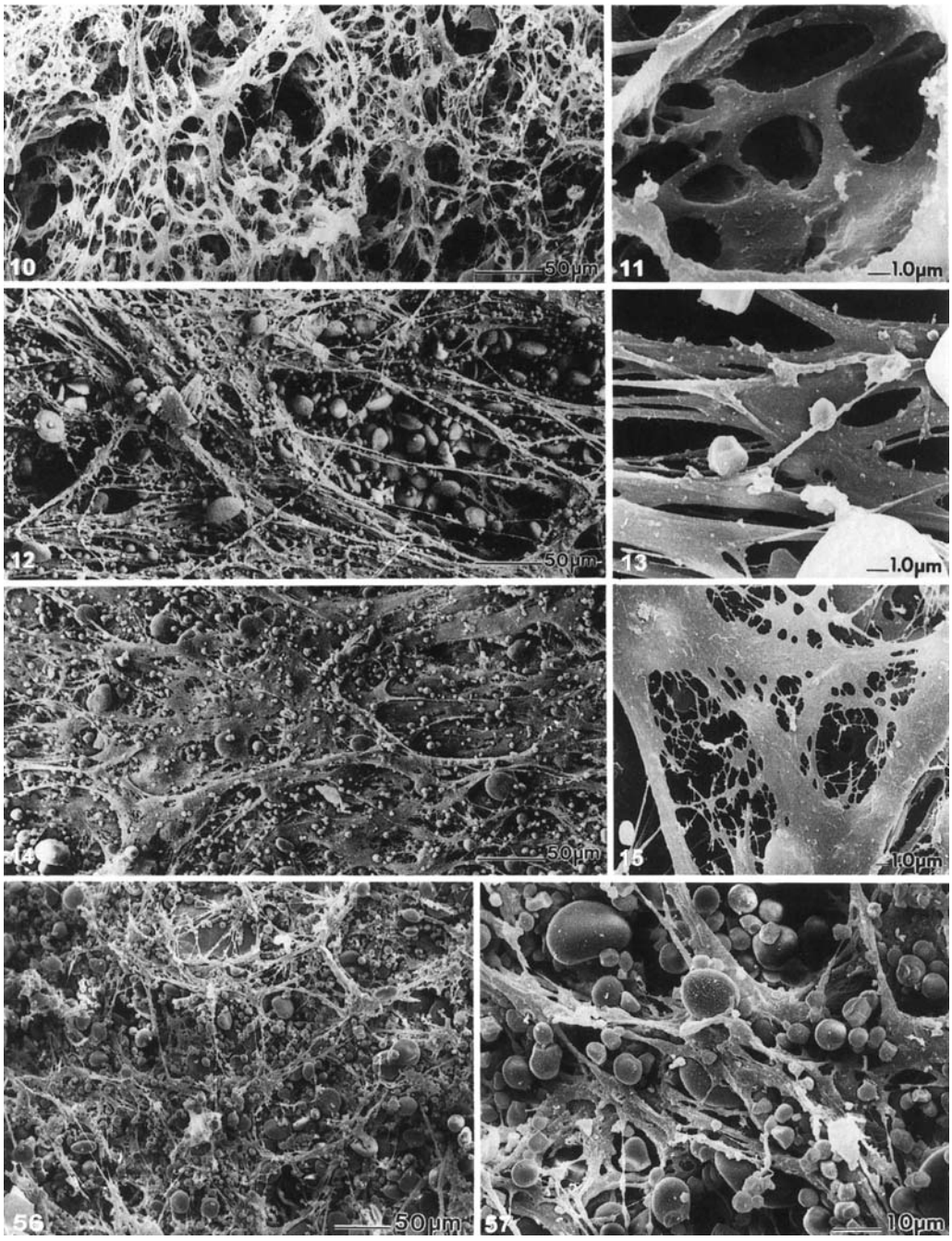


Fig. 15.44. (continued) *10*: Dough after addition of water (starch removed), not kneaded, practically unstretched, connected protein network. *11*: Detail from *10*. *12*: Kneaded dough with extended network. *13*: Detail from *12*, beginning film formation between protein strands. *14*: Optimally kneaded dough. *15*: Detail from *14* with partially perforated protein film. *56*: Highly overkneaded dough with short irregular protein strands. *57*: Detail from *56*.

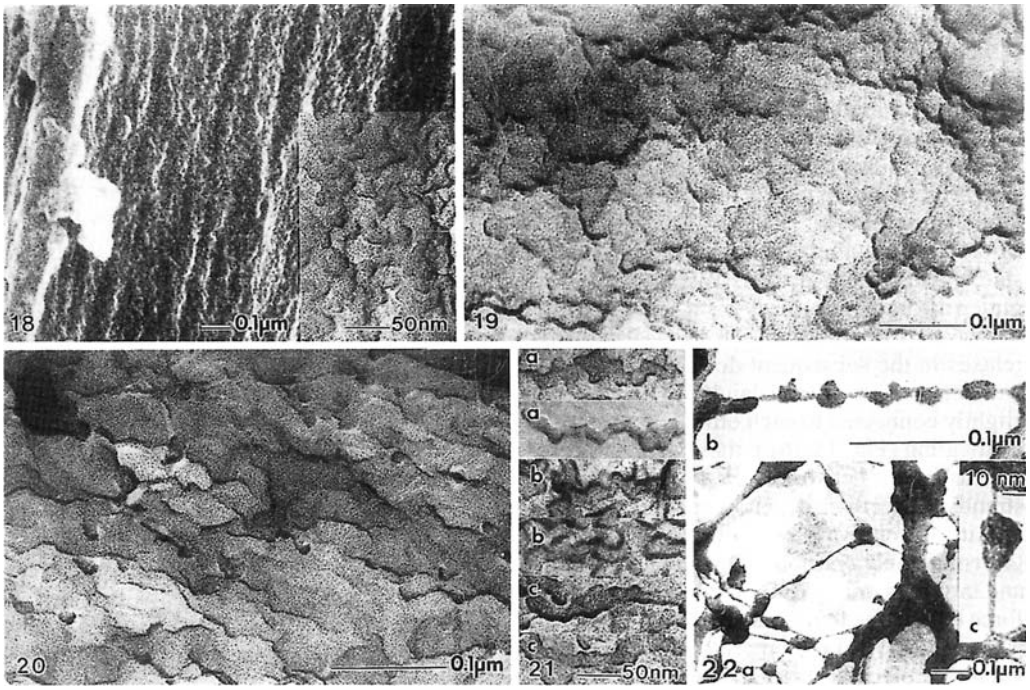


Fig. 15.44. (continued) *18–22*: *Transmission electron microscopy*. *18*: Slightly extended gluten protein strand with rough surface, enlarged section. *19*: Protein strand, more extended and with smoother surface compared with *18*. *20*: Platelet-like structures on a highly extended gluten film. *21*: Protein threads on a gluten film in a) water, b) triethylamine solution, c) dithioerythritol solution. *22*: a) Highly extended protein filbrils with thickenings, b,c) enlarged

mechanical stress and are stabilized in the form of superimposed layers due to intermolecular interactions.

These protein threads have a diameter of 10–30 nm and all look similar, irrespective of the type of preparation, e. g., in water (*21a*), in triethylamine (*21b*) or in dithioerythritol solution (*21c*). One-dimensional stretching causes individual protein threads to be partly stretched into fibrils, which, including the metal layers vapor deposited for stabilization, have a diameter of only 3 nm (*22a, b, c*).

Based on the microscope pictures, dough formation can be summarized as follows. The individual flour particles consist of a sponge-like protein matrix in which starch is embeded. After addition of water, the matrix protein becomes sticky and causes the flour particles to form a continuous structure on kneading. At the same time, the protein matrix is extended and protein films are formed at the branch points of the strands. In an optimally kneaded dough, the protein films are the predominant structural element and should contribute to the gas-holding capacity. Further kneading causes increased perforation of the films with formation of short, irregular protein strands, which are characteristic of overkneaded dough.

15.4.2.5.2 Dough Strengthening

A wheat dough is kneaded to the optimum and pressed, rolled or formed after a resting time of, e. g., up to 3 minutes or longer. This dough is subjected to a relatively weak shear compared with kneading. In this case, the resistance to extension is increased in tensile tests in the extensograph (Fig. 15.45).

Microscopic studies show that an unmixing of starch and gluten occurs. While starch and gluten are homogeneously distributed in freshly kneaded dough (Fig. 15.46a), the gluten relaxes in the sub-

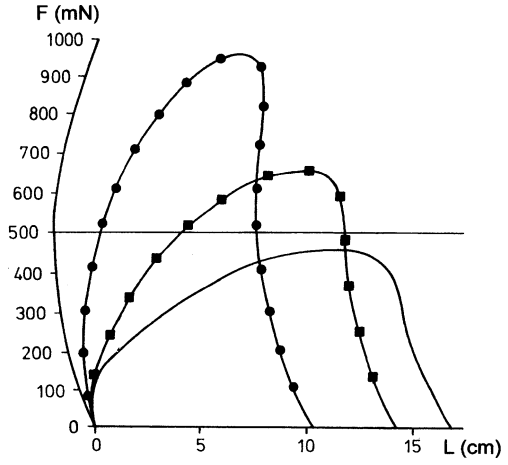


Fig. 15.45. Tensile tests with dough made of flour from the wheat cultivar Soisson (according to *Kieffer* and *Stein*, 1999). Dough after 45 min rest without shear (■–■), dough with shear after 135 min (●–●), dough without shear after 135 min (—)

sequent dough resting stage and contracts to form islands which are only slightly connected to each other (Fig. 15.46b). In shearing (Fig. 15.46c), these islands aggregate to form a network made of thicker gluten strands. The extent of the effect depends on the variety of wheat. In cultivars with weak gluten, the gluten is finely distributed even after shearing and the net is only weakly formed. The driving force behind the unmixing of starch and gluten is the tendency of gluten proteins to aggregate via intermolecular interactions, e. g., hydrogen bridges and hydrophobic interactions. Rye contains fewer gluten proteins than wheat. In dough development, its aggregation is additionally hindered by pentosans so that no gluten network can be formed.

Baking experiments have shown that the dough stability during fermentation is better, the baking form rounder and the baking volume larger if a clear unmixing of starch and gluten occurs due to the shearing of dough.

15.4.3 Baking Process

15.4.3.1 Conditions

The oven temperature and time of baking for some baked products are summarized in Table 15.50. Conditions for baking of rye and rye mix bread sometimes deviate from these values. They are prebaked at higher temperatures, for instance at 400 °C for 1–3 min, and then post-baked at 150 °C (for the effect on quality see Table 15.51). In a continuous process, tunnel-type ovens with circulation heaters are used. Gratings frequently serve as the conveyor band.

In an oven with the temperatures given in Table 15.50, since heat transfer occurs slowly in dough, there is a steep temperature gradient, 200 → 120 °C, inward from the crust of the dough piece. By the end of baking, a temperature of 96 °C is attained within the product. Higher temperatures up to 106 °C are found when the crust is able to resist the rise in inner steam pressure. The water evaporates only in the crust region during dough baking. Water diffusion towards the center of the bread can give the fresh crumb a higher moisture content than the dough. The steam concentration in the oven also affects the baking results. A steam header is provided in most oven designs to regulate oven moisture.

A baking weight loss is experienced as a result of water evaporation during crust formation. The extent of the loss is related to the form and size of the baked bread and is 8–14% of the fresh dough weight.

15.4.3.2 Chemical and Physical Changes – Formation of Crumb

The foamy texture of dough is changed into the spongy texture of crumb by baking. The following processes are involved in this conversion.

Up to ca. 50 °C, yeast produces CO_2 and ethanol at a rate that initially increases. At the same time, water and ethanol evaporate and, together with the liberated CO_2, expand the exisiting gas bubbles, further increasing the volume of the baked product. Parallel to this, the viscosity of the dough falls rapidly in the lower temperature range, reaches a minimum at ca. 60 °C, and then increases rapidly (Fig. 15.47). The increase is caused, on the one hand, by the swelling of starch and the accompanying release of amylose and, on the other hand, by protein denaturation. These processes result in a tremendous increase in the tensile stress of the dough and in the pressure in the gas bubbles at temperatures

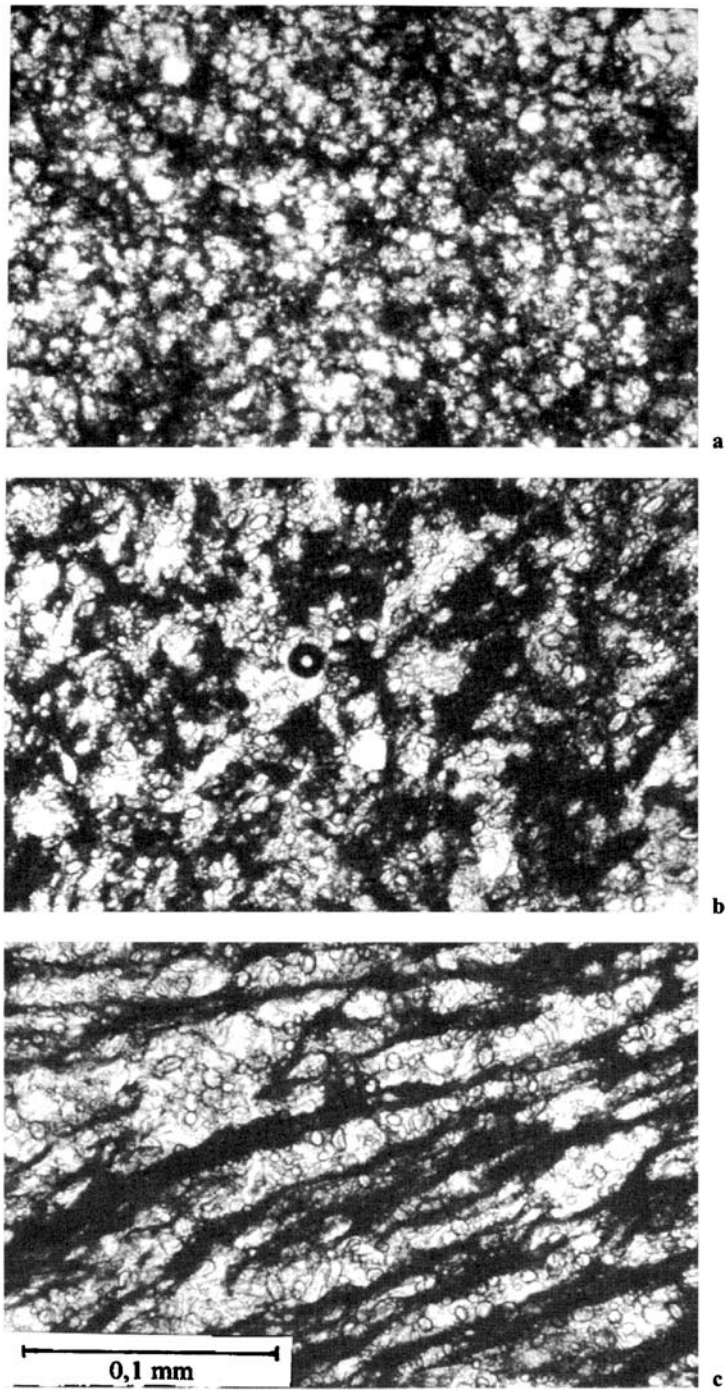


Fig. 15.46. Frozen section (thickness: 40 µm) of dough made of the flour Soisson (according to *Kieffer* and *Stein*, 1999). a) dough, freshly kneaded; b) dough, relaxed for 45 min; c) dough after 135 min and shearing

Table 15.50. Baking times and temperatures

Baked product	Weight (g)	Baking time (min)	Oven temperature (°C)
Buns, rolls and other small baked products	45	18–20	250–240
Wheat bread (self-supported dough)[a]	500	25–30	240–230
Wheat bread (pan-baked)[b]	500	35–40	240–230
Wheat bread (self-supported dough)	1000	40–50	240–220
Rye mix bread (self-supported dough)	1500	55–65	250–200
Rye bread (self-supported dough)	1500	60–70	260–200
Pumpernickel (pan-baked)	3000	16–14 hrs.	180–100

[a] Hearth bread.
[b] Pan bread.

Table 15.51. The effect of baking time and temperature on the quality of rye whole meal bread

Baking time (min)	90	180	270
Baking temperature (°C)	240–210	210–185	185–160
Bread yield (ml)	142	142	140
Crust strength (mm)	4	5	6
Taste	raw, slightly aromatic	aromatic	strongly aromatic

above ca. 60 °C (Fig. 15.47). The membranes give way and become permeable, allowing CO_2, ethanol, and water vapor to escape. The baking volume decreases slightly until the denatured proteins, with swollen and partially gelatinized starch, form a stable crumb framework, which contains pores down to 3 µm in diameter. Thin-walled membranes which can stand a greater increase in temperature on stretching, without becoming gas permeable; this is the prerequisite for a baked product with a large volume and uniform fine pores. A relatively large amount of high-molecular glutelins in gluten has a favorable effect. Dough made from wheat varieties with poor baking properties becomes gas permeable at a relatively low temperature and the baking volume remains correspondingly low. The extent of starch swelling depends on the available water. The water in dough is preferentially bound by prolamins, glutelins and pentosans. Part of this water becomes available to swell the starch during baking. Limited starch swelling results in a brittle crumb, whereas extensive swelling makes the crumb greasy or gluey.

In contrast to the crumb, the starch granules of the crust surface gelatinize almost completely. This is expecially the case when the oven humidity is high, e. g., when baking occurs below a steam header. Investigations involving gluten and starch mixtures to which the emulsifier stearyl-2-lactylate was added revealed that lipid transfer occurs from gluten to starch during heating of the mixture above 50 °C (Table 15.52). Apparently, the high swelling and gelatinization of the starch granules, which occurs above 50 °C (cf. Table 4.20), promotes lipid binding.

The specific volume of white bread is higher than that of rye bread (Table 15.53). The rye crumb is stronger and less elastic, suggesting that the pentosans can not fully compensate for the lack

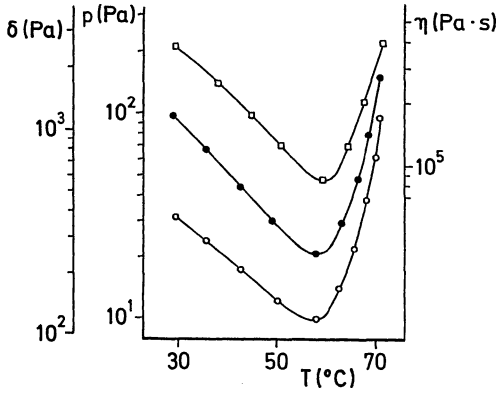


Fig. 15.47. Viscosity (η, □—□) and tensile stress (δ, ○—○) of a wheat dough as well as pressure (p, ●—●) in the gas bubbles as a function of temperature during the baking process (according to *Bloksma*, 1990)

of texturizing quality of rye proteins (cf. 15.1.5). Heating of a dough accelerates enzymatic reactions, e. g., starch degradation (cf. 15.4.2.4). Above the "temperature optimum" (cf. 2.5.4.3) the reactions are inhibited by denaturation of the enzymes.

The vitamins of the B group are lost to different extents during baking. In white bread, the losses amount to 20% (flour type 550)−50% (flour type 1150) of thiamine, 6–14% of riboflavin and 0–15% of pyridoxine.

Starch degrades to dextrins, mono- and disaccharides at the relatively high temperatures to which the outer part of the dough is exposed. Caramelization and nonenzymatic browning reactions also occur, providing the sweetness and color of the crust. The thickness of the crust is dependent on temperature and baking time (Table 15.51) and type of baked product (Table 15.54). The composition of some types of bread is presented in Table 15.55.

Table 15.52. The effect of temperature on stearyl-2-lactylate (SSL) binding in a blend of gluten and starch[a]

T (°C)	SSL free[b]	SSL bound[b] to	
		gluten	starch
30	22.0	64	14
40	20.0	66	14
50	22.0	62	16
60	20.0	6	74
70	16.0	6	78
80	12.0	8	80
90	12.0	2	86

[a] Blends of 17.9 g starch, 2.7 g gluten and 0.103 g SSL.
[b] Values in % of total SSL.

Table 15.53. Specific volumes[a] of bread

Bread variety	ml/g
Toast bread	3.5–4.0
White bread	3.3–3.7
White mix bread[b]	2.5–3.0
Rye mix bread[b]	2.1–2.6
Rye bread	1.9–2.4

[a] Specific volume = volume/weight.
[b] cf. Table 15.63.

Table 15.54. Crumb and crust ratios in different bread varieties

Bread variety	Crumb (%)	Crust (%)
Buns, rolls (50 g)	72.5	27.5
Stick (French) white bread	68.5	31.5
White bread, pan-baked (500 g)	75.0	25.0
White bread (self-supported dough, 500 g)	73.8	26.2
Rye mix bread (self-supported dough, 1000 g)	73.3	26.7
Rye mix bread (pan-baked, 1000 g)	84.5	15.5

15.4.3.3 Aroma

15.4.3.3.1 White Bread Crust

The substances which produce the aroma profile of a loaf of French bread (baguette) (Table 15.56) originate from the crust. They are listed in Table 15.57. 2-Acetyl-1-pyrroline produces the roasty note in the aroma profile and the *Strecker* aldehydes methylpropanal, 2- and 3-methylbutanal the malty note. The compounds (E)-2-nonenal and 1-octen-3-one are primarily responsible for the fatty impression.

The aroma of a baguette is not stable. Even four hours after the bread has left the oven, the intensities of the malty and sweet notes in the

Table 15.55. Chemical composition of some types of bread

Bread	Water	Protein (N × 5.8)	Available carbohydrates	Dietary fiber	Lipid	Minerals
	(%)	(%)	(%)	(%)	(%)	(%)
White bread	38.3	7.6	49.7	3.2	1.2	1.6
White mix bread	37.6	6.2	47.7	4.6	1.1	1.5
Rye mix bread	39.1	6.4	43.7	6.1	1.1	1.8
Rye bread	38.1	6.2	45.8	6.5	1.0	1.6
Rye whole grain bread	42.0	6.8	38.7	8.1	1.2	1.5
Crisp bread	7.0	9.4	66.1	14.6	1.4	2.3

Table 15.56. Aroma profile of baguette after 1 h and 4 h[a]

Aroma quality	Intensity[b] after	
	1 h	4 h
Roasty	1.8	1.9
Malty	1.9	0.4
Sweet	1.2	0
Fatty	1.0	2.3

[a] After leaving the oven the baguettes were cooled for 1 h at room temperature, then wrapped in aluminium foil and stored at room temperature for another 3 h.
[b] The intensity of each aroma quality was evaluated from 0–3 (strong). Average values of five testers.

Table 15.57. Odorants of the baguette crust[a]

Compound	Concentration (µg/kg)	Aroma-value[b]
Methylpropanal	1750	31
2-Methylbutanal	962	18
3-Methylbutanal	335	26
Methional	29	107
Dimethyl trisulfide	5.1	59
2,3-Butandione	1320	203
2-Acetyl-1-pyrroline	16	2191
2-Ethyl-3,5-dimethylpyrazine	3.2	19
Hexanal	214	7
1-Octen-3-one	6.6	150
(E)-2-Nonenal	87	164
(E,E)-2,4-Decadienal	56	21

[a] After leaving the oven the baguettes were cooled for 1 h at room temperature, then the crust was separated, frozen with liquid nitrogen and analyzed.
[b] On the basis of the odor threshold of the compound on starch.

aroma profile are greatly reduced and the fatty note predominates (Table 15.56). These changes are caused by the differences in the evaporation rates of the aroma substances. To determine these rates, the amounts of odorants which evaporate from a baguette in 15 min are collected at the times given in Table 15.58 and measured. The results in Table 15.58 show the evaporation rates of the malty smelling aldehydes methylpropanal, 2- and 3-methylbutanal decrease continuously in accordance with the changes in the aroma profile. This also results in the fact that odorants like the fatty smelling (E)-2-nonenal are more detectable with time. However, the intensity of the fatty note also increases because the evaporation rate of (E)-2-nonenal increases (Table 15.58), possibly due to the decomposition of the linoleic acid hydroperoxides formed during baking. 2-Acetyl-1-pyrroline evaporates uniformly (Table 15.58); the intensity of the roasty note is correspondingly stable during storage for 4 hours (Table 15.56). The losses of this odorant in the white bread crust on longer storage is shown in Table 15.59.

The aroma is influenced by the recipe but also by the fermentation, e. g., the *Strecker* aldehydes increase and those from lipid peroxidation decrease if the dough matures at lower temperatures (Table 15.60). An extension of the kneading process

Table 15.58. Concentrations of the odorants in the headspace of baguettes as a function of storage at room temperature[a]

Odorants	Concentration (ng/l air) after		
	1 h	2.5 h	4 h
Methylpropanal	830	536	400
2-Methylbutanal	320	230	170
3-Methylbutanal	150	85	68
2,3-Butandione	980	705	670
2-Acetyl-1-pyrroline	3.7	3.3	3.7
Hexanal	216	237	254
(E)-2-Nonenal	28	36	44
(E,E)-2,4-Decadienal	7.8	6.5	6.6

[a] To determine the concentration, the air above the baguette was collected for 15 min.

Table 15.59. Decrease (%) in 2-acetyl-1-pyrroline in the crust of white bread during storage

Time (h)	2-Acetyl-1-pyrroline
0	0
3	46
24	77
168	89

Table 15.60. Influence of the fermentation time and temperature on the concentrations of odorants in the baguette crust[a]

Odorant	Concentration (μg/kg)	
	Baguette I	Baguette II
2-Acetyl-1-pyrroline	16	14
Methylpropanal	1733	4331
2-Methylbutanal	1147	1487
3-Methylbutanal	426	680
Methional	31	49
1-Octen-3-one	3.8	2.1
(E)-2-Nonenal	61.8	40.4

[a] Dough I was fermented for 2 h 40 min at 26 °C, dough II for 2 h at 22 °C and then 18 h at 4 °C.

and the resulting increase in the dough temperature result in a decrease in the *Strecker* aldehydes in the crust (Fig. 15.48).

15.4.3.3.2 White Bread Crumb

In dilution analyses, 3-methylbutanol, 2-phenylethanol, methional, (E)-2-nonenal and (E,E)-2,4-decadienal were identified as the most important odorants in the baguette crumb. The odorants which produce the intense aroma note were detected in a comparison of two baguettes which were baked with two differently composed pre-fermented doughs. The crumb of baguette I had a pleasant intense odor, but in II this note was weak and a rancid aroma defect appeared. Table 15.61 shows that the concentrations of 2-phenylethanol and 3-methylbutanol, which have a flowery/intense and alcoholic odor, are higher in I than in II. The higher concentration of the sweaty 2-/3-methylbutyric acid in II produces the rancid aroma defect. A low yeast concentration in a liquid preliminary dough, which is only 1.5% based on the finished dough I compared with 4.6% in dough II, is the prerequisite for an optimal formation of both the alcohols shown in Fig. 15.49. The curves show that the concentrations of the two aroma substances reach a plateau after eight hours under the selected conditions. Their precursors phenylalanine and leucine, which originate in the flour and are degraded by yeast via the *Ehrlich* pathway to give the odorants (cf. Formula 15.8) are converted after this time or the bioconversion stops because important yeast nutrients are increasingly lacking.

Table 15.61. Odorants of white bread crumb – comparison of two kinds of bread subjected to different dough making[a]

Compound	Concentration (mg/kg)	
	Bread I	Bread II
2-Phenylethanol	11.8	2.87
3-Methylbutanol	18.1	9.7
2-/3-Methylbutyric acid	0.55	1.5

[a] Recipe (kg): flour (I: 4.15; II: 4.9), water (I: 2.27; II: 2.825), salt (I, II: 0.11), yeast (I: 0.125; II: 0.325), pre-ferment (I: 2.005 of A; II: 0.5 of B). Pre-ferment A: a suspension of flour (1 kg), water (1 kg) and yeast (5 g) was incubated for 15 h at 30 °C. Pre-ferment B: dough made of flour (250 g), water (175 g) and yeast (75 g) was incubated as in A.

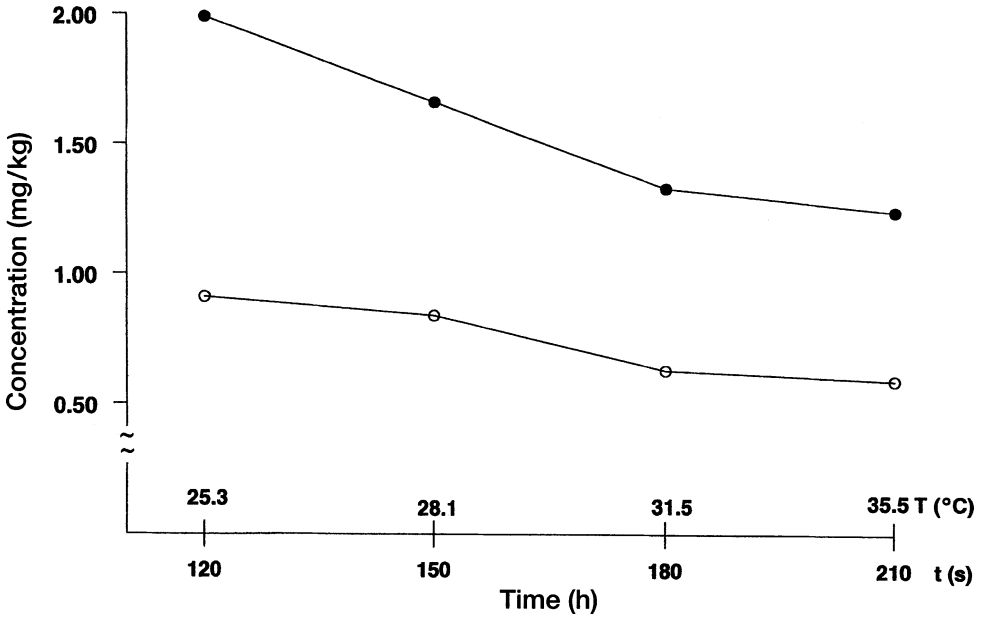
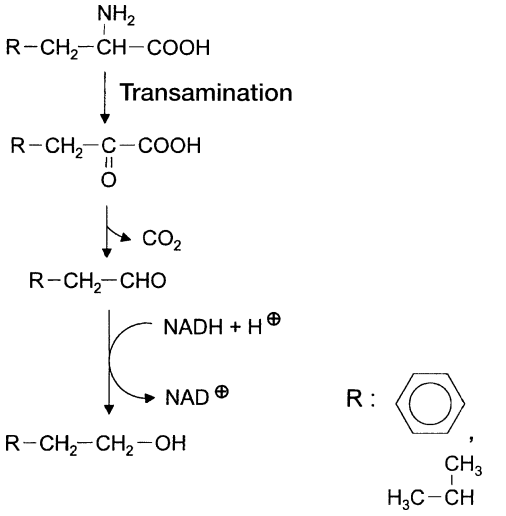


Fig. 15.48. Influence of the kneading intensity on the dough temperature and on the concentrations of 2- and 3-methylbutanal in the baguette crust. 2-Methylbutanal (●–●), 3-methylbutanal (○–○). *Abscissa*: kneading time (s) and dough temperature T (°C) (according to *Zehentbauer* and *Grosch*, 1998)



(15.8)

The crumb contains the precursors of the roasty odorants 2-acetyl-1-pyrroline and 2-acetyltetrahydropyridine (cf. 5.3.1.6), but the temperature in the baking process is sufficient to form these substances only in the crust. If white bread is toasted, the two odorants are formed with increasing browning of the toast (Fig. 15.50), whereby 2-acetyl-1-pyrroline increases much more. Of the odorants from the *Maillard* reaction, 4-hydroxy-2,5-dimethyl-3(2H)-furanone also appears with a high aroma value. In the case of fiber-enriched toast bread 2-/3-methylbutyric acid is a critical odorant. The addition of oat bran is preferable to wheat bran because it yields less 2-/3-methylbutyric acid and, consequently, a rancid/sweaty aroma defect is avoided.

Important precursors of 2-acetyl-1-pyrroline are ornithine and 2-oxopropanal (cf. 5.3.1.7), mainly originate from yeast metabolism. The concentrations of 2-acetyl-1-pyrroline and 2-acetyltetrahydropyridine in the crumb are less than those in the crust by a factor of about 30. The reason being that only in the crust area is the temperature high enough to release aroma substances or their precursors from yeast.

15.4.3.3.3 Rye Bread Crust

Dilution analyses show that the following compounds are involved in the aroma of rye bread

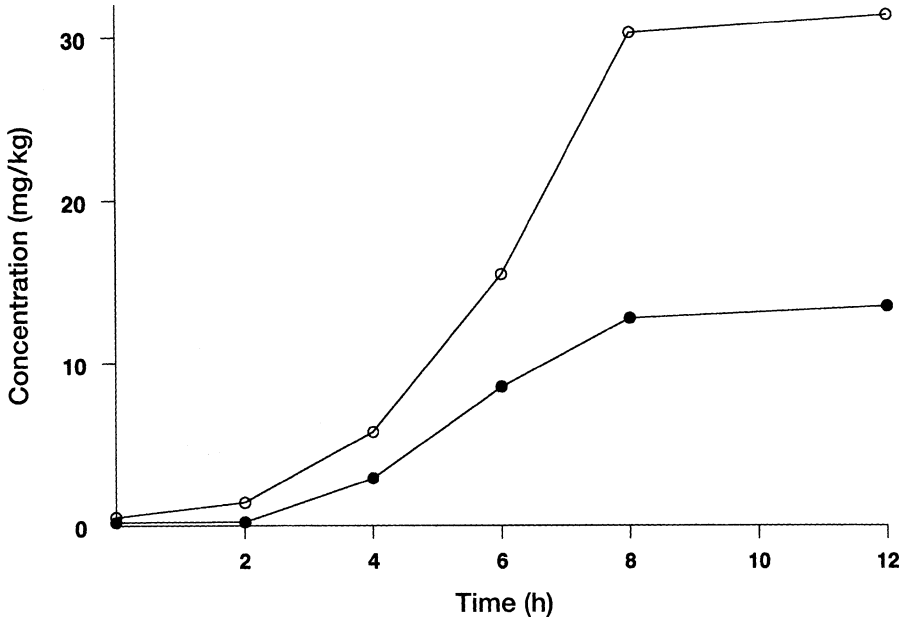


Fig. 15.49. Time curves of the formation of 2-phenylethanol (•–•) and 3-methylbutanol (○–○) in a prefermented dough (according to *Gassenmeier* and *Schieberle*, 1995): flour (59 g), water (50 g) and yeast (0.25 g) were incubated at 30 °C

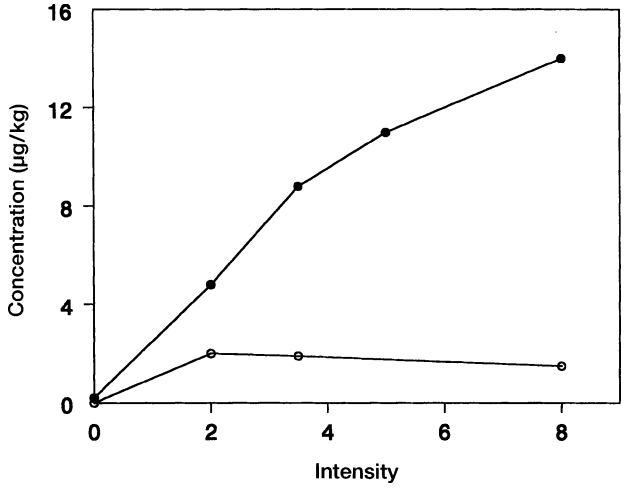


Fig. 15.50. Formation of 2-acetyl-1-pyrroline (•–•) and 2-acetyltetrahydropyridine (○–○) on toasting white bread (according to *Rychlik* and *Grosch*). Abscissa: intensity of browning (8: very strong).

crust with high FD values: methional, 2-/3-methylbutanal, 4-hydroxy-2,5-dimethyl-3(2H)-furanone (HD3F), 2-furfurylthiol, (Z)-4-heptenal, 1-octen-3-one, (Z)-1,5-octadien-3-one, phenylacetaldehyde, 2,3-diethyl-5-methylpyrazine and (E)-β-damascenone. The difference in the crust aroma of white and rye bread is due to the fact that the rye bread crust contains much more 3-methylbutanal, methional and HD3F but less 2-acetyl-1-pyrroline (Table 15.62). 2-Furfurylthiol also contributes only to the aroma of the rye bread crust.

Table 15.62. Concentrations of odorants in the crusts of white bread and rye bread

Compound	Concentration (μg/kg)	
	White bread	Rye bread
2-Acetyl-1-pyrroline	19	0.8
3-Methylbutanal	1406	3295
Methional	51	480
(E)-2-Nonenal	56	45
4-Hydroxy-2,5-dimethyl-3(2H)-furanone	1920	4310

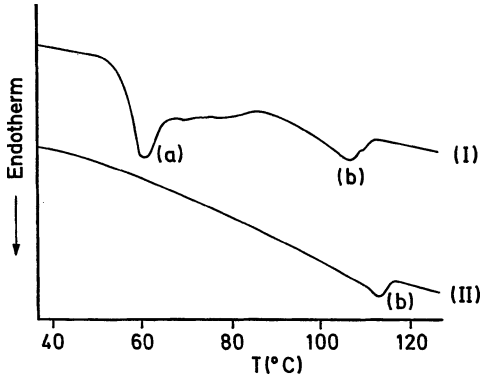


Fig. 15.51. DSC thermograms of wheat starch in water (45:55, g/g) I: native starch, II: gelatinized starch (according to *Slade, Levine*, 1991)

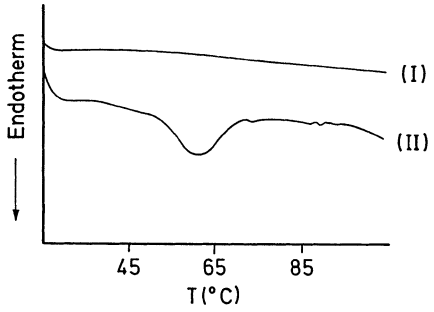


Fig. 15.52. DSC thermograms of white bread: I: fresh from the oven, II: after storage for 1 week at room temperature (according to *Slade, Levine*, 1991)

15.4.4 Changes During Storage

Bread quality changes rapidly during storage. Due to moisture adsorption, the crust loses its crispiness and glossyness. The aroma compounds of freshly baked bread evaporate or are entrapped preferentially by amylose helices which occur in the crumb. Repeated heating of aged bread releases these compounds. Very labile aroma compounds also contribute to the aroma of bread, e. g., 2-acetyl-1-pyrroline. They decrease rapidly on storage due to oxidation or other reactions (Table 15.59).

The crumb structure also changes, although at a lower rate. The crumb becomes firm, its elasticity and juiciness are lost, and it crumbles more easily. The so-called staling defect of the crumb is basically a starch retrogradation phenomenon (cf. 4.4.4.14.2) which proceeds at different rates with amylose and amylopectin. On cooling bread, the high-molecular amylose very rapidly forms a three-dimensional network and the crystalline states of order of amylose/lipid complexes increase. These processes stabilize the crumb.

On the other hand, the amylopectin is in an amorphous state because the crystalline regions present in flour melt on baking. This is in contrast to the behavior of crystalline amylose/lipid complexes. Thermograms of an aqueous starch suspension (Fig. 15.51) show the differences in the melting points. In comparison with native starch (I), the endotherm peak *a* at 60 °C caused by the melting of crystalline amylopectin is absent in the thermogram of gelatinized starch (II). However, the melting point of amylose/lipid complexes (ca. 110 °C, peak *b* in curve II) is not reached in the crumb on baking.

Staling of white-bread crumb begins with the formation of crystalline structures in amylopectin. The endotherm peak at 60 °C appears again in the thermogram of stored white bread (Fig. 15.52). A state of order arises which corresponds to that of B starch (cf. 4.4.4.14.2) and binds up to 27% of crystal water, which is withdrawn from amorphous starch and proteins. The crumb loses its elasticity and becomes stale. On storage of white bread, the amount of water that can freeze decreases corresponding to the conversion to nonfreezing crystal water (Fig. 15.53).

The formation of crystal nuclei, which proceeds very rapidly at 0 °C and does not occur at temperatures below −5 °C (Fig. 15.54), determines the rate of amylopectin retrogradation. The nuclei grow most rapidly shortly before the melting point (60 °C) is reached (Fig. 15.54).

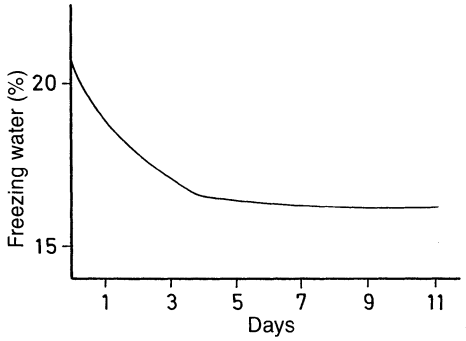


Fig. 15.53. Decrease in freezing water in the storage of white bread. The bread was stored at room temperature encapsulated to prevent drying (according to *Slade, Levine*, 1991)

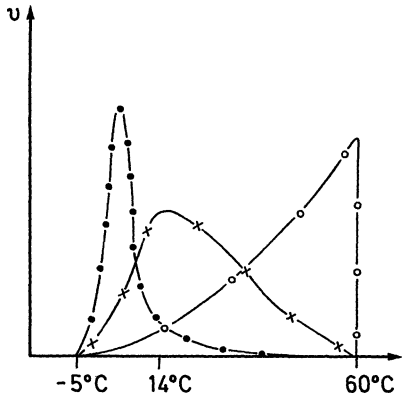


Fig. 15.54. Rate of crystallization of B starch as a function of temperature, (– • –•) formation of crystal nuclei, (–○ –○) crystal growth, (– × – × –) total crystal formation (according to *Slade, Levine*, 1991)

The ageing process resulting from these events reaches a maximum at ca. 14 °C. As a result of this course, the ageing of white-bread crumb can be prevented by storage at <-5 °C. But the temperature must very quickly fall below the critical temperature for nucleation.

Temperatures above 14 °C also inhibit staling, e. g., increasing the storage temperature from 21 to 35 °C decreases the rate of amylopectin retrogradation by a factor of 4 and improves freshness of the crumb, but the aroma is dissipated. Increased protein or pentosan content slows retrogradation. A choice – actually a rule – to extend the shelf life or freshness of the baked product is the use of emulsifiers, such as mono-

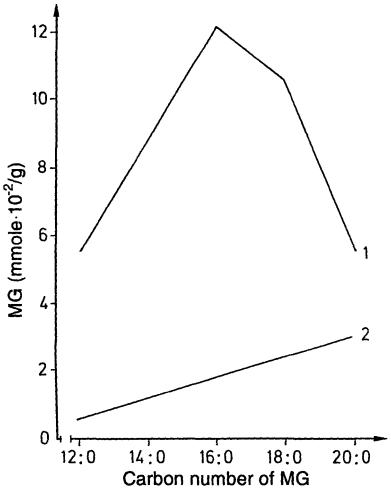


Fig. 15.55. Complex formation between monoacylglycerides (MG) and amylose (1) or amylopectin (2) (according to *Knightly*, 1977). *x-axis*: carbon number of the saturated acyl residue. *y-axis*: tendency of MG to form a complex with amylose or amylopectin (mmole $\cdot 10^{-2}$ MG/g polysaccharide)

acylglycerides or stearyl-2-lactylate. During baking the emulsifier will be complexed with both starch constituents, though to a different extents (Fig. 15.55). Such complexes retard starch retrogradation. Fewer carbohydrates can be extracted from starch/monoacylglyceride adducts than from starch alone. This effect probably contributes to the increase in the cooking stability of pasta after addition of monoacylglycerides (cf. 15.5).

The staling of crumb is also delayed by bacterial α-amylase. From amylopectin, this enzyme cleaves branched oligosaccharides that consist of 19–24 glucose units. Consequently, the formation of crystalline structures in amylopectin is hindered.

15.4.5 Bread Types

Only those bread types of significant economic importance are listed in Table 15.63. Corresponding data on chemical composition are given in Table 15.55.

Crisp bread (Knaeckebrot) and Pumpernickel are special rye breads.

Table 15.63. Bread varieties

No.	Bread variety	Formulation
1.	Wheat bread (white bread)	At least 90% wheat; middlings less than 10%; occasionally with addition of dairy products, sugar, shortenings.
2.	Wheat mix bread	50–89% wheat, the rest rye milling products and other ingredients as under 1.
3.	Rye mix bread	50–89% rye, the rest wheat milling products and others as under 1.
4.	Rye bread	At least 90% rye flour, up to 10% wheat flour; other ingredients as under 1.
5.	Rye whole grain bread	From whole rye meal including also whole kernels, other rye and wheat products less than 10%.

The flat crisp bread is produced mostly from whole rye meal with low α-amylase activity. The dough is ice-cooled and mixed using compressors until foaming occurs, then sheeted and baked for 8–10 min in a tunnel-type oven. Additional drying reduces moisture by 10–20% to a level of 5%. In addition to this mechanically leavened bread, made by mixing air or nitrogen into the dough, there are crisp breads in which biological leavening (yeast or rye sour) is used. Flat bread is also produced in fully automatic cooker-extruders. The heart of these systems is represented by single-screw or double-screw extruders with co- or counter-rotating screws. This is mainly a high-temperature, short-time heating process. The material is degraded to some extent (partial starch gelatinization amongst others) by a combination of pressure, temperature, and shear forces and then deformed by the nozzle head plate. The sudden drop in pressure at the nozzle mouth results in expansion. Water then evaporates and causes the formation of the desired light and bubbly structure.

Pumpernickel bread originates from Westphalia. The sour rye dough, heated in sealed ovens, is more steam-cooked than baked (cf. Table 15.50). Prolonged heating considerably degrades the starch into dextrins and maltose, which are responsible for the sweet taste. The increased buildup of melanoidin pigments accounts for the dark color.

15.4.6 Fine Bakery Products

Until a few years ago, the production of fine bakery products was the domain of confectioners. Today, the importance of the industrial production of these products has grown substantially. In general, the process techniques described for the production of bread can be adapted for fine bakery products. Thus, the relevant machine-building companies offer practically automatic production lines for various fine and stable bakery products.

15.5 Pasta Products

15.5.1 Raw Materials

Pasta products are made of wheat semolina and grist (cf. 15.3.1.3), in which the flour extraction grade is less than 70%, and may incorporate egg. The preferred ingredient is durum wheat semolina rather than the soft wheat counterpart (farina) since the former has better cooking and biting strengths and also has a higher content of carotenoids (cf. 15.2.5) which provide the yellow color of pasta products. In wheat mixtures, the soft wheat characteristics emerge when the soft wheat content is higher than 30%. In egg-pasta products (chemical composition in Table 15.64), 2–4 eggs/kg semolina provide a pasta with improved cooking strength and color.

Table 15.64. Composition of pasta products containing eggs (4 eggs per 1 kg flour)

Constituent	%	Constituent	%
Water	11.1	Available carbohydrates	70.0
Protein (N × 5.8)	12.3	Dietary fiber	3.4
Fat	2.9	Minerals	1.0

15.5.2 Additives

Cysteine hydrochloride (about 0.01%) lowers the mixing/kneading time by 15–20% (cf. 15.4.1.4.4). The cysteine also inhibits melanoidin build-up due to nonenzymatic browning, and suppresses the greyish-brown pigmentation. Addition of monoglycerides (about 0.4%) brings about amylose and amylopectin complexing, thereby increasing cooking strength (cf. 15.4.4). Through competitive inhibition, ascorbic acid prevents the action of lipoxygenase (Fig. 15.56). Although the enzyme is a lipoxygenase with high regio- and stereospecificity (cf. 3.7.2.2) and only slowly cooxidizes carotenoids, the low enzyme activity can still destroy the pigments because pasta production is a relatively long process. Addition of ascorbic acid inhibits this cooxidation (Fig. 15.57).

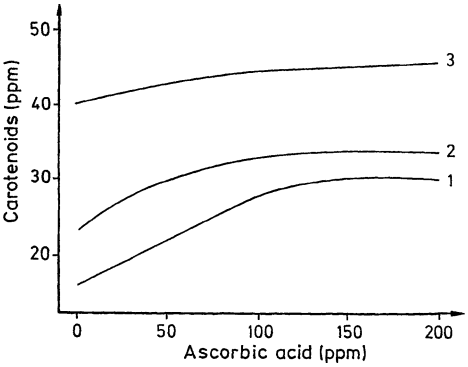


Fig. 15.57. Carotenoid stability in pasta products made of three Durum wheat cultivars as affected by added ascorbic acid (according to *Walsh* et al., 1970). 1–3 wheat cv. Durum

15.5.3 Production

Pasta products are manufactured continuously by a vacuum extruder, which consists of a mixing trough and press segments. The vacuum is used to retard oxidative degradation of carotenoids.
The semolina and added water (30%) and, when necessary, egg or egg powder are mixed in a mixing trough to form a crumb dough (diameter 1–3 mm), pressed at 150–200 bar into a uniform paste and then pressed through an extruder pressure head die to provide the familiar pasta strings.
Drying is the most demanding stage of pasta manufacturing. The surface of a pasta product must not be allowed to harden prior to the interior core, otherwise cracks, fractures or bursts develop. The freshly extruded strings are initially dried from the outside until they are no longer sticky, then drying is continued at 45–60 °C, either very slowly or stepwise. The moisture content drops to 20–24% after such a predrying process. The moisture is then allowed to equilibrate between inner and outer parts, which brings the content of the final dried product to 11–13%.

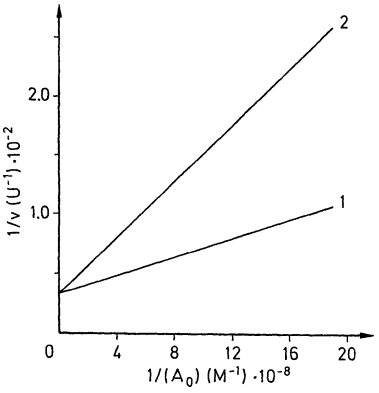


Fig. 15.56. Competitive inhibition of wheat lipoxy-genase by ascorbic acid (according to *Walsh* et al., 1970). Activity assay with linoleic acid as a substrate (1) without, and (2) in the presence of ascorbic acid ($2 \cdot 10^{-6}$mol/l)

15.6 References

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