18 Fruits and Fruit Products

18.1 Fruits

18.1.1 Foreword

Fruits include both true fruits and spurious fruits, as well as seeds of cultivated and wild perennial plants. Fruits are commonly classified as pomaceous fruits, stone fruits, berries, tropical and subtropical fruits, hard-shelled dry fruits and wild fruits. The most important fruits are presented in Table 18.1 with pertinent data on botanical classification and use. Table 18.2 provides data about fruit production.

18.1.2 Composition

Fruit composition can be strongly influenced by the variety and ripeness, thus data given should be used only as a guide. Table 18.3 shows that the dry matter content of fruits (berries and pomme, stone, citrus and tropical fruits) varies between 10–20%. The major constituents are sugars, polysaccharides and organic acids, while N-compounds and lipids are present in lesser amounts. Minor constituents include pigments and aroma substances of importance to organoleptic quality, and vitamins and minerals of nutritional importance. Nuts are highly variable in composition (Table 18.4). Their moisture content is below 10%, N-compounds are about 20% and lipids are as high as 50%.

18.1.2.1 N-Containing Compounds

Fruits contain 0.1–1.5% N-compounds, of which 35–75% is protein. Free amino acids are also widely distributed. Other nitrogen compounds are only minor constituents. The special value of nuts, with their high protein content, has already been outlined.

18.1.2.1.1 Proteins, Enzymes

The protein fraction varies greatly with fruit variety and ripeness. This fraction is primarily enzymes. Besides those involved in carbohydrate metabolism (e. g., pectinolytic enzymes, cellulases, amylases, phosphorylases, saccharases, enzymes of the pentose phosphate cycle, aldolases), there are enzymes involved in lipid

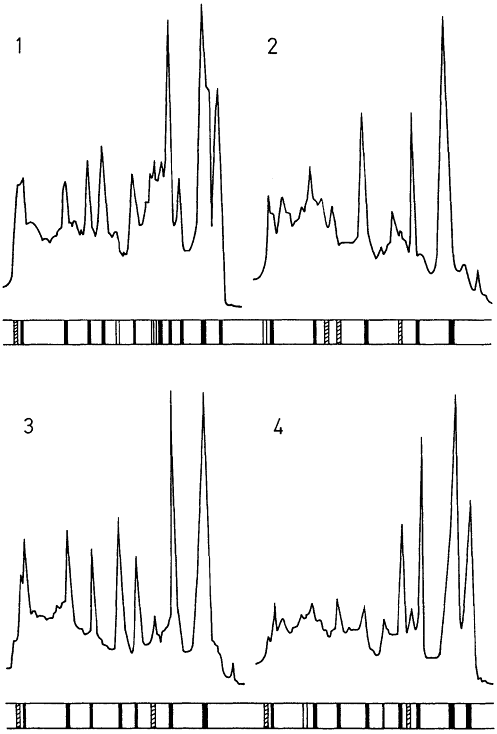


Fig. 18.1. Protein patterns of various wine cultivars obtained by isoelectric focussing (pH 3–10) using Sephadex G-75 as a gel support medium. Staining was done by Coomassie Blue. The figures show the electropherograms and the corresponding densitograms. Cultivation region South Palatinate; *1* Morio Muscat, *2* Mueller-Thurgau, *3* Rulaender, *4* Sylvaner (according to *Drawert* and *Mueller*, 1973)

Table 18.1. Eddible fruits: a classification

Number	Common name	Latin name	Family/ subfamily	Form of consumption
Pomme fruits				
1	Apple	*Malus sylvestris*	Rosaceae	Fresh, dried, purée, jelly, juice, apple cider, brandy
2	Pear	*Pyrus communis*	Rosaceae	Fresh, dried, compote, brandy
3	Quince	*Cydonia oblonga*	Rosaceae	Jelly, ingredient of apple purée
	apple shaped	*var. maliformis*		
	pear shaped	*var. pyriformis*		
Stone fruits				
4	Apricot	*Prunus armeniaca*	Rosaceae	Fresh, dried, compote, jam, juice, seed for persipan, brandy
5	Peach	*Prunus persica*	Rosaceae	Fresh, compote, juice, brandy
6	Prune/plum	*Prunus domestica*	Rosaceae	Fresh, dried, compote, jam, brandy
7	Sour cherry	*Prunus cerasus*	Rosaceae	Fresh, compote, jam, juice, brandy
8	Sweet cherry	*Prunus avium*	Rosaceae	Fresh, candied, compote
Berry fruits				
9	Blackberry	*Rubus fruticosus*	Rosaceae	Fresh, jam, jelly, juice, wine, liqueur
10	Strawberry	*Fragaria vesca*	Rosaceae	Fresh, compote, jam, brandy
11	Bilberry	*Vaccinium myrtillus*	Ericaceae	Fresh, compote, jam, brandy
12	Raspberry	*Rubus idaeus*	Rosaceae	Fresh, jam, jelly syrup, brandy
13	Red currant	*Ribes rubrum*	Saxifragaceae	Fresh, jelly, juice, brandy
14	Black currant	*Ribes nigrum*	Saxifragaceae	Fresh, juice, liqueur
15	Cranberry	*Vaccinium vitis-idaea*	Ericaeae	Compote
16	Gooseberry	*Ribes uva-crispa*	Saxifragaceae	Unripe: compote; ripe: fresh, jam, juice
17	Grapes	*Vites vinifera ssp. vinifera*	Vitaceae	Fresh, dried (raisins) juice, wine, brandy
Citrus fruits				
18	Orange	*Citrus sinensis*	Rutaceae	Fresh, juice, marmelade
19	Grapefruit	*Citrus paradisi*	Rutaceae	Fresh, juice
20	Kumquat	*Fortunella margarita*	Rutaceae	Fresh, compote, jam
21	Mandarine	*Citrus reticulata*	Rutaceae	Fresh, compote
22	Pomelo	*Citrus maxima*	Rutaceae	Fresh, juice
23	Seville orange	*Citrus aurantium ssp. aurantium*	Rutaceae	Candied, marmalade
24	Lemon	*Citrus limon*	Rutaceae	Juice
25	Citron	*Citrus medica*	Rutaceae	Peel candied (citronat)
Other tropical/ subtropical fruits				
26	Acerola	*Malpighia emarginata*	Malpighiaceae	Fresh, compote, juice
27	Pineapple	*Ananas comosus*	Bromeliaceae	Fresh, compote, jam, juice
28	Avocado	*Persea americana*	Lauraceae	Fresh
29	Banana	*Musa*	Musaceae	Fresh, dried, cooked, baked
30	Cherimoya	*Annona cherimola*	Annonaceae	Fresh
31	Date	*Phoenix dactylifera*	Arecaceae	Fresh, dried
32	Fig	*Ficus carica*	Moraceae	Fresh, dried, jam, dessert wine
33	Indian fig	*Opuntia ficus-indica*	Cactaceae	Fresh
34	Guava	*Psidium guajava*	Myrtaceae	Compote, juice
35	Persimmon	*Diospyros kaki*	Ebenaceae	Fresh, candied, compote

Table 18.1. (Continued)

Number	Common name	Latin name	Family/ subfamily	Form of consumption
36	Kiwi	*Actinidia chinensis*	Actinidiaceae	Fresh, compote
37	Litchi	*Litchi chinensis*	Sapindaceae	Fresh, dried, compote
38	Mango	*Mangifera indica*	Anacardiaceae	Fresh, compote, juice
39	Melons			
	cantaloups	*Cucumis melo*	Cucurbitaceae	Fresh
	watermelon	*Citrullus lanatus*	Cucurbitaceae	Fresh
40	Papaya	*Carica papaya*	Caricaceae	Fresh, compote, juice
41	Passion fruit	*Passiflora edulis*	Passifloraceae	Fresh, juice
42	Golden shower	*Cassia fistula*	Caesalpiniaceae	Fresh
Shell(nut) fruits				
43	Cashew nut	*Anacardium occidentale*	Anacardiaceae	Roasted
44	Peanut	*Arachis hypogaea*	Fabaceae	Roasted, salted
45	Hazel-nut (Filbert)	*Corylus avellana*	Betulaceae	Fresh, baked and confectionary products (nougat, crocant)
46	Almond sweet bitter	*Prunus dulcis* *var. dulcis* *var. amara*	Rosaceae	Baked and confectionary products (marzipan); flavoring of baked and confectionary products
47	Brazil nut	*Bertholletia excelsa*	Lecythidaceae	Fresh
48	Pistachio	*Pistacia vera*	Anacardiaceae	Fresh, salted, sausage flavoring, decoration of baked products
49	Walnut	*Juglans regia*	Juglandaceae	Fresh, baked and confectionary products, unripe fruits in vinegar and sugar-containing preserves
Wild fruits				
50	Rose hips	*Rosa sp.*	Rosaceae	Jam, wine
51	Elderberry	*Sambucus nigra*	Caprifoliaceae	Juice, jam
52	Seabuckthorn	*Hippophae rhamnoides*	Elaeagnaceae	Jam, juice

metabolism (e. g. lipases, lipoxygenases, enzymes involved in lipid biosynthesis), and in the citric acid and glyoxylate cycles, and many other enzymes such as acid phosphatases, ribonucleases, esterases, catalases, peroxidases, phenoloxidases and O-methyl transferases.

Protein and enzyme patterns, which can be obtained, for example, by electrophoretic separation, are generally highly specific for fruits and can be utilized for analytical differentiation of the species and variety. Figure 18.1 shows protein patterns of various grape species and Fig. 18.2 presents enzyme patterns of various species and cultivars of strawberries.

18.1.2.1.2 Free Amino Acids

Free amino acids are on average 50% of the soluble N-compounds. The amino acid pattern is typical of a fruit and hence can be utilized for the analytical characterization of a fruit product. Table 18.5 provides some relevant data.

In addition to common protein-building amino acids, there are nonprotein amino acids present in fruits, as in other plant tissues. Examples are the toxic 2-(methylene cyclopropyl)-glycine (I) in litchi fruits (*Litchi sinensis*), the toxic hypoglycine A (II) in akee (*Blighia sapida*), l-aminocyclopropane-l-carboxylic acid (X) in apples and pears, trans-4-methylproline (XXII), 4-hydroxymethylprolines (XXIII–XXV) and 4-methyleneproline (XXVI) in apples and in loquat fruits (*Eviobotrya japonica*), 3,4-dihydroxyglutamic acid (XXXV) in red currants, 4-methyleneglutamic acid (XXXI) and 4-methyleneglutamine (XXXII) in peanuts and 3-amino-3-carboxypyrrolidine (LIV) in cashew. The nonprotein amino acids are discussed in more detail in Section 17.1.2.1.2. The Roman

Table 18.2. Production of fruits in 2006 (1000 t)

Continent	Fruits[a], grand total	Nuts, grand total	Grapes	Raisins	Dates
World	526,496	11,106	68,953	1189	6704
Africa	67,848	1676	3822	41	2413
America, Central	106,024	208	260	4	3
America, North	25,316	1305	6172	320	15
America, South and Caribbean	106,024	599	6999	85	3
Asia	244,643	6403	20,740	635	4261
Europe	73,058	1070	29,097	79	13
Oceania	6965	52	2123	30	–

Continent	Apples	Pears	Peaches + nectarines	Plums + sloes	Oranges
World	63,805	19,540	17,189	9431	64,795
Africa	2006	651	810	244	5620
America, Central	632	30	223	74	5260
America, North	4909	770	941	415	9000
America, South and Caribbean	4368	827	1166	505	26,118
Asia	36,768	13,906	9639	5505	16,721
Europe	14,952	3212	4515	2727	6757
Oceania	800	174	119	34	580

Continent	Mandarins[b]	Lemons and limes	Grapefruit	Apricots	Avocado
World	25,660	12,990	4563	3251	3317
Africa	1483	832	665	502	396
America, Central	342	2087	465	2	1201
America, North	417	942	1118	41	247
America, South and Caribbean	2800	5295	1093	54	165
Asia	18,008	4324	1616	1735	429
Europe	2843	1552	60	895	94
Oceania	109	46	13	23	57

Continent	Guavas, mangoes	Pineapples	Bananas	Papaya
World	30,541	18,261	70,756	6591
Africa	3003	2598	7755	1422
America, Central	2342	2191	7137	964
America, North	3	192	9	13
America, South and Caribbean	5098	6060	24,897	134
Asia	22,383	9273	36,457	1926
Europe	–	2	393	–
Oceania	55	135	1244	12

Table 18.2. (Continued)

Continent	Strawberries	Raspberries and other berries	Currants	Almonds	Pistachios
World	4082	1155	760	1766	576
Africa	227	3	–	214	1
America, Central	202	8	–	–	–
America, North	1279	109	–	716	122
America, South and Caribbean	297	14	–	10,651	–
Asia	711	510	2	418	440
Europe	1539	411	748	396	12
Oceania	29	108	9	12	–

Continent	Hazelnuts	Chestnuts	Cashew nuts	Walnuts
World	961	1180	3103	1664
Africa	–	–	1059	42
America, Central	–	–	8	80
America, North	41	–	–	308
America, South and Caribbean	–	42	247	107
Asia	737	1013	1797	891
Europe	183	125	–	316
Oceania	–	–	–	–

Country	Fruits, grand total
China	93,410
India	43,525
Brazil	37,736
USA	27,328
Italy	17,812
Spain	16,514
Indonesia	15,406
Mexico	15,385
Iran	13,848
Philippines	13,582
Turkey	12,563
Nigeria	9874
Uganda	9731
France	9682
Thailand	8648
Argentina	8351
Egypt	8196
Colombia	7910
Ecuador	7536
Pakistan	6379
Vietnam	5691
South Africa	5690
$\sum$ (%)[c]	75

Country	Nuts, grand total
China	1625
USA	1305
India	1092
Turkey	1000
Vietnam	950
Nigeria	727
Iran	507
Italy	328
Brazil	271
Spain	268
Indonesia	264
$\sum$ (%)[c]	75

Country	Grapes
Italy	8326
France	6693
Spain	6402
China	6375
USA	6094
Turkey	4000
Iran	2964
Argentina	2881
Chile	2250
Japan	2098
Australia	1981
South Africa	1550
$\sum$ (%)[c]	75

Table 18.2. (Continued)

Country	Raisins	Country	Dates	Country	Apples
Turkey	376	Egypt	1170	China	26,066
USA	320	Iran	997	USA	4569
Iran	146	Saudi Arabia	970	Iran	2662
Greece	77	Pakistan	507	Poland	2305
Chile	64	Algeria	491	Italy	2113
South Africa	40	Sudan	328	Turkey	2002
Uzbekistan	39	Oman	259	India	1739
Australia	30	Libya	181	France	1705
Argentina	17	China	125	Russian Fed.	1617
Syria	12	Tunisia	125	Chile	1350
$\sum (\%)^{c}$	94	$\sum (\%)^{c}$	77	Argentina	1272
				Germany	948
				$\sum (\%)^{c}$	76

Country	Pears	Country	Peaches + nectarines	Country	Plums + sloes
China	11,988	China	7510	China	4535
Italy	907	Italy	1665	Romania	599
USA	758	Spain	1256	Serbia, Rep.	556
Spain	590	USA	916	USA	412
Argentina	510	Greece	864	Chile	255
Korea, Rep.	431	Turkey	553	France	230
Japan	319	Iran	456	Turkey	214
Turkey	318	France	401	Italy	180
South Africa	316	Egypt	360	Spain	160
Netherlands	222	Chile	315	Iran	146
$\sum (\%)^{c}$	84	$\sum (\%)^{c}$	83	$\sum (\%)^{c}$	83

Country	Oranges	Country	Mandarins	Country	Lemons and limes
Brazil	18,059	China	13,240	Mexico	1866
USA	9000	Spain	2000	India	1618
Mexico	3980	Brazil	1233	Argentina	1393
India	3469	Japan	842	Brazil	1031
Spain	3211	Turkey	791	USA	942
China	2765	Iran	702	Spain	868
Italy	2356	Thailand	670	China	783
Iran	2253	Egypt	665	Turkey	710
Indonesia	2214	Argentina	660	Iran	615
Egypt	1789	Pakistan	639	Italy	583
$\sum (\%)^{c}$	76	$\sum (\%)^{c}$	84	$\sum (\%)^{c}$	80

numerals given in brackets above correspond to Tables 17.5 and 17.6.

18.1.2.1.3 Amines

A number of aliphatic and aromatic amines are found in various fruits and vegetables (Tables 18.6 and 18.7 and 18.1.4.2.1). They are formed in part by amino acid decarboxylation such as in apples, or by amination (cf. Reaction 18.1) or transamination of aldehydes (cf. Reaction 18.2).

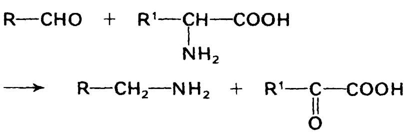
$$R{-}CHO \xrightarrow[2\,[H]]{NH_3} R{-}CH_2{-}NH_2 \qquad (18.1)$$

Table 18.2. (Continued)

Country	Grapefruit	Country	Apricots	Country	Avocado
USA	1118	Turkey	460	Mexico	1137
China	505	Iran	276	USA	247
South Africa	415	Uzbekistan	236	Indonesia	228
Mexico	380	Italy	222	Colombia	186
Syria	282	Pakistan	190	Brazil	169
Israel	266	France	180	Chile	163
Argentina	191	Algeria	167	Dominican Rep.	114
Turkey	180	Spain	141	Peru	103
Cuba	170	Morocco	129	China	90
India	154	Japan	120	Ethiopia	83
∑ (%)[c]	80	Syria	101	∑ (%)[c]	76
		China	85		
		South Africa	84		
		Greece	73		
		Egypt	73		
		∑ (%)[c]	83		

Country	Guavas, mangoes	Country	Pineapples	Country	Bananas
India	11,140	Thailand	2705	India	11,710
China	3550	Brazil	2487	Brazil	7088
Pakistan	2243	Philippines	1834	China	7053
Mexico	2050	China	1400	Philippines	6795
Thailand	1800	India	1229	Ecuador	6118
Indonesia	1413	Costa Rica	1200	Indonesia	5178
Brazil	1348	Indonesia	925	Costa Rica	2353
Philippines	937	Nigeria	895	Mexico	2197
Nigeria	732	Mexico	628	Thailand	1865
Egypt	380	Kenya	600	Colombia	1765
∑ (%)[c]	84	∑ (%)[c]	76	Burundi	1539
				∑ (%)[c]	76

Country	Papaya	Country	Strawberries
Brazil	1574	USA	1259
Mexico	806	Spain	334
India	783	Russian Fed.	235
Nigeria	759	Turkey	211
Indonesia	549	Korea, Rep.	205
Ethiopia	259	Poland	194
Congo	218	Mexico	192
Peru	171	Japan	191
Philippines	157	Germany	173
Venezuela	151	Italy	131
∑ (%)[c]	82	∑ (%)[c]	77



$$\mathrm{R{-}CHO} + \mathrm{R^1{-}\underset{\underset{\textstyle NH_2}{|}}{C}H{-}COOH} \longrightarrow \mathrm{R{-}CH_2{-}NH_2} + \mathrm{R^1{-}\underset{\underset{\textstyle O}{\|}}{C}{-}COOH} \qquad (18.2)$$

Some amines are derived from tyramine (e. g., hordenine, synephrine, octopamine, dopamine and noradrenaline; cf. Formula 18.3) and others from tryptophan (serotonin, tryptamine, melatonin; Formula 18.4). The occurrence of

Table 18.2. (Continued)

Country	Raspberries and other berries
Iran	212
Russian Fed.	184
Vietnam	106
USA	99
Serbia, Rep.	80
Turkey	55
Poland	53
China	40
Ukraine	19
Armenia	12
UK	10
∑ (%)[c]	75

Country	Currants
Russian Fed.	435
Poland	195
UK	21
Austria	19
Ukraine	16
Czech Rep.	12
Germany	11
Denmark	10
New Zealand	8
Lithuania	6
∑ (%)[c]	96

Country	Almonds
USA	716
Spain	220
Syria	120
Italy	113
Iran	109
Morocco	83
Algeria	54
Tunisia	50
Greece	47
Turkey	43
∑ (%)[c]	88

Country	Pistachios
Iran	230
USA	122
Turkey	110
Syria	60
China	36
Greece	9
Italy	3
Tunisia	1
Pakistan	1
∑ (%)[c]	100

Country	Hazelnuts
Turkey	661
Italy	142
USA	41
Spain	25
Azerbaijan, Rep.	25
Iran	18
Georgia	17
China	14
France	6
Poland	3
∑ (%)[c]	99

Country	Chestnuts
China	850
Korea, Rep.	76
Turkey	54
Italy	52
Bolivia	41
Portugal	29
Japan	23
Greece	21
France	10
Spain	10
∑ (%)[c]	99

Country	Cashewnuts
Vietnam	942
Nigeria	636
India	573
Brazil	236
Indonesia	122
Philippines	113
Côte d'Ivoire	94
Tanzania	90
Guinea-Bissau	85
Mozambique	68
∑ (%)[c]	95

Country	Walnuts
China	499
USA	308
Iran	150
Turkey	130
Mexico	80
Ukraine	60
Romania	38
France	36
India	36
Egypt	32
∑ (%)[c]	80

[a] Without melons and nuts.

[b] Inclusive tangerines, clementines and satsumas.

[c] World production = 100%.

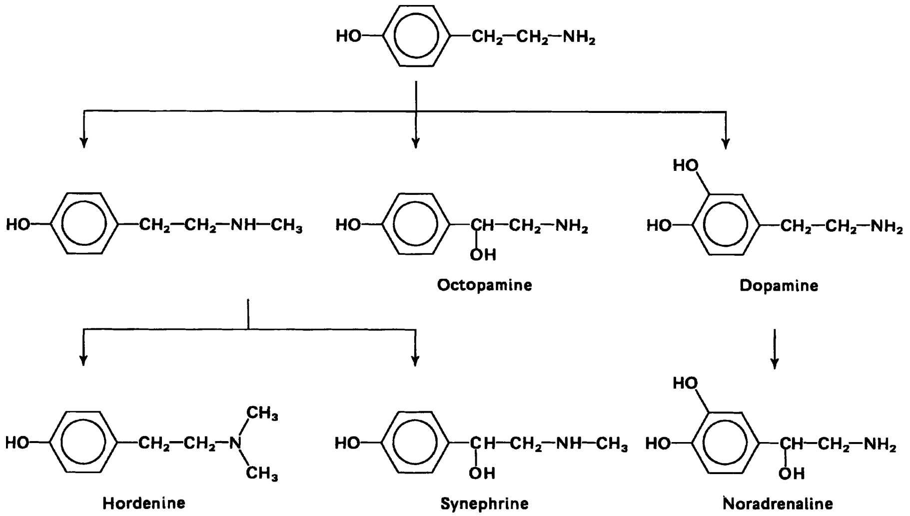
Table 18.3. Average chemical composition of fruits (as % of fresh edible portion)

Fruit	Dry matter	Total sugar	Titratable acidity[a]	Dietary fiber	Pectin[b]	Ash	pH
Apple	16.0	11.1	0.6	2.1	0.6	0.3	3.3
Pear	17.5	12.4	0.2	3.1	0.5	0.4	3.9
Apricot	14.7	8.5	1.4	1.6	1.0	0.6	3.7
Sour cherry	14.7	9.9	1.8	1.0	0.3	0.5	3.4
Sweet cherry	17.2	13.3	1.0	1.3	0.3	0.6	4.0
Peach	12.9	8.5	0.6	1.9	0.5	0.5	3.7
Plum/prune	16.3	10.2	1.5 (Ä)[c]	1.6	0.9	0.5	3.3
Blackberry	15.3	6.2	1.7	3.2	0.5	0.5	3.4
Strawberry	10.2	5.7	1.1	1.6	0.5	0.5	
Currant, red	15.3	4.8	2.3 (C)[c]	3.5	0.9	0.6	3.0
Currant, black	18.7	6.3	2.6 (C)[c]	6.8	1.7	0.8	3.3
Raspberry	15.5	4.5	2.1 (C)[c]	4.7	0.4	0.5	3.4
Grapes	18.9	15.2	0.9 (W)[c]	1.5	0.3	0.5	3.3
Orange	14.3	8.3	1.1	1.6		0.5	3.3
Grapefruit	11.4	7.4	1.5	1.6		0.4	3.3
Lemon	9.8	3.2	4.9			0.5	2.5
Pineapple	15.4	12.3	0.7	1.0		0.4	3.4
Banana	26.4	20.0	0.6 (Ä)[c]	1.8	0.9	0.8	4.7
Cherimoya	25.9	13	0.2			0.9	
Date	80	65.1	1.3	8.7		1.8	
Fig	20	13	0.4	2.0	0.6	0.7	
Guava	17	5.8	0.9	5.2	0.7	0.7	
Mango	19	12.5	0.3	1.7	0.5	0.5	
Papaya	11	7.1	0.1	1.7	0.6	0.6	

[a] Sum: citric acid + malic acid + tartaric acid.

[b] Results are expressed as calcium pectate.

[c] Calculated as malic (M), citric (C), or tartaric acid (T).



(18.3)

Table 18.4. Proximate composition of shell-nut fruit (as % of fresh edible portion)

Fruit	Moisture	N-Compounds ($N \times 5.3$)	Lipids	Available carbohydrates	Ash	Dietary fiber
Cashewnut	4.0	16	42.2	30.5	2.9	2.9
Peanut	5.0	25.3	47.5	7.5	2.2	11.7
Hazelnut	5.2	12.0	66.0	10.5	2.5	8.2
Pistachio	5.9	17.6	53.5	11.6	2.7	10.6
Almond	5.7	20.5	56.0	5.4	2.7	13.5
Walnut	4.4	15.0	64.4	10.6	2.0	6.1

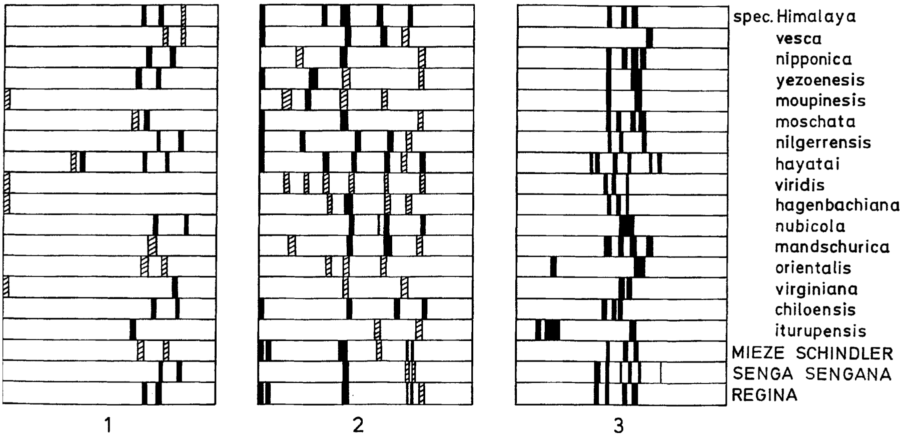


Fig. 18.2. Enzyme patterns of some strawberry species (*Fragaria sp.*) and (*Fragaria ananas*) obtained by PAGE disc gel electrophoresis. Large pore concentrating gel pH 6.7, small pore separating gel, pH 8.9. *1* Peroxidase: incubation with o-toluidine/H_2O_2 at pH 7. *2* Esterase: incubation with α-naphthylacetate at pH 7, the released α-naphthol is diazotized and then coupled with p-chloroaniline. *3* Malate-dehydrogenase: incubation with malate, nitro-blue-tetrazolium chloride and NAD at pH 7.5. (according to *Drawert* et al., 1974)

Table 18.5. Free amino acids in fruits (as % of total free amino acids)

Fruit	Asp	Asn	Glu	Gln	Ser	Thr	Pro	Ala	Abu[b]	His	Arg	Pip[c]
Apple (juice)	21	17	15		10	3	2	7	5			
Pear (juice)	10	9	10		11	2	14	9	3			
Grapes	3		13			6	31	9	6		27	
Currant black		7	17	24	5		8	17	12			
Orange[a]	7–115	20–188	6–93	3–63	4–37		8–79	3–26	4–73		0–23	
Grapefruit[a]	34–99		8–90		310	10		4–27		76	20–45	
Lemon[a]	19–60		6–35		12–28			1–31	4–20		25–106	
Banana	5–10	15		10–15					5–10	10–15		5–10

[a] Values in mg/100 ml juice.
[b] γ-Aminobutyric acid.
[c] Pipecolinic acid.

Table 18.6. Amines in fruit

Fruit	Amines
Apple	Methylamine, ethylamine, propylamine, butylamine, hexylamine, octylamine, dimethylamine, spermine, spermidine
Plum/prune	Dopamine
Orange	Feruloylputrescine, methyltyramine, synephrine
Grapefruit	Feruloylputrescine
Lemon	Tyramine, synephrine, octopamine
Pineapple	Tyramine, serotonin
Avocado	Tyramine, dopamine
Banana	Methylamine, ethylamine, isobutylamine, isoamylamine, dimethylamine, putrescine, spermidine, ethanolamine, propanolamine, histamine, 2-phenylethylamine, tyramine, dopamine, noradrenaline, serotonin

these biologically active amines in fruits and vegetables (Table 18.7) could influence their concentrations in human serum.

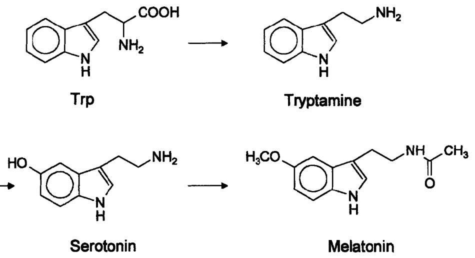


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Table 18.7. Concentrations of tryptamine, serotonin and melatonin in fruits and vegetables[a]

Fruit/ Vegetable	Serotonin (mg/kg)	Tryptamine (mg/kg)	Melatonin (ng/kg)
Banana	11.7	0.03	466
Kiwi	6.2	4.2	
Pineapple	29.0	1.4	
Cherry			2–15
Walnut	278.9		
Cucumber			86
Tomato		2.9	112–506

[a] Reference: fresh weight.

18.1.2.2 Carbohydrates

18.1.2.2.1 Monosaccharides

In addition to glucose and fructose, the ratios of which vary greatly in various fruits (Table 18.8), other monosaccharides occur only in trace amounts. For example, arabinose and xylose have been found in several fruits. An exceptional case is avocado in which a number of higher sugars are present at 0.2 to 5.0% of the fresh weight (D-manno-heptulose, D-talo-heptulose, D-glycero-D-galacto-heptose, D-glycero-D-manno-octulose, D-glycero-L-galacto-octulose, D-erythro-L-gluco-nonulose and D-erythro-L-galacto-nonulose). Small amounts of heptuloses have been found in the fruit flesh of apples, peaches and strawberries, and in the peels of grapefruit, peaches and grapes.

18.1.2.2.2 Oligosaccharides

Saccharose (sucrose) is the dominant oligosaccharide. Other disaccharides do not have quantitative importance. Maltose occurs in small amounts in grapes, bananas and guava. Melibiose, raffinose and stachyose have also been detected in grapes. 6-Kestose has been identified in ripe bananas.

Other oligosaccharides occur only in trace amounts. The proportion of reducing sugars to saccharose can vary greatly (Table 18.8). Some fruits have no saccharose (e. g., cherries, grapes and figs), while in some the saccharose content is significantly higher than the reducing sugar content (e. g., apricots, peaches and pineapples).

18.1.2.2.3 Sugar Alcohols

D-Sorbitol is abundant in *Rosaceae* fruits (pomme fruits, stone fruits). For example, its concentration is 300–800 mg/100 ml in apple juice. Since fruits such as berries, citrus fruits, pineapples or bananas do not contain sorbitol, its detection is of analytical importance in the evaluation of wine and other fruit products. Meso-inositol also occurs in fruits; in orange juice it ranges from 130–170 mg/100 ml.

Table 18.8. Sugar content in various fruits (as % of the edible portion)

Fruit	Glucose	Fructose	Saccharose
Apple	1.8	5.7	2.4
Pear	1.8	6.7	1.8
Apricot	1.9	0.9	5.1
Cherry	6.9	6.1	0.2
Peach	1.0	1.2	5.7
Plum/prune	3.5	2.0	3.4
Blackberry	3.2	2.9	0.2
Strawberry	2.2	2.3	1.3
Currant, red	2.0	2.5	0.3
Currant, black	2.4	3.1	0.7
Raspberry	1.8	2.1	1.0
Grapes	7.2	7.4	0.4
Orange	2.4	2.4	3.4
Grapefruit	2.0	2.1	2.9
Lemon	1.4	1.4	0.4
Pineapple	2.3	2.4	7.9
Banana	3.5	3.4	10.3
Date	25.0	24.9	13.8
Fig	5.5	4.0	0.0

18.1.2.2.4 Polysaccharides

All fruits contain cellulose, hemicellulose (pentosans) and pectins. The building blocks of these polysaccharides are glucose, galactose, mannose, arabinose, xylose, rhamnose, fucose and galacturonic and glucuronic acids. The pectin fractions of fruits are particularly affected by ripening. A decrease in insoluble pectin is accompanied by an increase in the soluble pectin fraction. The total pectin content can also decrease. Starch is present primarily in unripe fruits and its content decreases to a negligible level as ripening proceeds. Exceptions are bananas, in which the starch content can be 3% or more even in ripe bananas, and various nuts such as cashew and Brazil nuts.

18.1.2.3 Lipids

The lipid content of fruits is generally low, 0.1–0.5% of the fresh weight. Only fruit seeds and nuts contain significantly higher levels of lipids (cf. Table 18.4). The fruit flesh of avocado is also rich in fat. The lipid fraction of fruits consists of triacylglycerols, glyco- and phospholipids, carotenoids, triterpenoids and waxes.

Table 18.9. Lipids of apple flesh (as % of the total lipids)

Triacylglycerols	5	Sterols	15
Glycolipids	17	Sterol esters	2
Phospholipids	47	Sulfolipids	1
		Others	15

18.1.2.3.1 Fruit Flesh Lipids (Other than Carotenoids and Triterpenoids)

Table 18.9 presents the lipid fractions of apple flesh. Phospholipids, about 50% of the lipid fraction, are predominant. The most abundant fatty acids are palmitic, oleic and linoleic acids (Table 18.10).

18.1.2.3.2 Carotenoids

Carotenoids are widespread in fruits and, in a number of fruits, such as citrus fruits, peaches and sweet melons, their presence is the main factor determining color. The most important carotenoids found in fruits are compiled in Table 18.11, while Table 18.12 gives the carotenoid composition of some fruits.
Fruits can be divided into various classes according to the content and distribution pattern of carotenoids:

- Fruits with low content of carotenoids (occurring mostly in chloroplasts) such as β-carotene, lutein, violaxanthin, neoxanthin (e. g., pineapples, bananas, figs and grapes).

Table 18.10. Fatty acid composition of some fruit flesh lipids (as % of the total fatty acids)

Fatty acid	Avocado	Apple	Banana
12:0	+[a]	0.6	+
14:0	+	0.6	0.6
16:0	15	30	58
16:1	4	0.5	8.3
18:0	+	6.4	2.5
18:1	69	18.5	15
18:2	11	42.5	10.6
18:3	+	1	3.6

[a] Traces.

Table 18.11. Carotenoids occurring in fruit (Roman numerals refer to their structures shown in 3.8.4)

Number	Carotenoid
1	Phytoene (I)
2	Phytofluene (II)
3	ζ-Carotene (III)
4	Lycopene (IV)
5	α-Carotene (VI)
6	β-Carotene (VII)
7	β-Zeacarotene (Va)
8	Lycoxanthin (16-hydroxylycopene)
9	α-Cryptoxanthin (3-hydroxy-α-carotene)
10	β-Cryptoxanthin (3-hydroxy-β-carotene)
11	β-Carotene-5,6-epoxide
12	Mutatochrome (β-carotene-5,8-epoxide)
13	Lutein (IX)
14	Zeaxanthin (VIII)
15	Cryptoflavin (α-cryptoxanthin-5,8-epoxide)
16	β-Carotene-5,6,5′,6′-diepoxide
17	Antheraxanthin (zeaxanthin-5,6-epoxide)
18	Lutein-5,6-epoxide
19	Mutatoxanthin (XVI)
20	Lutein-5,8-epoxide
21	Cryptoxanthin-5,8,5′,8′-diepoxide
22	Violaxanthin (XIII)
23	Luteoxanthin (XIV)
24	Auroxanthin(zeaxanthin-5,8,5′,8′-diepoxide)
25	Neoxanthin (XX)
26	Capsanthin (X)

Table 18.12. Carotenoid patterns of various fruits

Fruit	Carotenoid Content[a]	Compounds[b]
Pineapple		6, 13
Orange	24	1, 2, 3, 4, 6, 10, 11, 12, 15, 17, 20, 21, 22, 23, 24
Banana		6, 13
Pear	0.3–1.3	2, 3, 6, 7, 8, 11, 12, 13, 14, 16, 18, 20, 24, 25
Fig	8.5	1, 2, 5, 6, 13, 14, 22, 23, 25
Guava		5, 6
Peach	27	1, 2, 3, 5, 6, 9, 10, 13, 14, 17, 18, 19, 22, 23, 24
Plum/ prune		1, 2, 3, 5, 6, 9, 10, 12, 14, 15, 17, 18, 19, 20, 22, 23, 25
Grapes	1.8	1, 2, 4, 5, 13, 14, 22, 23
Cantaloupe	20–30	1, 2, 3, 5, 6, 13, 14, 22, 23

[a] mg/kg fresh weight.

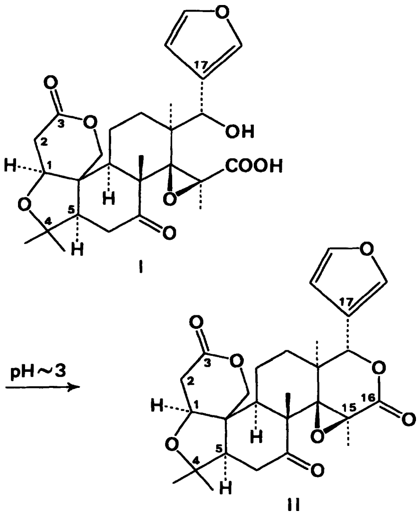
[b] The numerals refer to Arabic numerals in Table 18.11.

- Fruits with relatively high contents of lycopene, phytoene, phytofluene, ζ-carotene and neurosporene, e. g., peaches.
- Fruits with relatively high contents of β-carotene, cryptoxanthin and zeaxanthin. This class includes oranges, pears, peaches and sweet melons.
- Fruits with high amounts of epoxides, e. g., oranges and pears.
- Fruits which contain unusual carotenoids, e. g., oranges.

The compositional pattern of carotenoids which can be readily analyzed by HPLC is important for analytical characterization of fruit products.

18.1.2.3.3 Triterpenoids

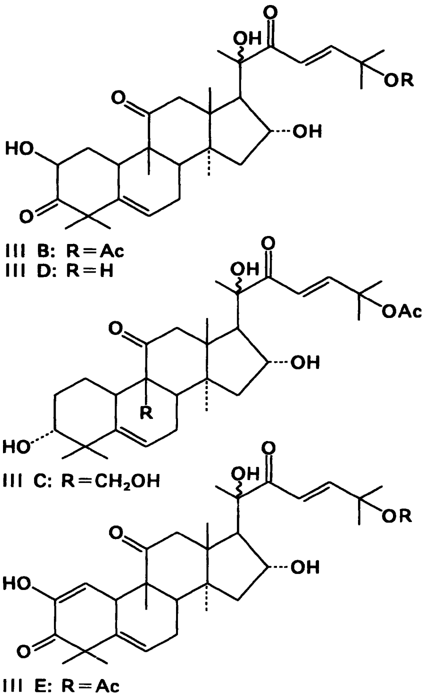
This fraction contains bitter compounds of special interest, limonoids and cucurbitacins. Limonoids are found in the flesh and seeds of *Rutaceae* fruits. For example, limonin (II) is present in seeds, juice, and fruit flesh of oranges and grapefruit. The limonin content decreases with fruit ripening in oranges but remains constant in grapefruit. Development of a bitter taste in heated orange juice is a processing problem. Limonin monolactone (I), a nonbitter compound which is stable in the neutral pH range, is present in orange albedo and endocarp. During production of orange juice it is transferred to the juice in which, due to the lower pH, it is transformed



(18.5)

into the bitter tasting dilactone, limonin (II; cf. Formula 18.5).

Bitter and nonbitter forms of the many *Cucurbitaceae* are known. The bitter forms contain cucurbitacins (III) in fruits and seeds. For example, *Citrullus lanatus* (watermelon) contains IIIE in glycosidic form; while *Cucumis sativus* (cucumber) contains IIIC and *Cucurbita* spp. (pumpkin) contains IIIB, D, E and I (cf. Formula 18.6).


III B: R=Ac
III D: R=H
III C: R=CH₂OH
III E: R=Ac
III I: R=H

(18.6)

The common precursor in the biosynthesis of limonoids and cucurbitacins is squalene-2,3-oxide (IV). Based on some identified intermediary compounds, the biosynthetic pathway is probably as postulated in Reaction 18.7.

18.1.2.3.4 Fruit Waxes

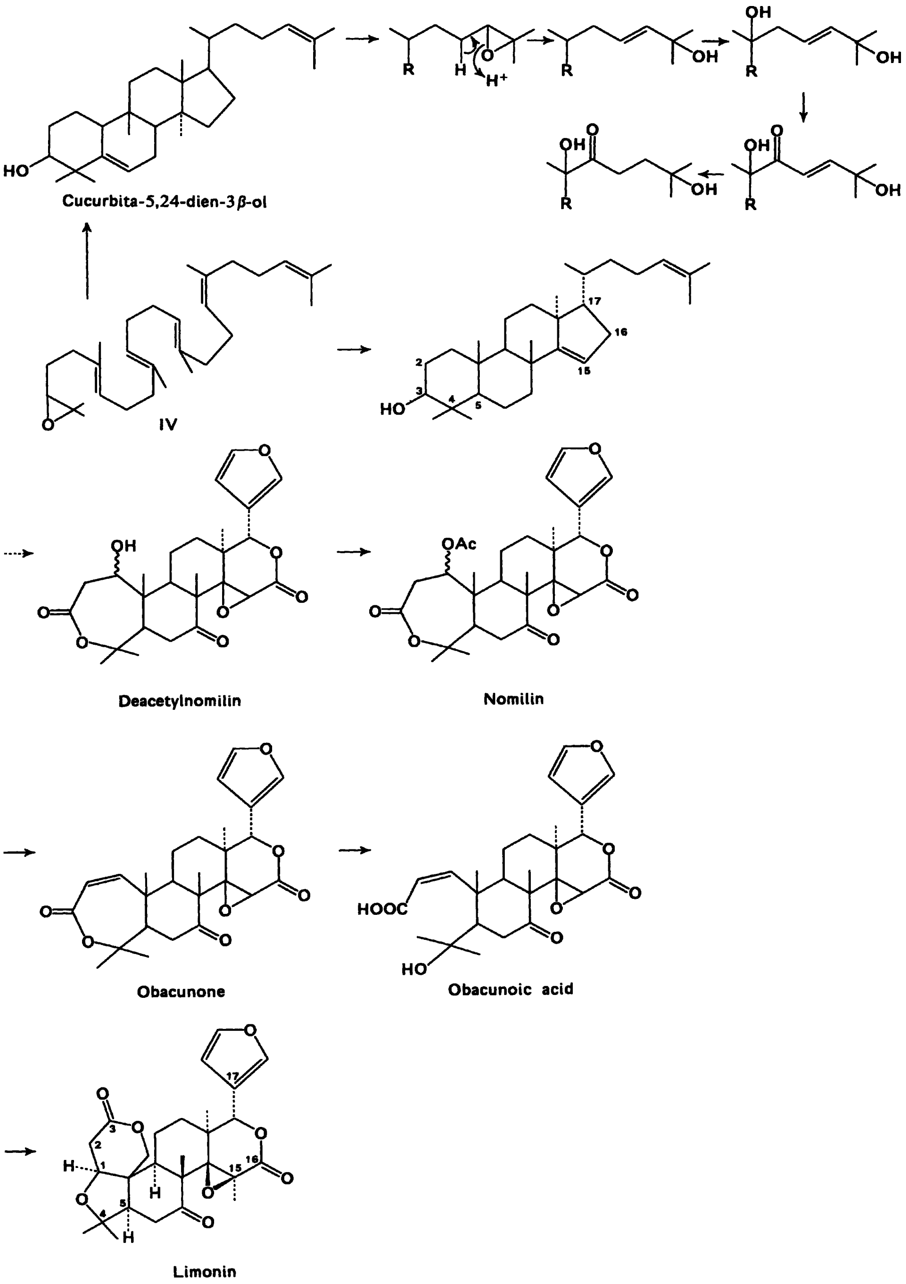
The fruit peel is often coated with a waxy layer. In addition to the esters of higher fatty acids with higher alcohols, these waxes contain hydrocarbons, free fatty acids, free alcohols, ketones and aldehydes. The ester fraction in apples and grapes predominantly consists of alcohols of 24, 26 and 28 carbons, but their fatty acid patterns differ. Apples contain mostly 18:1, 18:2, 16:0 and 18:0 fatty acids, while grapes contain 20:0, 18:0, 22:0 and 24:0 fatty acids.

18.1.2.4 Organic Acids

L-Malic and citric acids are the major organic acids of fruits (Table 18.13). Malic acid is predominant in pomme and stone fruits, while citric acid is most abundant in berries, citrus and tropical fruits. (2R:3R)-Tartaric acid occurs only in grapes. Many other acids, including the acids in the citric acid cycle, occur only in low amounts. Examples are cis-aconitic, succinic, pyruvic, citramalic, fumaric, glyceric, glycolic, glyoxylic, isocitric, lactic, oxalacetic, oxalic and 2-oxoglutaric acids. In fruit juices, the ratio of citric acid to isocitric acid (examples in Table 18.14) serves as an indicator of dilution with an aqueous solution of citric acid.

Table 18.13. Organic acids in various fruits (milliequivalents/100 g fresh weight)

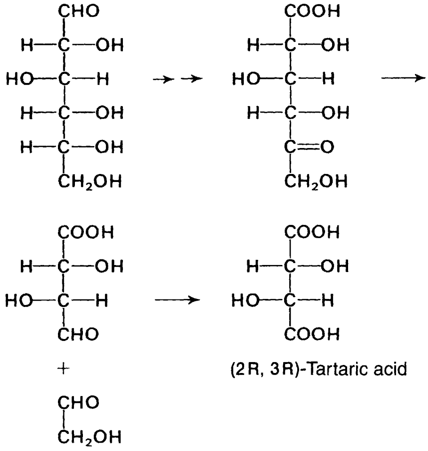
Fruit	Major acid	Other acids
Apple	Malic 3–19	Quinic (in unripe fruits)
Pear	Malic 1–2	Citric
Apricot	Malic 12	Citric 12, quinic 2–3
Cherry	Malic 5–9	Citric, quinic, and shikimic
Peach	Malic 4	Citric 4
Plum/prune	Malic 4–6	Quinic (especially in unripe fruits)
Strawberry	Citric 10–18	Malic 1–3, quinic 0.1, succinic 0.1
Raspberry	Citric 24	Malic 1
Currant, red	Citric 21–28	Malic 2–4, succinic, oxalic
Currant, black	Citric 43	Malic 6
Gooseberry	Citric 11–14	Malic 10–13, shikimic 1–2
Grapes	Tartaric 1.5–2	Malic 1.5–2
Orange	Citric 15	Malic 3, quinic
Lemon	Citric 73	Malic 4, quinic
Pineapple	Citric 6–20	Malic 1.5–7
Banana	Malic 4	
Fig	Citric 6	Malic, acetic
Guava	Citric 10–20	Malic



(18.7)

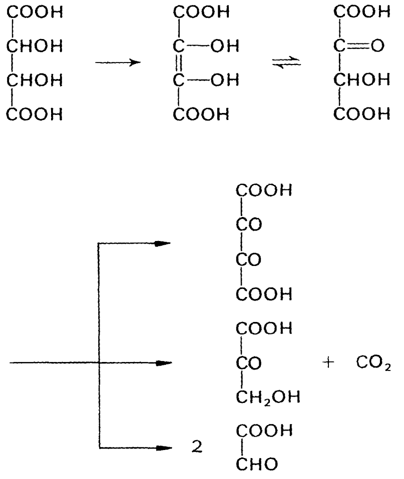
Important phenolic acids, dealt with in Section 18.1.2.5.1, are quinic, caffeic, chlorogenic and shikimic acids. Galacturonic and glucuronic acids are also found.

Tartaric acid biosynthesis in *Vitis* spp. starts from glucose or fructose and probably proceeds through 5–oxogluconic acid or ascorbic acid respectively:



(18.8)

Human and animal metabolism oxidatively degrade (2R:3R)-tartaric and meso-tartaric acids into glyoxylic and hydroxypyruvic acids respectively:



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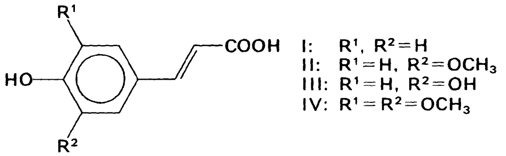

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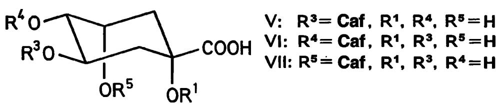

(18.11)

Table 18.14. Ratio of citric acid (C) to isocitric acid (I) in fruit juices

Fruit juice	C/I
Orange	80–130
Currant	60–140
Grapefruit	50–90
Raspberry	80–200
Lemon	$\leq$250
Blackberry	ca. 0.25

18.1.2.5 Phenolic Compounds

In plant foods, several hundred polyphenols have been identified, which are classified according to the number of phenol rings and their linkage, as presented in Fig. 18.3. The flavonoids exhibit a great multiplicity. According to Fig. 18.4, they are divided into six subclasses. The polyphenols are mostly present as glycosides, and partly also as esters. They are antioxidatively active, their activity depending on the number and position of the OH-groups and on the pH (cf. 3.7.3.2.1). As antioxidants, they are of interest from

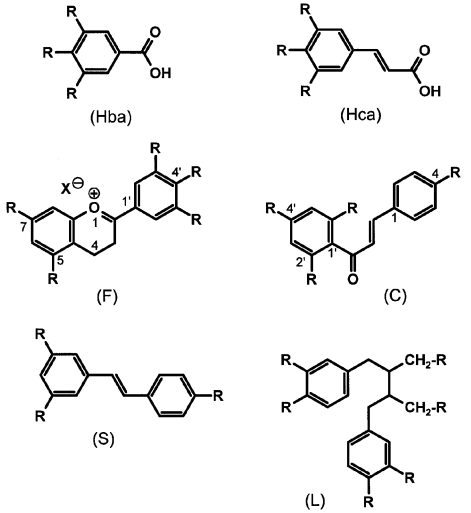

Fig. 18.3. Chemical structures of polyphenols Hydroxybenzoic acids (Hba), Hydroxycinammic acids (Hca), Flavonoids (F), Chalcones (C), Stilbenes (S, cf. 20.2.6.6), Lignans (L). R: H, OH or OCH_3

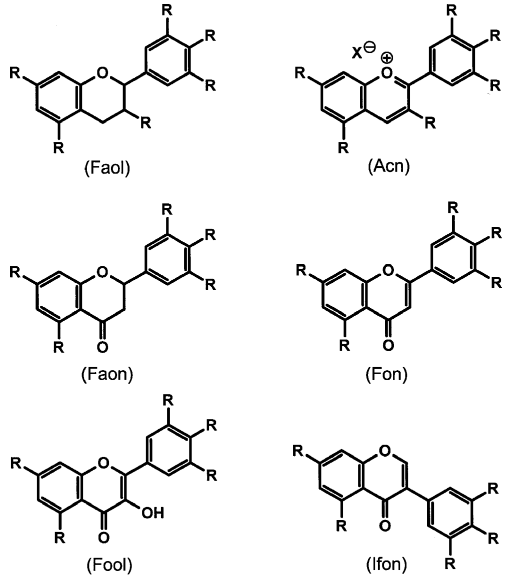

Fig. 18.4. Chemical structures of flavonoids
Flavanols (Faol), Anthocyanidines (Acn), Flavanones (Faon), Flavones (Fon), Flavonols (Fool), Isoflavones (Ifon, cf. 16.2.9). R: H, OH or OCH_3

a nutritional and physiological viewpoint. Up to now, however, unambiguous evidence of a health-building effect is lacking (literature till 2006). The phenolic compounds contribute to the color and taste of many types of fruit. In processing, they can cause discoloration by the formation of metal complexes and turbidity by complexation of proteins. Table 18.15 shows the polyphenol content of foods, which is strongly dependent on the variety, climate and degree of ripeness, among other factors. For instance, their content in apples varies from 1.3 g/kg (*Golden Delicious*) to 6 g/kg (*Jeanne Renard*) and can even rise to 10 g/kg in this variety.

18.1.2.5.1 Hydroxycinammic Acids, Hydroxycoumarins and Hydroxybenzoic Acids

p-Coumaric (I), ferulic (II), caffeic (III) and sinapic (IV) acids are widespread in fruits and vegetables.

These hydroxycinnamic acids are present mainly as derivatives. The most common are

Table 18.15. Polyphenol content of foods

Compound[a]	Food	Content[b]
Hydroxybenzoic acids (Hba)	Blackberries	80–270
	Raspberries	60–100
	Black currants	40–130
	Strawberries	20–90
Hydroxycinammic acids (Hca)	Bilberries	2000–2200
	Kiwi	600–1000
	Cherry	180–1150
	Plum	140–1140
	Apple	50–600
	Pear	15–600
	Aubergine	600–660
	Artichoke	450
	Chicory	200–500
	Potato	100–190
Flavanols[c] (monomer) (Faol)	Apricot	100–250
	Cherry	50–250
	Grape	30–175
	Peach	50–140
	Blackberry	130
	Apple	20–120
Anthocyans (Acn-glycoside)	Blackberry	1000–4000
	Black currant	1300–4000
	Bilberry	250–5000
	Red grape	300–7500
	Cherry	350–4500
	Rhubarb	2000
	Strawberry	150–750
	Plum	20–250
	Red cabbage	250
Flavanones[c] (Faon)	Orange (juice)	215–685
	Grapefruit (juice)	100–650
	Lemon (juice)	50–300
Flavones[c] (Fon)	Parsley	240–1850
	Celery	20–140
Flavonols[c] (Fool)	Bilberry	30–160
	Black currant	30–70
	Apricot	25–50
	Apple	20–40
	Red grape	15–40
	Kale	300–600
	Leek	30–225
	Broccoli	40–100
	Bean, green	10–50
	Tomato	2–15

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[a] The numbers and abbreviations refer to the formulas in Fig. 18.5 and 18.6.

[b] Values in mg/kg fresh weight or mg/l juice.

[c] Concentration of the aglycone.

Table 18.16. Derivatives of hydroxycinnamic acid in pomme and stone fruits[a]

Compound	Apple	Pear	Sweet cherry	Sour cherry	Plum	Peach	Apricot
5-Caffeoylquinic acid	62–385[b]	64–280	11–40	50–140	15–142	43–282	37–123
4-Caffeoylquinic acid	2	–	+	+	9	–	–
3-Caffeoylquinic acid	–	–	73–628	82–536	88–771	33–142	26–132
3-p-Coumaroylquinic acid	–	–	81–450	40–226	4–40	2	2–9
3-Feruloylquinic acid	–	–	4	1	13	1	7
p-Coumaroylglucose	4	+	–	–	15	–	–
Feruloylglucose	3	–	–	–	5	–	–

[a] mg/kg of fresh weight,
[b] variety "Boskop": 400–500 mg/kg.

Table 18.17. Derivatives of hydroxycinnamic acid in berries[a]

Compound	Strawberry	Raspberry	Blackberry	Red currant	Black currant	Gooseberry	Cultured blueberry
Caffeoylquinic acid	–	1	45–53	1	45–52	3	1860–2080
p-Coumaroylquinic acid	–	1	2–5	+	14–23	1	2–5
Feruloylquinic acid	–	+	2–4	2	4	1	8
Caffeoylglucose	1	3–7	3–6	2–5	19–30	5–13	+
p-Coumaroylglucose	14–17	6–14	4–11	1	10–14	7	+
Feruloylglucose	1	4–7	2–6	+	11–15	1–6	+
Caffeic acid-4-O-glucoside	–	–	–	2	2	2	3
p-Coumaric acid-O-glucoside	+	5–10	2–5	5–16	4–10	6–8	3–15
Ferulic acid-O-glucoside	–	+	–	–	3	2–7	8–10

[a] mg/kg of fresh weight. The hydroxycinnamoylquinic acids are present mostly as the 3-isomers, but in blueberries as the 5-isomer.

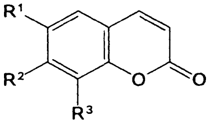
esters of caffeic, coumaric, and ferulic acids with D-quinic and, in addition, with D-glucose (Tables 18.16 and 18.17). Since quinic acid has four OH groups, four bonding possibilities exist (R^1, R^3–R^5 in Formula 18.11), the 3- and 5-isomers being preferred. According to IUPAC nomenclature for cyclitols, the 3-, 4-, and 5-caffeoylquinic acids are identical to neochlorogenic acid (V), cryptochlorogenic acid (VI), and chlorogenic acid (VII). Isochlorogenic acid is a mixture of di-O-caffeoylquinic acids. Apart from quinic acid and glucose, other alcoholic components are shikimic, malic and tartaric acids and meso-inositol. Sinapine, which is found in mustard seed, is the counter ion of the glucosinolate sinalbin and is the choline ester of sinapic acid, which is as bitter as caffeine. Hydroxycinnamic acid amides are also found in plants.

Scopoletin (VIII, Formula 18.12) in esterified form is the only hydroxycoumarin (Table 18.18) which has been found, in small amounts, in plums and apricots.

Table 18.18. Hydroxycoumarins in fruit (VIII)[a]

Compound	Substitution pattern		
	R^1	R^2	R^3
Coumarin	H	H	H
Umbelliferone	H	OH	H
Herniarin	H	OCH$_3$	H
Aesculetin	OH	OH	H
Scopoletin	OCH$_3$	OH	H
Fraxetin	OCH$_3$	OH	OH

[a] See Formula 18.12.



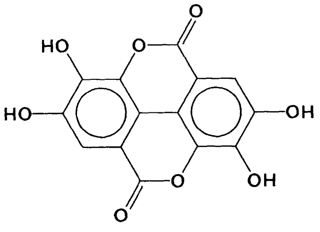
VIII (18.12)

Table 18.19. Occurrence of hydroxybenzoic acids in fruit[a]

Type of fruit	4-Hydroxy-benzoic acid	Protoca-techuic acid	Gallic acid
Blackberry	10–16	68–189	8–67
Black currant	0–6	10–52	30–62
Raspberry	15–27	25–37	19–38
Red currant	10–23	3–08	
Strawberry	10–36		11–44
White currant	5–19		3–38

[a] After hydrolysis; values in mg/kg fresh weight.

The hydroxybenzoic acids that are found in various fruits and occur mostly as esters include: salicylic acid (2-hydroxybenzoic acid), 4-hydroxybenzoic acid, gentisic acid (2,4-dihydroxybenzoic acid), protocatechuic acid (3,4-dihydroxybenzoic acid), gallic acid (3,4,5-trihydroxybenzoic acid), vanillic acid (3-methoxy-4-hydroxybenzoic acid) and ellagic acid (IX, Formula 18.13), the dilactone of hexahydroxydiphenic acid (Table 18.19). Table 18.19 shows the most important sources of 4-hydroxybenzoic acid, protocatechuic acid and gallic acid. Strawberries (0.2–0.5), raspberries (1.2) and blackberries (1.9–2.0) contain higher concentrations of free and bound ellagic acid (g/kg).

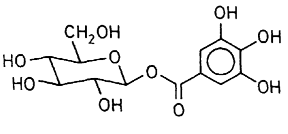


IX (18.13)

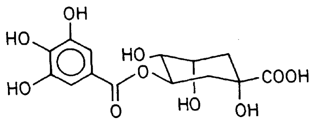
Apart from the proanthocyanidins (cf. 18.1.2.5.2), esters of gallic acid and hexahydroxydiphenic acid form one of the two main classes of plant tanning agents, the “hydrolyzable tanning agents” or tannins. In addition to simple esters with different hydroxy components, such as β-D-glucogallin (X in Formula 18.14), theogallin (XI) and the flavan-3-olgallates XII and XIII, found, e. g., in tea leaves, complex polyesters with D-glucose are known.

They have molecular weights of M_r 500–3000, are generally readily soluble, and contribute their astringent properties to the taste of foods of plant origin.

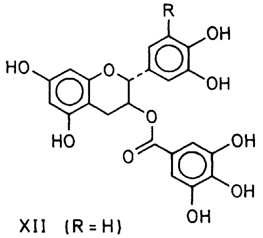
Apart from gallic acid, most of the tanning agents of this type contain as acyl residues intermolecular gallic acid esters (depsides XIV), their ethers (depsidones, XV), and hexahydroxydiphenic acid (XVI) formed by oxidative coupling of two gallic acids. Some of the polyphenols derived from β-pentagalloyl-D-glucose are shown



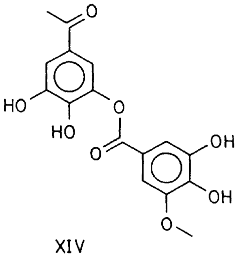
X



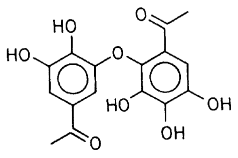
XI



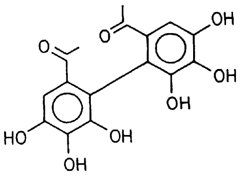
XII (R = H)
XIII (R = OH)



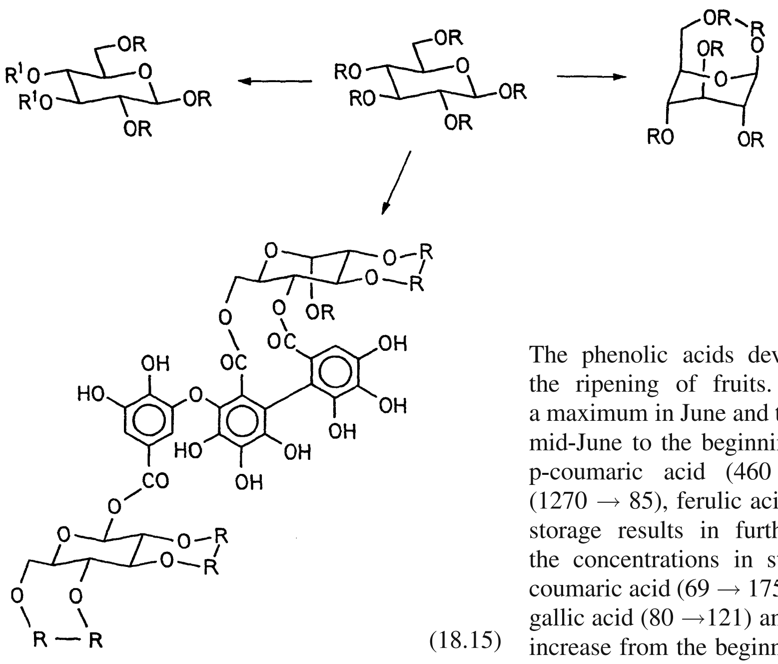
XIV



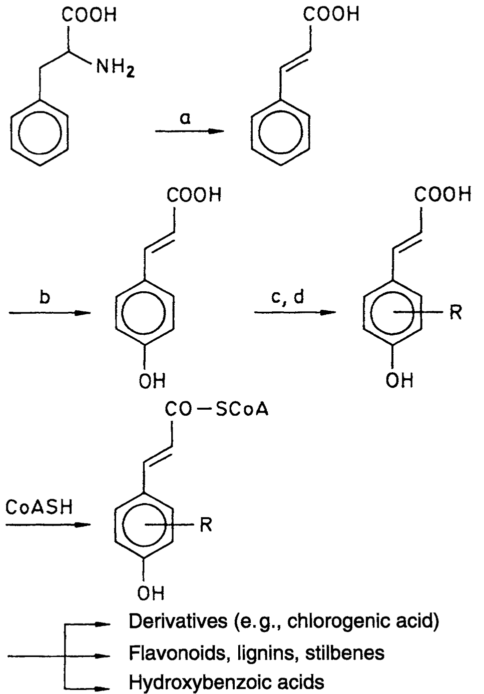
XV



XVI (18.14)



(18.15)

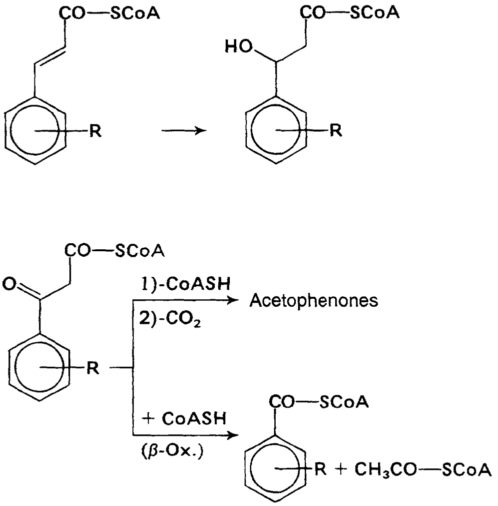


(18.16)

in Formula 18.15. They have been found in various *Rosaceae*, e. g., raspberries and blackberries, and contain the structural elements mentioned above.

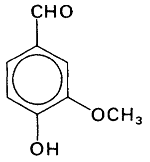
The phenolic acids develop differently during the ripening of fruits. In apples, they reach a maximum in June and then decrease, e. g., from mid-June to the beginning of October (mg/kg): p-coumaric acid (460 → 15), caffeic acid (1270 → 85), ferulic acid (95 → 4). Subsequent storage results in further losses. In contrast, the concentrations in strawberries of, e. g., β-coumaric acid (69 → 175), caffeic acid (15→39), gallic acid (80 →121) and vanillic acid (3 → 34) increase from the beginning of June till ripening in the beginning of July (mg/kg). Hydroxycinnamic acid biosynthesis starts with phenylalanine [cf. Reaction route 18.16: a) phenylalanine-ammonia lyase; b) cinnamic acid 4-hydroxylase; c) phenolases; d) methyl transferases, R: OH and OCH_3 in various positions].

The hydroxybenzoic acids are derived from hydroxycinnamic acids by a pathway analogous to β-oxidation of fatty acids:

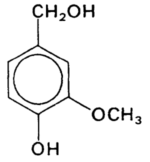


(18.17)

Reduction of the benzoic acid carboxyl groups yields the corresponding aldehydes and alcohols, as for instance vanillin and vanillyl alcohol (XVII and XVIII respectively in Formula 18.18) from 3-methoxy-4-hydroxybenzoic acid and coniferyl alcohol from ferulic acid.

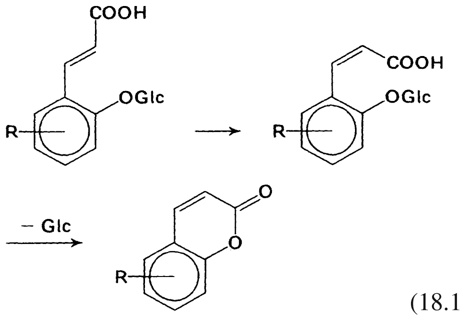


XVII



XVIII (18.18)

The glucosides of cis-o-coumaric acid are the precursors of coumarins. Disintegration of plant tissue releases the free acids from the glucosides. The acids then close spontaneously to the ring forms (R: OH and OCH_3 in various positions):



(18.19)

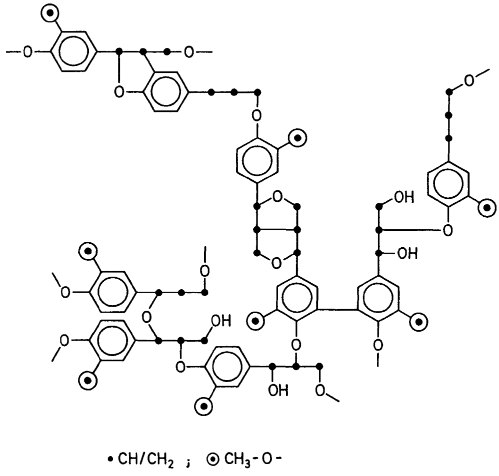
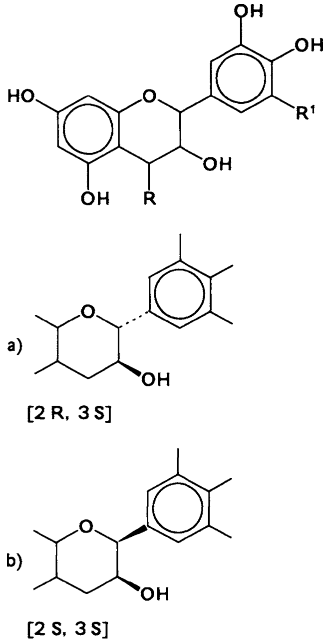


Fig. 18.5. Section of the structure of a lignin (according to *Kindl* and *Wöber*, 1975)

Lignin is formed by the dehydrogenative polymerization of coniferyl, sinapyl, and p-coumaryl alcohol, which is catalyzed by a peroxidase and requires H_2O_2. A section of the structure of lignin formed by the polymerization of coniferyl alcohol is shown in Fig. 18.5. Lignins strengthen the walls of plant cells. They play a role as fiber in foods (cf. 15.2.4.2).

18.1.2.5.2 Flavan-3-ols (Catechins), Flavan-3,4-diols, and Proanthocyanidins (Condensed Tanning Agents)

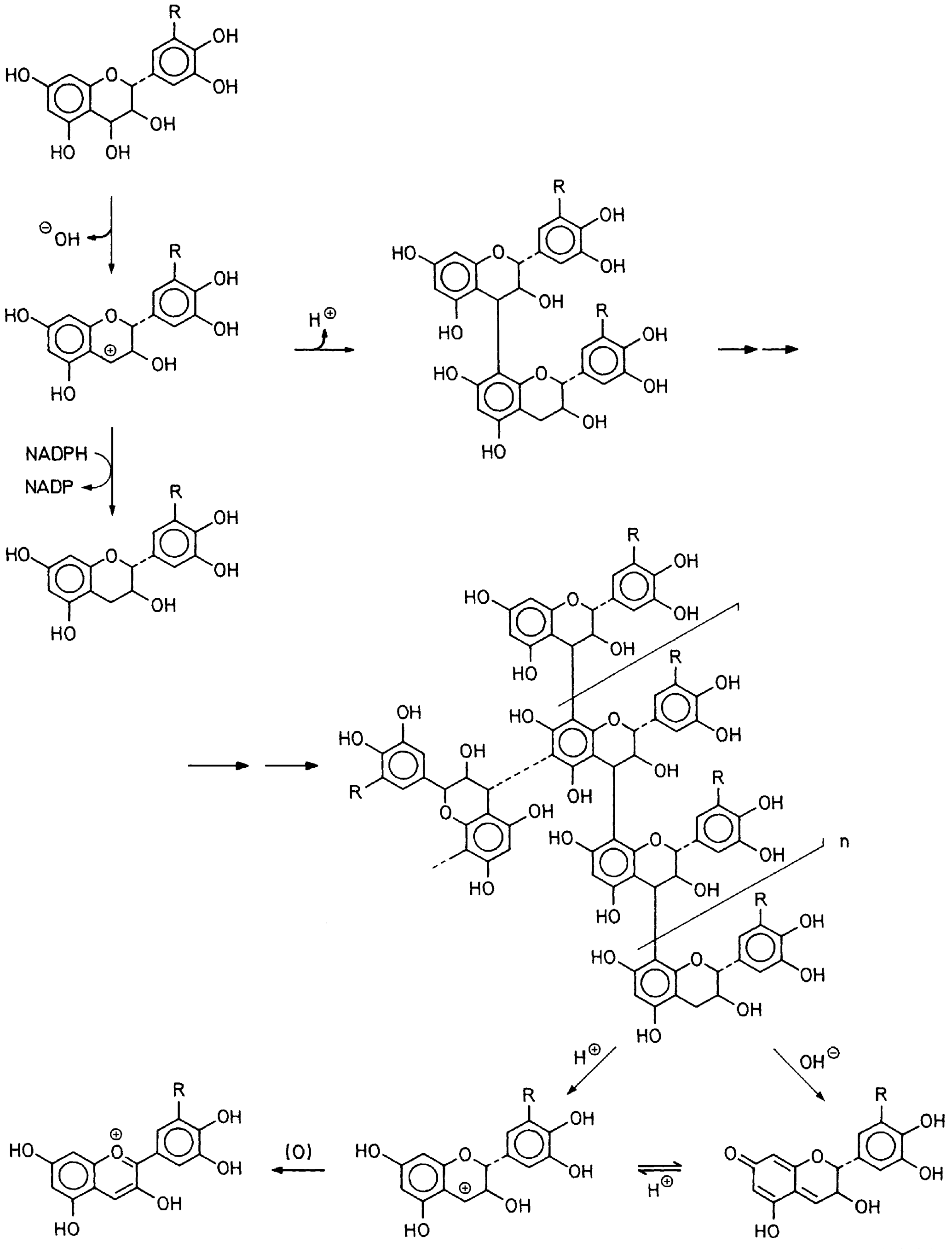
These colorless compounds are the following: [R, R^1 = H: a) catechin, b) epicatechin; R = H, R^1 = OH: gallocatechin, epigallocatechin; R = OH: flavan-3,4-diols]:



(18.20)

Table 18.20 shows the occurrence of catechin and epicatechin in fruit.

In flavonoid biosynthesis, flavan-3,4-diols can be converted to flavan-3-ols (cf. 18.1.2.5.7). The intermediate is assumed to be a carbocation which is reduced to flavan-3-ol (Formula 18.21). When the reducing agent, e.g., NADPH, is limited, the cation can react with flavan-3-ol to



(18.21)

Table 18.20. Occurrence of catechin and epicatechin in foods[a]

Food	(+)Catechin	(-)Epicatechin
Apple	4–15	67–103
Apricot	50	61
Blackberry	7	181
Bilberry	n.d.	11
Sweet cherry	22	95
Black currant	7	5
Red currant	12	n.d.
Kiwi	n.d.	5
Mango	17	n.d.
Peach	23	n.d.
Pear	1–2	29–37
Plum	33	28
Strawberry	44	n.d.

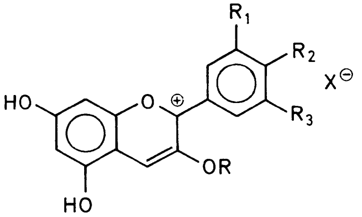
[a] Values in mg/kg fresh weight.
n.d.: not detected.

give dimers and higher oligomers, which are called proanthocyanidins. As “condensed tanning agents”, they contribute to the astringent taste of fruits. The spectrum of oligomers depends on the ratio of the rate of formation to the rate of reduction of the cation. The proanthocyanidins are soluble up to $M_r \sim 7000$, corresponding to ca. 20 flavanol units. Plant tissues also contain insoluble polymeric forms which frequently even predominate and can be covalently bound to the polysaccharide matrix of the cell. Procyanidins (Formula 18.21, R = H) are the most common group of proanthocyanidins; prodelphinidins (R = OH) also occur.

The name proanthocyanidins, previously called leucoanthocyanidins, implies that these are colorless precursors of anthocyanidins. On heating in acidic solution, the C—C bond made during formation is cleaved and terminal flavan units are released from the oligomers as carbocations, which are then oxidized to colored anthocyanidins (cf. 18.1.2.5.3) by atmospheric oxygen (Formula 18.21). Base-catalyzed cleavage via the quinone methode is also possible.

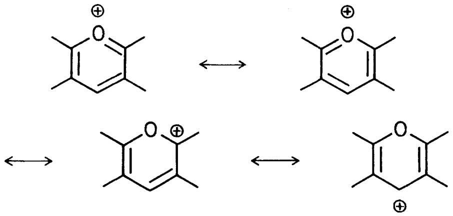
18.1.2.5.3 Anthocyanidins

These red, blue or violet colored benzopyrylium and flavylium salts (Formula 18.22) occur in the form of glycosides, the anthocyanins, in most commonly grown fruit varieties (Table 18.21) and also in tropical fruits; approximately 70 have been identified up to now.



(18.22)

The cation is to be regarded as a resonance hybrid of the following oxonium and carbenium forms:



(18.23)

The sugar residues at the 3 or 5 position are easily cleaved in an acid catalyzed reaction with the formation of the corresponding aglycones (anthocyanidins).

Table 18.22 provides data on the structure and absorption maxima of the most important antho-

Table 18.21. Anthocyan content of fruit[a,b]

Type of fruit	Dp	Cy	Pt	Pg	Pn	Mv
Apple						
Gala	–	2.3	–	–	–	–
Red Delicious	–	12	–	–	0.2	–
Blackberry	–	244	–	0.7	–	–
Bilberry	120	29	72	–	34	131
Cherry, sweet	–	113	–	1.4	7.5	–
Black currant	333	133	7.3	1.9	1	–
Red currant	0.1	13	–	–	–	–
Red grape	1.1	3.9	1.1	–	10	10
Peach	–	4.8	–	–	–	–
Plum	–	19	–	–	–	–
Raspberry	–	90	–	1.9	–	–
Strawberry	–	1.2	–	20	–	–

[a] Values in mg/kg fresh weight.
[b] Dp, delphinidin; Cy, cyanidin; Pt, petunidin; Pg, pelargonidin; Pn, peonidin; Mv, malvidin.
– not detected.

cyanidins. Increasing hydroxylation results in a shift towards blue color (pelargonidin → cyanidin → delphinidin), whereas glycoside formation and methylation results in a shift towards red color (pelargonidin → pelargonidin-3-glucoside; cyanidin → peonidin). The visual detection threshold (VDT) is also influenced by the glycoside residue, as shown by the following examples (VDT in mg/l water): cyanidin-3-sophorosyl-5-glucoside (3.6), cyanidin-3-glucoside (1.3), cyanidin-3-xylosylgalactoside (0.9).

The color of an anthocyanin changes with the pH of the medium (R = sugar moiety; cf. Formula 18.24).

Table 18.22. Anthocyanidins: absorption maxima in the visible spectrum

Compound (Formula 18.22)	R^1	R^2	R^3	λ_{max} (nm)[a] R = H	R = Glc[b]
Pelargonidin	H	OH	H	520	506
Cyanidin	OH	OH	H	535[c]	525[c]
Peonidin	OCH_3	OH	H	532	523
Delphinidin	OH	OH	OH	544[c]	535[c]
Petunidin	OCH_3	OH	OH	543[c]	535[c]
Malvidin	OCH_3	OH	OCH_3	542	535

[a] In methanol with 0.01% HCl.

[b] 3-Glucoside.

[c] $AlCl_3$ shifts the absorption towards the blue region of the spectrum by 14 to 23 nm.

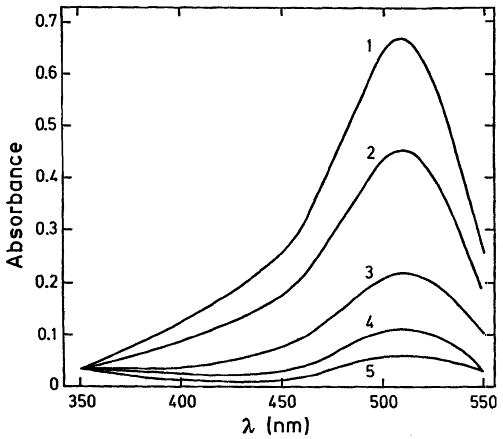
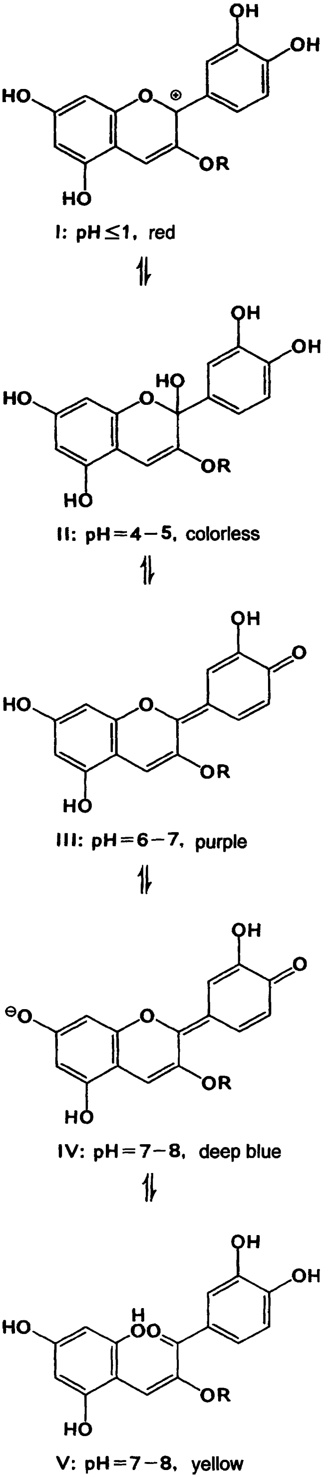
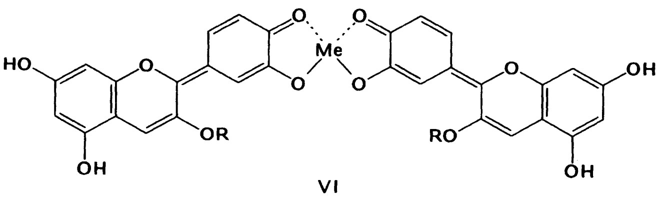


Fig. 18.6. Absorption spectra of cyanidin-3-rhamnoglucoside (16 mg/l) in aqueous buffered solution at pH 0.71 (1), pH 2.53 (2), pH 3.31 (3), pH 3.70 (4), and pH 4.02 (5). (According to *Jurd*, 1964)

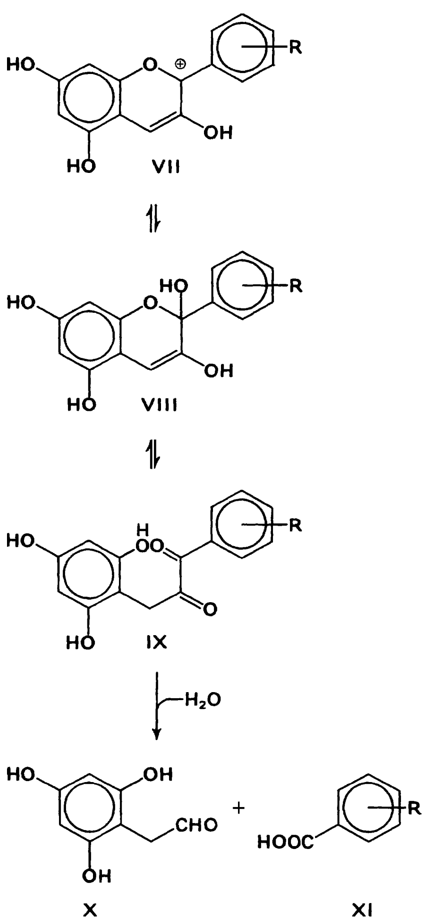


(18.24)



(18.25)

The flavylium cation (I) is stable only at very low pH. As the pH increases it is transformed into colorless chromenol (II). Figure 18.6 shows the decrease in absorption in the visible spectrum at various pH's, reflecting these transformations. Formation of a quinoidal (III) and ionic anhydro base (IV) at pH 6–8 intensifies the color. At pH 7–8 structure IV is transformed through ring opening to yellow chalcone (V). At higher pH's the color can be stabilized by the presence of multivalent metal ions (Me: Al^{3+}, Fe^{3+}). The complexes formed are deep blue (cf. Formula 18.25). Figure 18.7 illustrates the shift in absorption maximum from 510 to 558 nm for cyanidin-3-glucoside over the pH range of 1.9–5.4. Readings were taken in the presence of aluminium chloride. At higher pH's free anthocyanidins (VII, Formula 18.26) are degraded via chromenols (VIII) and α-diketones (IX) to aldehydes (X) and carboxylic acids (XI):



(18.26)

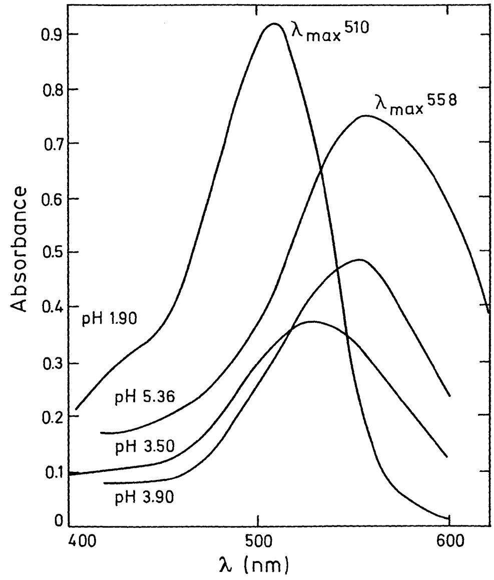
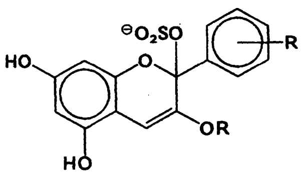
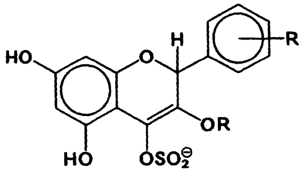


Fig. 18.7. Absorption spectra of cyanidin-3-glucoside (35 µmole/l + 830 µmole/l $AlCl_3$) in aqueous buffered solutions at pH 1.90, pH 3.50, pH 3.90, and pH 5.36. (According to *Jurd* and *Asen*, 1966)

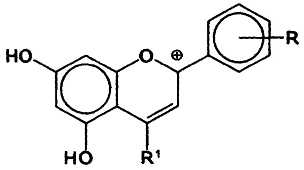
Addition of SO_2 bleaches anthocyanins. The flavylium cation reacts to form a carbinol base corresponding to compounds XII or XIII (Formula 18.27). The color is restored by acidification to pH 1 or by addition of a carbonyl compound (e. g. ethanal). Since compounds of type XIV ($R^1 = CH_3$, C_2H_5) are not affected by SO_2, it appears that compound XIII is involved in such bleaching reactions.



XII



XIII

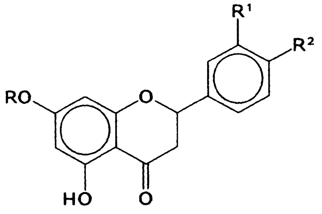


XIV

(18.27)

18.1.2.5.4 Flavanones

Flavanones (Formula 18.28: $R^1 = H$, $R^2 = OCH_3$: isosacuranetin; $R^1 = H$, $R^2 = OH$: naringenin; $R^1 = OH$, $R^2 = OCH_3$: hesperitin; R^1, $R^2 = OH$: eriodictyol) occur mostly as glycosides in citrus fruits (Table 18.23):



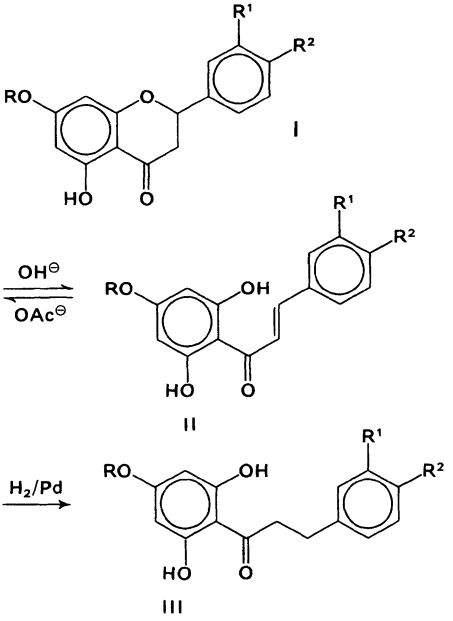
(18.28)

Table 18.24 shows that flavanone-7-rutinosides are usually nonbitter, whereas flavanone-7-neohesperidosides are generally bitter. The intensity of the bitter taste is influenced by the substitution pattern. Compounds with $R^1 = H$, $R^2 = OH, OCH_3$ (e. g., naringin, poncirin) are an order of magnitude more bitter than those with $R^1 = OH$, $R^2 = OH, OCH_3$ (e. g., neohesperidin, neoeriocitrin). Naringenin-7-neohesperidoside (naringin) is the bitter constituent of grapefruit. Hesperetin-7-neohesperidoside (neohesperidin) is the bitter compound of bitter oranges (*Citrus auranticus*). The nonbitter isomer, hesperitin-7-rutinoside (hesperidin) occurs in oranges (*Citrus sinensis*) (cf. Table 18.23).

Removal of the bitter taste of citrus juices and citrus fruit pulps is possible by enzymatic cleavage of the sugar moiety using a mixture of α-rhamnosidase and β-glucosidase. These enzymes are isolated from microorganisms such as *Phomopsis citri, Cochliobolus miyabeanus* or *Rhizoctonia solanii*:

$$\text{Naringin} \longrightarrow \text{Naringenin} + \text{Rhamnose} + \text{Glucose}$$

A number of neutral or bitter flavanone glycosides can be converted through ring opening to sweet chalcones (II) which, by additional hydrogenation, can be stabilized as sweet dihydrochalcones (III):



(18.29)

The presence of a free OH-group in position R^1 or R^2 is necessary for a sweet taste. Table 18.25 shows that the dihydrochalcone of naringin corresponds to saccharin in sweetness intensity, whereas the dihydrochalcone of neohesperidin is sweeter than saccharin by a factor of 20.

Conversion of naringin to highly sweet neohesperidin dihydrochalcone (VII) is possible by al-

Table 18.23. Flavanones and flavones in citrus fruits[a]

Polyphenol glucoside[b]	Orange, sweet[c]		Bitter orange		Grapefruit		Lemon	
	Fruit	Peel	Fruit	Peel	Fruit	Peel	Fruit	Peel
Flavanones								
Eriocitrin (Eri-7-rut)	159	59	49	38	183	92	1020	1320
Neoeriocitrin (Eri-7-neo)	27	n.d.	2100	2200	n.d.	n.d.	n.d.	n.d.
Narirutin (Nar-7-rut)	1660	665	170	220	1700	1900	114	225
Naringin (Nar-7-neo)	n.d.[d]	n.d.	9790	14,700	13,600	21,000	n.d.	n.d.
Hesperidin (Hes-7-rut)	9620	14,100	n.d.	n.d.	n.d.	n.d.	3560	711
Neohesperidin (Hes-7-neo)	n.d.	n.d.	6840	10,900	210	203	n.d.	n.d.
Neoponcirin (Isa-7-rut)	571	421	16	27	53	84	n.d.	n.d.
Poncirin (Isa-7-neo)	n.d.	n.d.	2820	5670	3040	462	n.d.	n.d.
Flavones								
Rutin (Que-3-rut)	108	n.d.	290	473	51	51	n.d.	n.d.
Isorhoifolin (Api-7-rut)	3	11	20	37	n.d.	n.d.	158	355
Rhoifolin (Api-7-neo)	15	58	566	1080	95	184	13	29
Diosmin (Dio-7-rut)	14	55	16	38	n.d.	n.d.	208	432
Neodiosmin (Dio-7-neo)	77	30	173	438	185	110	n.d.	n.d.

[a] Values in mg/kg fresh weight; n.d., not detected.

[b] Api: apigenin, Dio: diosmetin, Eri: eriodictyol, Hes: hesperitin, Isa: isosakuranetin, Nar: naringenin, Que: quercetin, rut: rutinose (O-α-L-Rha$_p$-(1 → 6)-D-Glc$_p$), neo: neophesperidose (O-α-L-Rha$_p$(1 → 2)-D-Glc$_p$)

[c] *C. sinensis* cv. Valencia

[d] *C. sinensis* var Brasiliensis cv. Morita contained 14 mg/kg naringin

Table 18.24. Taste of flavanone glycosides[a]

Compound	R	R^1	R^2	Taste	
				quality	intensity[b]
Naringenin-rutinoside	rut[c]	H	OH	neutral	–
Naringin	neo[d]	H	OH	bitter	20
Isosacuranetin-rutinoside	rut	H	OCH$_3$	neutral	–
Poncirin	neo	H	OCH$_3$	bitter	20
Hesperidin	rut	OH	OCH$_3$	neutral	–
Neohesperidin	neo	OH	OCH$_3$	bitter	2
Eriocitrin	rut	OH	OH	neutral	–
Neoeriocitrin	neo	OH	OH	bitter	2

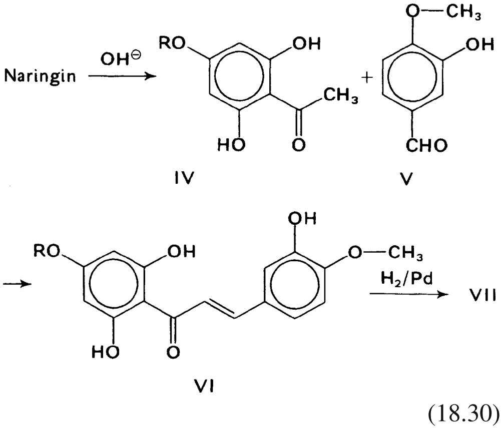
[a] Data for R, R^1 and R^2 refer to Formula 18.28.

[b] Relative bitterness refers to quinine hydrochloride = 100.

[c] Rutinosyl.

[d] Neohesperidosyl.

kali fragmentation to a methylketone (IV), condensation with isovanillin (V) to the corresponding chalcone (VI), then hydrogenation:



(18.30)

A sweet compound can be obtained from the neutral-tasting hesperidin of oranges by first converting hesperidin to another neutraltasting compound, hesperidin dihydrochalcone. The latter can then be hydrolyzed, by acidic or enzymatic catalysis, to remove the rhamnose residue, yielding hesperidin dihydrochalcone glucoside, which is sweet. The use of dihydrochalcones as sweeteners is discussed in Section 8.8.11.

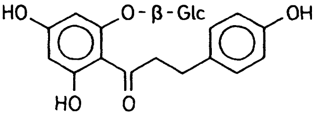
Table 18.25. Taste of dihydrochalcones

Dihydrochalcone from	Tastes		
	quality	intensity[a] (µmole/l)	Relative intensity[b]
Naringin	sweet	200	1
Neohesperidin	sweet	10	20
Neoeriocitrin	slightly sweet	–	–
Poncirin	slightly bitter	–	–
Saccharin (Sodium salt)	sweet	200	1

[a] Concentration of iso-sweet solutions.

[b] Related to saccharin.

The dihydrochalcone glycoside phloridzin (Formula 18.31) occurs in apples.



(18.31)

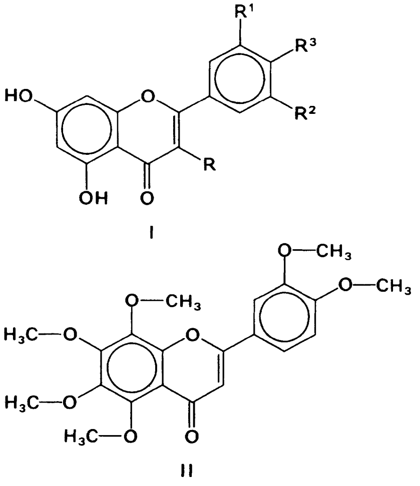
18.1.2.5.5 Flavones, Flavonols

Flavones (Formula 18.32: I, R = H; R^1, R^2 = H, R^3 = OH: apigenin; R^1, R^2 = OH, R^3 = H: luteolin; R^1 = OH, R^2 = H, R^3 = OCH_3: diosmetin; R^1 = OCH_3, R^2 = H, R^3 = OH: chrysoeriol; II: nobiletin) and flavonols (Formula 18.32: I, R, R^3 = OH; R^1, R^2 = H: kaempferol; R^1 = OH, R^2 = H: quercetin; R^1, R^2 = OH: myricetin; R^1 = OCH_3, R^2 = H: isorhamnetin) occur in all common fruits and citrus and tropical fruits as the 3-glycosides and, less frequently, as the 7-glycosides (Tables 18.23 und 18.26). Quercetin is a very effective antioxidant (cf. 3.7.3.2.1). Higher concentrations (mg/kg) have been found in quince (180), elderberry (170), cranberry (130), raspberry (70), apple (49), cherry (14) and red/blackcurrant (13).

Table 18.26. Occurrence of flavonols in fruit

Fruit	Flavonols
Apple	Que-3-gal, Que-3-glc, Que-3-rha, Que-3-rha-glc, Que-3-ara, Que-3-xyl
Pear	Que-3-glc
Peach	Que-3-glc
Apricot	Que-3-glc, Kaem-gly
Plum/prune	Que-3-glc, Que-3-rha, Que-3-ara
Sour cherry	
Sweet cherry	Que-3-glc
Blackberry	Que-3-glc
Strawberry	
Currant, black	Que-3-glc, Kaem-3-glc, Myr-3-glc, further Que-glc, Kaem-glc
Raspberry	
Grapes	Que-3-rha, Que-3-glc, Que-3-rha-glc

Kaem: kaempferol, Myr: myricetin, Que: quercetin. ara: arabinoside, gal: galactoside, glc: glucoside, gly: glycoside, rha: rhamnoside, and xyl: xyloside.



(18.32)

They are faintly yellow compounds.

Table 18.27. Lignans in foods[a,b]

Food	Pino (I)	Lari (II)	Seco (III)	Mat (IV)	Sum
Linseed	33	30	2942	5	3011
Sesame	293	94	0.7	5	393
Bread, wholemeal wheat	0.3	0.7	0.2	n.d.	1.2
Bread, Rye, dark	1.7	1.2	0.1	0.1	3.2
Broccoli	3.2	9.7	0.4	n.d.	13.3
Garlic	2.0	2.9	0.5	n.d.	5.4
Apricot	3.1	1.1	0.3	n.d.	4.5
Strawberry	2.1	1.2	0.05	n.d.	3.3
Peach	1.9	0.8	0.3	n.d.	2.9

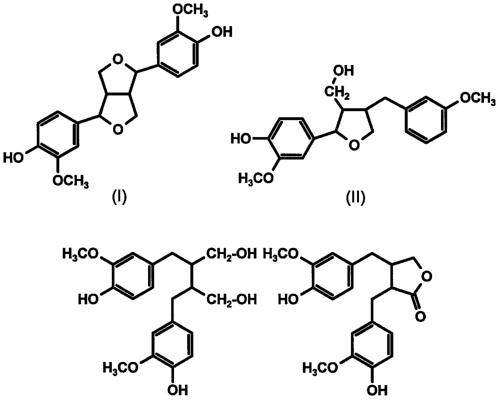
[a] Values in mg/kg fresh weight.

[b] Structures see Formula 18.33, Name: pinoresinol (I), lariciresinol (II), secoisolariciresinol (III), matairesinol (IV)

n.d.: not detected

18.1.2.5.6 Lignans

Lignans are polyphenols which belong to the group of phytoestrogens (cf. 16.2.9). Four compounds (I–IV in Formula 18.33) will be presented here. Pinoresinol (I) is a dimer of coniferyl alcohol. Lignans widely occur in low concentrations in food (examples in Table 18.29), linseed and sesame being especially rich.



(I) (II) (III) (IV) (18.33)

18.1.2.5.7 Flavonoid Biosynthesis

Flavonoid biosynthesis (cf. Formula 18.34) occurs through the stepwise condensation of activated hydroxycinnamic acid (I) with three activated malonic acid molecules (II). The primary condensation product, a chalcone (III), is in equilibrium with a flavanone (IV) with the equilibrium shifted toward product IV. The condensation directly yields a flavanone, hence chalcone is not an obligatory intermediary product.

A 2,7-cyclization yields stilbenes (IIIa).

One pathway converts flavanones (IV) to flavones (V) and, through another pathway, flavanones are converted to flavanonols (VI). The latter compounds are converted to flavandiols (VII), flavanols (VIII) and flavonols (IX), as well as anthocyanidins (XII) via endiols (X) and enols (XI).

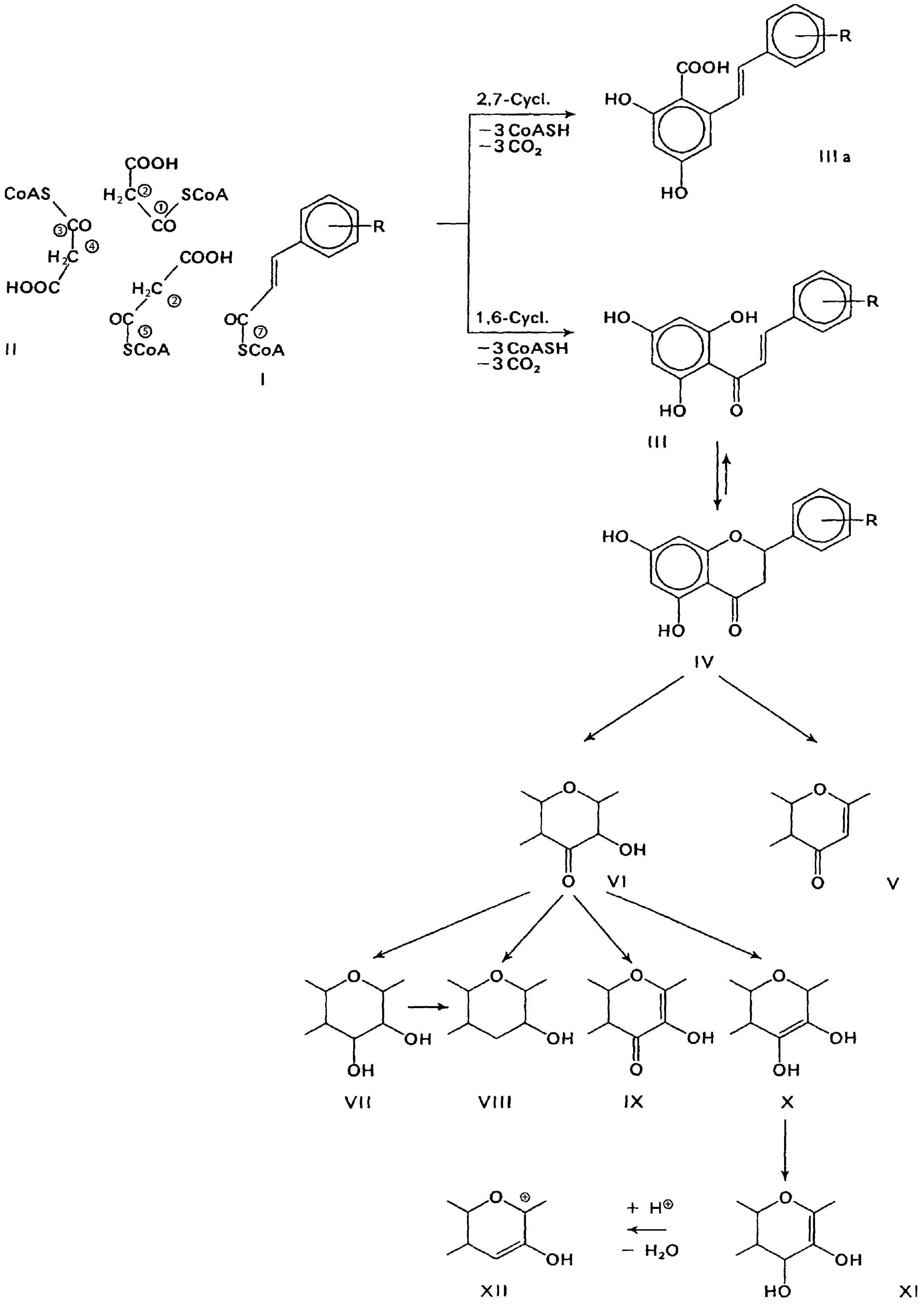
18.1.2.5.8 Technological Importance of Phenolic Compounds

The taste of fruits is influenced by phenolic compounds. The presence of tannins yields an astringent, harsh taste, similar to an unripe apple (or an apple variety suitable only for processing). Table quality apples are low in phenolic compounds. Flavanones (naringin, neohesperidin) are the bitter compounds of citrus fruits.

Phenolic compounds are substrates for polyphenol oxidases. These enzymes hydroxylate monophenols to o-diphenols and also oxidize o-diphenols to o-quinones (cf. 2.3.3.2).

o-Quinones can enter into a number of other reactions, thus giving the undesired brown discoloration of fruits and fruit products. Protective measures against discoloration include inactivation of enzymes by heat treatment, use of reductive agents such as SO_2 or ascorbic acid, or removal of available oxygen.

Polyvalent phenols form colored complexes with metal ions. For example, at $pH > 4$, Fe^{3+} forms


CoAS
COOH
H₂C②
SCoA
①
③CO
CO
H₂C ④
HOOC
COOH
H₂C
②
OC
⑤
SCoA
OC
⑦
SCoA
II
I
R
2,7-Cycl.
−3 CoASH
−3 CO₂
1,6-Cycl.
−3 CoASH
−3 CO₂
COOH
HO
HO
III a
HO
OH
HO
O
III
HO
O
HO
O
IV
O
OH
O
VI
O
O
V
OH
OH
VII
OH
VIII
OH
O
IX
OH
OH
X
O ⊕
OH
XII
+ H⊕
− H₂O
OH
HO
XI

(18.34)

complexes which are bluish-gray or bluish-black in color. Al^{3+} and Sn^{2+} also form intensely colored complexes. Leucoanthocyanins, when heated in the presence of an acid, are converted into anthocyanins. The red color of apples and pears, which is formed during cooking, is derived from leucoanthocyanins.

Phenolic compounds can also form complexes with proteins. These complexes increase the turbidity of fruit juices, beer and wine. The tendency to form complexes of this type increases with increasing degree of polymerization of the phenols; even dimeric procyanidins are active, e. g., procyanidin B2 (epicatechin-epicatechin) in apple juice. Based on model experiments, it is thought that especially the amino acid proline should be involved in complex formation, its ring system forming a π-complex with that of the phenols. Hydrogen bridges are also supposed to contribute to stabilization of the complexes. In the pH range 4.0–4.2, the amount of precipitate is maximum, being 7 times higher than at pH 3.0. In a similar manner as proteins and peptides, polyvinylpolypyrrolidone (PVPP) binds polyphenols. Therefore, it is especially suitable for the separation of haze active polyphenols.

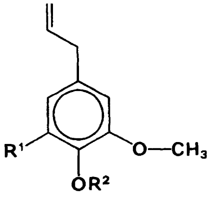
18.1.2.6 Aroma Compounds

Aroma compounds contribute significantly to the importance of fruits in human nutrition. The aroma substances of selected fruits will be outlined below in more detail. The structures and synthesis pathways of common aroma substances are explained in Chapter 5.

The aroma of fruits can change on heating due to the liberation of aroma substances from glycosidic precursors (cf. 5.3.2.4), oxidation, water addition, and cyclization of individual compounds (cf. 5.5.4).

18.1.2.6.1 Bananas

The characteristic aroma compound of bananas is isopentyl acetate. Some esters of pentanol, such as those of acetic, propionic and butyric acids, also contribute to the typical aroma of bananas, while esters of butanol and hexanol with acetic and butyric acids are generally fruity in character. An important contribution to the complete, mild banana aroma is supposed to be provided by eugenol (1), O-methyleugenol (II) and elemicin (III):



I: $R^1, R^2 = H$
II: $R^1 = H, R^2 = CH_3$
III: $R^1 = OCH_3, R^2 = CH_3$ (18.35)

18.1.2.6.2 Grapes

The compounds responsible for the typical aromas of different grape varieties has not been clarified in each case. Esters contribute to the fruity notes. The flowery-fruity aroma note of American grapes (*Vitis labrusca*) is based on 2-aminobenzoic acid methylester (methyl anthranilate), which is not found in European varieties, 2-Isobutyl-3-methoxypyrazine is responsible for the green paprika-like aroma note of Cabernet Sauvignon grapes.

18.1.2.6.3 Citrus Fruits

The aroma of the most important citrus fruit, the orange, has been analyzed in detail. The potent aroma substances identified in the freshly pressed juice of the variety *Valencia late* by dilution analyses are shown in Table 18.28.

On the basis of high orthonasal aroma values, it is expected that (S)-2-methylbutyric acid ethylester, ethyl butyrate, (Z)-3-hexenal, isobutyric acid ethylester, acetaldehyde and (R)-limonene are especially important for the aroma of orange juice (Table 18.28). Based on the retronasal odor threshold, the group of important compounds is enlarged to include 1-octen-3-one, trans-4,5-epoxy-(E)-2-decenal and ethyl caproate. A mixture of the odorants listed in Table 18.28, in which only wine lactone was missing, reproduced and aroma of orange juice. Omission experiments showed that the key aroma substances of the orange are acetalde-

Table 18.28. Odorants in fresh orange juice[a]

Compound	Concentration (µg/kg)	Aroma value[b] Ortho-nasal	Retro-nasal
Acetaldehyde	8305	332	831
Isobutyric acid ethylester	8.8	440	293
(R)-α-Pinene	308	62	9
Ethyl butyrate	1192	1192	11,920
(S)-2-Methylbutyric acid ethylester	48	8000	12,000
Hexanal	197	19	19
(Z)-3-Hexenal	187	747	6227
Myrcene	594	42	36
(R)-Limonene	85,598	228	1339
3-Methylbutanol	639	<1	2.6
2-Methylbutanol	270	<1	n.b.
Ethyl caproate	63	13	125
Octanal	25	3.2	<1
1-Octen-3-one	4.1	4.1	410
Nonanal	13	2.7	3.8
Methional	0.4	<1	10
Decanal	45	9	6
(E)-2-Nonenal	0.6	<1	8
(S)-Linalool	81	13	54
3-Hydroxyhexanoic acid ethylester	1136	4	18
(E,E)-2,4-Decadienal	1.2	6	24
trans-4,5-Epoxy-(E)-2-decenal	4.3	36	287
Wine lactone	0.8	n.b.	94
Vanillin	67	3	2

[a] Variety: *Valencia late.*

[b] Aroma value: the ratio of the concentration to ortho- or retronasal odor threshold value of the substance in water.

n.d.: not determined.

hyde, (Z)-3-hexenal, decanal, (R)-limonene and trans-4,5-epoxy-(E)-2-decenal. It is remarkable that these substances include decanal although its aroma value is fairly low (Table 18.28). Esters are also indispensable, but the aroma of the recombined mixture is not impaired when a member of this group is missing. The contribution of (R)-α-pinene and myrcene is negligible.

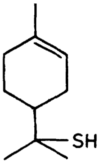
The concentrations of the odorants in juice differ depending on the variety. Thus, the weaker citrus note of *Navel* oranges compared with the variety *Valencia late* is due to a 70% lower content of (R)-limonene.

The aroma of oranges changes on storage. In the juice of oranges stored for three weeks at 4°C, the concentrations of esters and especially aldehydes were much lower than in the fresh juice. For instance, the content of (Z)-3-hexenal was only 15%.

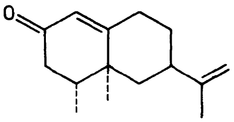
Orange juice from rediluted concentrate differs in its aroma. This can be the result of big losses of acetaldehyde and (Z)-3-hexenal, the formation of carvone by peroxidation of limonene and a large increase in the vanillin concentration, probably due to the degradation of ferulic acid.

Dilution analyses of grapefruit juice gave high FD factors (definition in 5.2.2.1) for ethyl butyrate, (Z)-3-hexenal, 1-hepten-3-one, 4-mercapto-4-methylpentan-2-one and 1-p-menthene-8-thiol (IV, probably the R enantiomer). The concentrations of the two sulfur compounds in juices were 0.4–0.8 µg/l and 0.007–0.1 µg/l respectively. Omission experiments (cf. 5.2.7) indicate that the grapefruit aroma note is produced by 4-mercapto-4-methylpentan-2-one. 1-p-Menthene-8-thiol, which occurs in even lower concentrations in oranges, contributes to the aroma but is not typical. It is possibly formed by the addition of H_2S to limonene. Traces of hydrogen sulfide occur in all citrus juices.

Grapefruit juice differs from orange juice also in the considerably lower limonene content. (+)-Nootkatone (V) only contributes to the aroma of grapefruit peel-oil, but not to that of the juice.



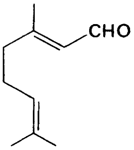
IV



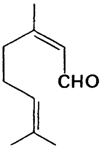
V

(18.36)

Citral, which is actually a mixture of two stereoisomers, geranial (VIa) and neral (VIb), is the character impact compound of lemon oil (cf. 5.5.1.5):



VIa



VIIb

(18.37)

Linalool, myrcene, and limonene also have high aroma values.

18.1.2.6.4 Apples, Pears

The potent odorants identified in two apple varieties with a fruity/green (*Elstar*) and fruity/sweet/aromatic (*Cox Orange*) odor are shown in Table 18.29.

The fruity note in the aroma profile of both varieties is produced by acetic acid esters. On the other hand, there is a decrease in the ethyl esters, which are more odor active than the acetates (cf. 5.3.2.2) and dominate in some other fruits, e. g., oranges and olives. Hexanal, (Z)-3-hexenal and (Z)-3-nonenal are responsible for the green/apple-like note. (E)-β-Damascenone, which smells of cooked apples, has the highest aroma value in both varieties due to its much lower odor threshold. Eugenol and (E)-anethol contribute to the aniseed-like note which is a characteristic especially of the aroma of the peel of the *Cox Orange*.

The aroma of the pear Williams Christ is characterized by esters produced by the degradation of unsaturated fatty acids (example in 5.3.2.2): ethyl esters of (E,Z)-2,4-decadienoic acid, (E)-2-octenoic acid, and (Z)-4-decenoic acid, as well as hexyl acetate. In fact, butyl acetate and ethyl butyrate are also involved in the fruity odor note.

18.1.2.6.5 Raspberries

The character impact compound is the "raspberry ketone", i. e. 1-(p-hydroxyphenyl)-3-butanone (VII). Its concentration is 2 mg/kg and its odor threshold is 5 μg/kg (water). The starting point for the biosynthesis of VII is the condensation reaction of p-cumaroyl-CoA with malonyl-CoA (cf. Formula 18.38). Additional aroma notes are provided by (Z)-3-hexenol, α- and β-ionone.

In addition, the ethyl esters of 5-hydroxyoctanoic acid and 5-hydroxydecanoic acid should contribute to the aroma. A part of the esters hydrolyzes during cooking and the hydroxy acids released cyclize to the corresponding lactones.

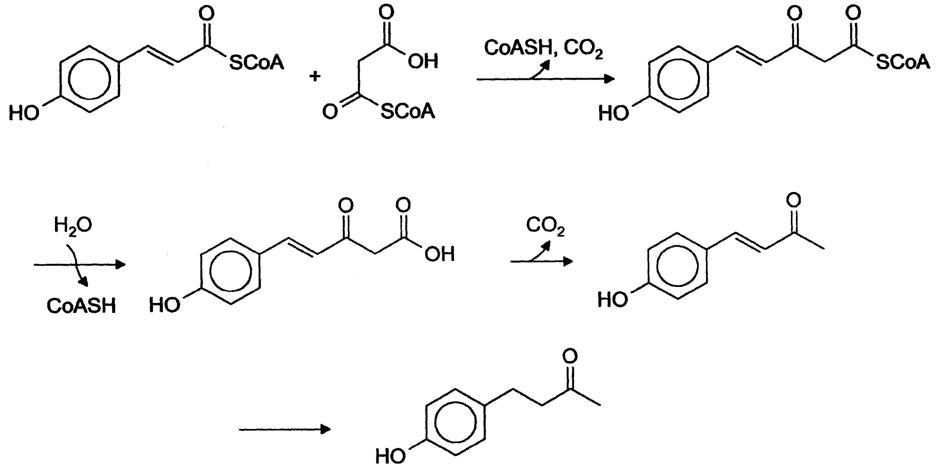
18.1.2.6.6 Apricots

The following compounds are discussed as contributors to the aroma: myrcene, limonene, p-cymene, terpinolene, α-terpineol, geranial, geraniol, linalool, acids (acetic and 2-methylbutyric acids) alcohols, e. g., trans-2-hexenol; and a number of γ- and δ-lactones, e. g., γ-caprolactone,

Table 18.29. Odorants of the apple varieties *Elstar* and *Cox Orange*

Compound	*Elstar*		*Cox Orange*	
	Concentration (μg/kg)	Aroma value[a]	Concentration (μg/kg)	Aroma value[a]
(E)-β-Damascenone	1.4	1813	0.99	1320
2-Methylbutyric acid methylester	0.2	<1	1.8	7
Ethyl butyrate	0.7	7	0.3	3
Hexyl acetate	5595	112	1500	30
Butyl acetate	4640	93	1595	32
Acetic acid 2-methylbutylester	240	48	217	43
Hexanal	85	19	48	11
(E)-2-Hexenal	77	2	114	2
(Z)-3-Hexenal	6.4	25	30	120
(Z)-2-Nonenal	8.8	440	1.1	55
Butanol	4860	10	975	2
Hexanol	1390	3	350	<1
Linalool	9.3	19	4.5	9

[a] Aroma value: ratio of the concentration to the orthonasal odor threshold value of the substance in water.



(VII) (18.38)

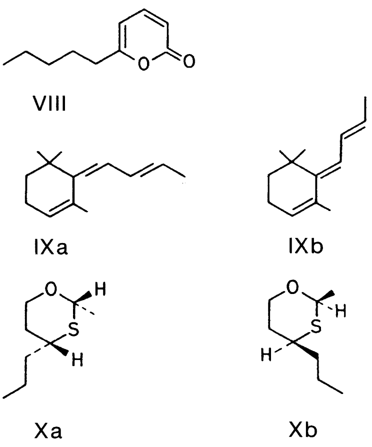
γ-octalactone, γ-decalactone, γ-dodecalactone, δ-octalactone and δ-decalactone.

18.1.2.6.7 Peaches

The aroma of peaches is characterized by γ-lactones (C_6–C_{12}) and δ-lactones (C_{10} and C_{12}). The main compound in the lactone fraction is (R)-1,4-decanolide, which has a creamy, fruity, peach-like odor. Other important compounds should be benzaldehyde, benzyl alcohol, ethyl cinnamate, isopentyl acetate, linalool, α-terpineol, α- and β-ionone, 6-pentyl-α-pyrone (Formula 18.39, VIII), hexanal, (Z)-3-hexenal, and (E)-2-hexenal. Aroma differences in different varieties of peaches are correlated with the different proportions of the esters and monoterpenes. In the case of nectarines (*Prunus persica* L., Batsch var. nucipersica Schneid), the lactones γ-C_8–C_{12} and δ-C_{10} belong to the compounds with the highest aroma values.

18.1.2.6.8 Passion Fruit

The aroma of the yellow fruit (*Passiflora edulis* var. *flavica*) is supposed to be superior to that of the crimson fruit (*Passiflora edulis* var. *edulis*). Compounds that contribute to the aroma of both varieties are β-ionone and the following esters (% of the volatile fraction): ethyl butyrate (1.4), ethyl hexanoate (9.7), hexyl butyrate (13.9), and hexyl hexanoate (69.6).



(18.39)

Four stereoisomeric megastigmatrienes have been found in crimson passion fruit. A mixture of the isomers IXa and IXb (Formula 18.39) gives a rose-like aroma, that has a hint of strawberries in it (threshold = 100 μg/kg; water).

The following S-containing aroma substances have been isolated from the yellow fruit: 3-methylthiohexane-1-ol which probably gives rise to 2-methyl-4-propyl-1,3-oxathianes (cis/trans isomers in the ratio of 10:1) (Xa, b: Formula 18.39). Of the two cis isomers, only the 2R,4S-isomer (Xb), which has a sulfurous herb-like odor (threshold = 4 μg/kg; water), has been found in the fruit. However, the aroma note more typical of passion fruit is exhibited by the 2S,4R-isomer (Xa).

18.1.2.6.9 Strawberries

The concentrations of the odorants in strawberry juice are given in Table 18.30. With a solution of the first 11 compounds listed in the table, the original aroma was largely approximated. If HD3F was missing, the mixture smelt green and fruity and if (Z)-3-hexenal was missing, the caramel-like/sweetish note of HD3F dominated.

The HD3F concentration depends on the variety of strawberry. Values between 1.1 and 33.8 mg/kg were found. The red parts of the fruit are richer in HD3F than the white parts. The strawberry aroma changes on heating due to an increase in HD3F, formation of (E)-β-damascenone, (E,E)-2,4-decadienal and guaiacol as well as great losses of (Z)-3-hexenal and the esters (Table 18.30). A freeze/thaw process also changes the aroma as a result of a great increase in HD3F and degradation of (Z)-3-hexenal.

18.1.2.6.10 Pineapples

A model on the basis of the compounds listed in Table 18.31 reproduces the aroma of pineapples.

Table 18.30. Concentrations of odorants in fresh and heated strawberry juice

Compound	Concentration (mg/kg)	
	Fresh	Heated[a]
4-Hydroxy-2,5-dimethyl-3(2H)-furanone (HD3F)	16.2	29.4
(Z)-3-Hexenal	0.333	0.025
Methyl butyrate	5.0	1.0
Ethyl butyrate	0.41	0.048
Isobutyric acid ethylester	0.043	0.012
2-/3-Methylbutyric acid methylester	0.048	0.007
2-/3-Methylbutyric acid ethylester	0.007	0.0012
Acetic acid	74.5	74.9
2,3-Butandione	1.29	0.85
Butyric acid	1.83	1.79
2-/3-Methylbutyric acid	2.24	2.20
(E)-β-Damascenone	<0.1	5.4
(E,E)-2,4-Decadienal	<0.1	4.1
Guaiacol	0.8	2.8

[a] 100°C, 30 min (reflux).

Table 18.31. Odorants of pineapples

Compound	Concentration (μg/kg)	Aroma value[a]
4-Hydroxy-2,5-dimethyl-3(2H)-furanone	26,800	2680
2-Methylpropionic acid ethyl ester	48	1400
2-Methylbutyric acid ethyl ester	157	1050
2-Methylbutyric acid methyl ester	1190	595
(E,Z)-1,3,5-Undecatriene	8.9	445
β-Damascenone	0.083	111
Butyric acid ethyl ester	75	75
2-Methylpropionic acid methyl ester	154	24
Octanal	19	2
δ-Ocalactone	78	<1
δ-Decalactone	32.7	<1
Vanillin	6	<1

[a] Aroma value: quotient of the concentration and orthonasal odor threshold value in water.

Omission experiments have shown the five odorants with the highest aroma values shown in Table 18.31 are the key aroma substances.

18.1.2.6.11 Cherries, Plums

The compounds essentially involved in the aroma of cherries are benzaldehyde, linalool, hexanal, (E)-2-hexenal, phenylacetaldehyde, (E,Z)-2,6-nonadienal, and eugenol (Table 18.32). On heating cherry juice or in the making of jams, the concentration of benzaldehyde increases due to the hydrolysis of amygdalin and prunasin

Table 18.32. Odorants of cherry juice and jams made from it[a]

Aroma substance	Juice (μg/kg)	Jam (μg/kg)
Benzaldehyde	202	1510
Linalool	1.1	13.1
Hexanal	5.6	0.2
(E)-2-Hexenal	8.5	3.8
Eugenol	10.0	4.9

[a] Fruit content: 50 w/w per cent.

(cf. 16.2.6) and the concentration of linalool increases due to the hydrolysis of the corresponding glycoside (Table 18.32). Since the C_6-aldehydes and nonadienal decrease simultaneously, the fruity-flowery aroma notes are enhanced and the "green" notes diminished.

The important compounds in plums are linalool, benzaldehyde, methyl cinnamate, and γ-decalactone together with the C_6-aldehydes. Benzaldehyde, nonanal, and benzyl acetate contribute to the aroma of canned plums.

18.1.2.6.12 Litchi

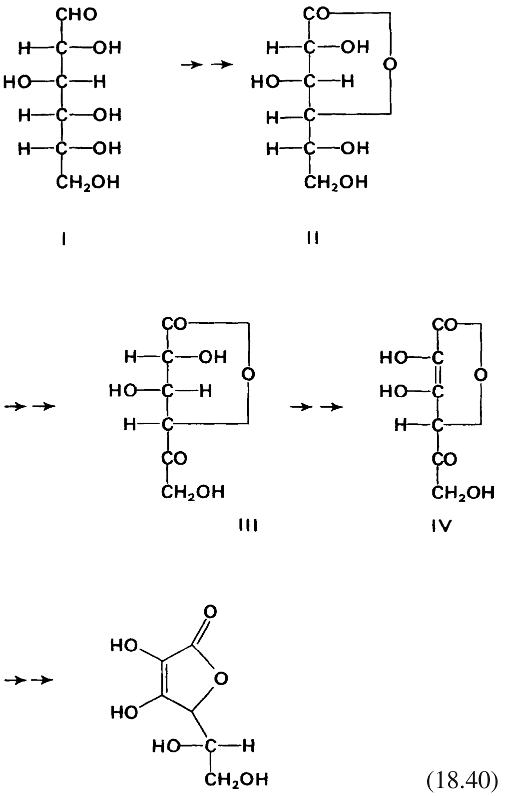
The compounds acetic acid isobutylester, guaiacol, cis-rose oxide, 2-acetylthiazoline, (E)-β-damascenone, 4-hydroxy-2,5-dimethyl-3(2H)-furanone, linalool, geraniol and 2-phenylethanol exhibit the highest aroma activity.

18.1.2.7 Vitamins

Many fruits are important sources of vitamin C (Table 18.33). Its biosynthesis in plants starts from hexoses, e. g., glucose. It is postulated that following C-1 oxidation and cyclization to 1,4-lactone (II), the 5-keto compound (III) appears as an intermediary product which is oxidized to the 2,3-endiol (IV) then reduced stereospecifically to L-ascorbic acid (V) (cf. Formula 18.40).

Table 18.33. Ascorbic acid in various fruits (mg/100 g edible portion)

Fruit	Ascorbic acid	Fruit	Ascorbic acid
Apple	3–35	Currant, black	177
Pear	1–4		
Apricot	5–15	Orange	50
Cherry	8–37	Grapefruit	40
Peach	5–29	Lemon	50
Plum/prune	2–14	Acerola	1000–2000
Blackberry	17	Pineapple	25
Strawberry	60	Banana	7–21
Raspberry	25	Guava	300
Currant, red	40	Melons	6–32

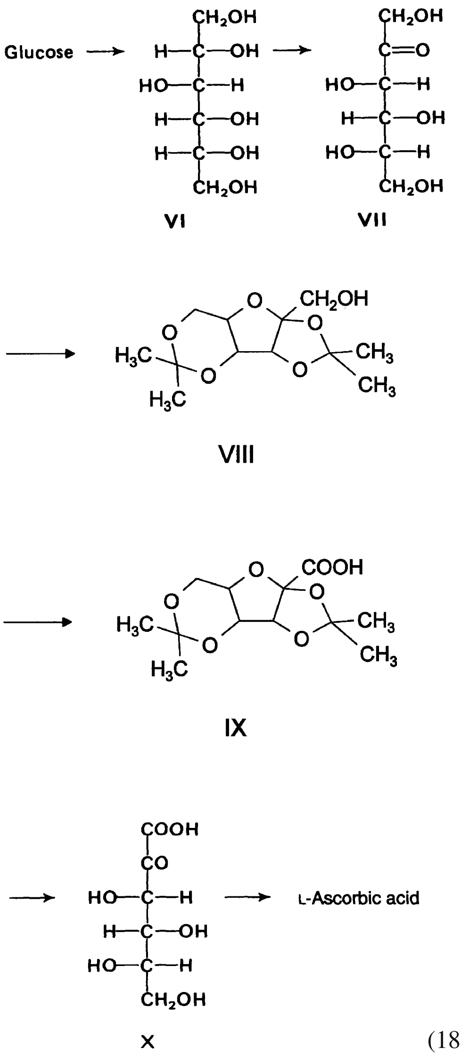


(18.40)

Industrial-scale production of ascorbic acid also starts with glucose. The sugar is first reduced to sorbitol (VI) and then oxidized with *Acetobacter suboxidans* to L-sorbose (VII) which after cyclization and conversion to the diisopropylidene derivative (VIII) is oxidized to the corresponding derivative of L-2-oxogulonic acid (IX). After removal of the protecting isopropylidene groups, L-ascorbic acid (vitamin C) is obtained via L-2-oxogulonic acid (X; cf. Reaction 18.41).

The synthesis can be shortened with a genetically modified strain of the bacterium *Erwinia herbicola* which directly converts D-glucose to L-2-oxogulonic acid (X).

β-Carotene (provitamin A) occurs in large amounts in apricots, cherries, cantaloups and peaches. B-vitamins present in some fruits (apricots, citrus fruits, figs, black currants and gooseberries) are pantothenic acid and biotin. Other B-group vitamins occur at levels of no nutritional significance. Vitamins B_{12} and D and tocopherols are found in no more than trace amounts.



(18.41)

18.1.2.8 Minerals

Table 18.34 gives the composition of the ash of orange juice and apples. The most important cation is potassium and the most important inorganic anion is phosphate.

Table 18.34. Minerals in fruit

Element	Orange juice (% in ash)	Apple (mg/100g dry matter)
Potassium	40	840
Sodium	0.3	7.9
Calcium	2.8	38
Magnesium	3.0	40
Iron	0.06	1.6
Aluminium	0.12	0.43
Phosphorus	3.8	73
Sulfur	0.8	
Chlorine	1.0	
Zinc, titanium, barium, copper, manganese, tin	≤ 0.03	Zinc 0.65 Manganese 0.3
Boron	≤ 0.01	Copper 0.35

18.1.3 Chemical Changes During Ripening of Fruit

Ripening of fruit involves highly complex changes in physical and chemical properties. Softening, increasing sweetness, aroma and color changes are among the most striking phenomena related to ripening. Some changes will be outlined below in more detail.

18.1.3.1 Changes in Respiration Rate

The respiration rate is affected by the development stage of the fruit. A rise in respiration rate occurs with growth. This is followed by a slow decrease in respiration rate until the fruit is fully ripe. In a number of fruits ripening is associated with a renewed rise in respiration rate, which is often denoted as a climacteric rise. Maximal CO_2 production occurs in the climacteric stage. De-

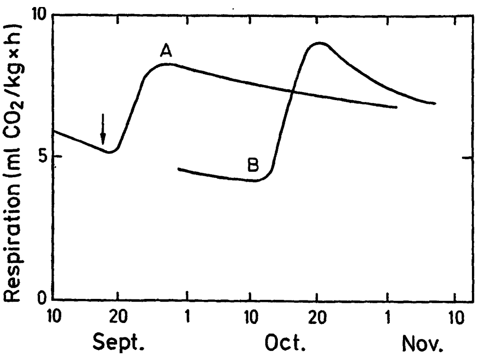


Fig. 18.8. Respiration rise in apples, Bramsley's seedlings (according to *Hulme*, 1963.) A, apple picked →, B, left on tree to ripen

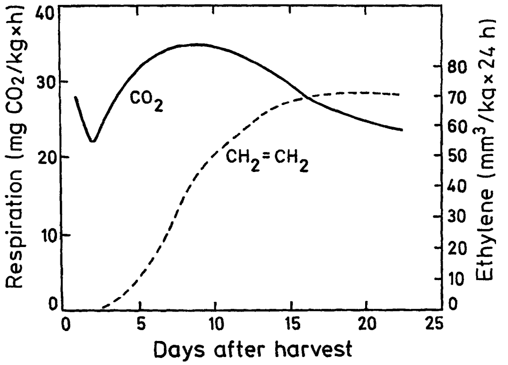


Fig. 18.9. Respiration rise in tomatoes —— : CO_2, – – – : Ethylene

pending on the fruit, this can occur before or after harvesting. Figures 18.8 and 18.9 show that such a rise occurs a short time after harvest for apples and tomatoes and is accompanied by increased ethylene production.

The climacteric respiration rise is so specific that fruits can be divided into:

- *Climacteric types*, such as apples, apricots, avocados, bananas, pears, mangoes, papaya, passion fruit, peaches, plums/prunes and tomatoes; and
- *Nonclimacteric types*, which include pineapples, oranges, strawberries, figs, grapefruit, cucumbers, cherries, cantaloupes, melons, grapes and lemons.

It should be emphasized that nonclimacteric fruits generally ripen on the plants and contain no starch. The differing effects of ethylene on the two types of fruits are covered in Section 18.1.4.2.

Fruits can also be classified according to respiration behavior after harvesting. Three fruit types are distinguished:

Type 1: A slow drop in CO_2 production during ripening (as illustrated by citrus fruits).

Type 2: A temporary rise in CO_2 production. The fruits are fully ripe after this increase reaches a maximum (e. g., avocados, bananas, mangoes or tomatoes).

Type 3: Maximum CO_2 production in the fully ripe stage, until the fruit is overripe (e. g. strawberries and peaches).

The reason for the increase in CO_2 production is not yet fully elucidated. Physical and chemical factors are involved. For example, a change in permeability for gases occurs in fruit peels. With increasing age the peel cuticle becomes thicker and is more strongly impregnated with fluid waxes and oils. Thus, the total permeability drops, while the CO_2 concentration within the fruit increases. Three possibilities are usually considered for the rise in CO_2 production. The first is related to increased protein biosynthesis coupled with increased ATP consumption thus stimulating enhanced respiration. Secondly, since the respiratory quotient (RQ) increases from 1 to 1.4–1.6, it is assumed that the additional CO_2 source is not due to respiration but to decarboxylation of malate and pyruvate, i.e. there is a switch from the citric acid cycle to malate degradation. Another possibility is the partial uncoupling of respiration from phosphorylation by an unknown decoupler.

New concepts involving structural factors suggest that fruit flesh possesses marked photosynthetic activity which is then associated with CO_2 uptake. With the onset of ripening, an increased disorganization occurs in chloroplasts and other cell organelles. Photosynthetic activity decreases and finally stops completely. The same is the case for other synthetic activities. Catabolic processes, catalyzed by cytoplasmic enzymes, become dominant. Based on such a perception (*Phan et al.*, 1975) the "climacteric is seen as an indication of the natural end of a period of active synthesis and maintenance, and the beginning of the actual senescence of the fruit".

18.1.3.2 Changes in Metabolic Pathways

Metabolic shifts may occur in several fruits during ripening. For example, during ripening of bananas, there is a marked rise in aldolase and carboxylase activities and thus it appears that at this stage the *Embden–Meyerhoff* pathway becomes dominant and the pentose-phosphate pathway is suppressed.

An increase in malate and pyruvate decarboxylase activities is observed in apples during the climacteric stage. The activities drop as

CO_2 production decreases. This provides an explanation for the change in RQ during the climacteric stage. CO_2 production increases more rapidly than O_2 uptake, thus the RQ is greater than 1. The shift from the citric acid cycle to malate degradation in apples is also reflected by the effect of citrate and malate on succinate production. As ripening proceeds, production of succinate from citrate drops to zero. An increase in succinate content after addition of malate in the initial stage of ripening is probably a feedback reaction. In this case, a decrease is also observed later on, suggesting a greater change in metabolic patterns.

18.1.3.3 Changes in Individual Constituents

18.1.3.3.1 Carbohydrates

During ripening of fruits, significant changes occur in the carbohydrate fraction. For example, between picking and onset of decay in apples about 20% of the available carbohydrates have been utilized.

During the growth of apples on trees, the starch content rises and then drops to a negligible level by the time of harvest. This drop appears to be related to the increase in climacteric respiration. Contrary to starch, the sugar content rises. Other sources in addition to starch should be available for conversion to sugars. A decrease in hemicelluloses suggests that they are a possible source. Organic acids may also be an additional source of sugars.

A marked decrease in starch in bananas parallels an increase in the contents of glucose, fructose and saccharose. Biosynthesis of the latter occurs by two pathways:

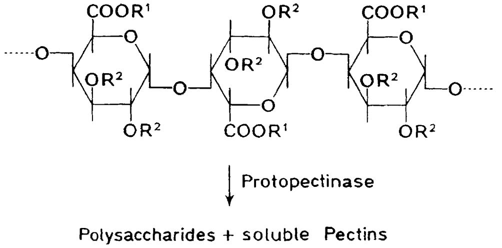
$$\begin{aligned} &1)\ \text{UDPG} + \text{Fru-6-p} \rightarrow \text{UDP} + \text{Sac-6}^{\text{F}}\text{-P} \\ &\qquad \rightarrow \text{Sac} + \text{P}_{\text{in}} \\ &2)\ \text{UDPG} + \text{Fru} \rightarrow \text{UDP} + \text{Sac} \qquad (18.42) \end{aligned}$$

The content of hemicelluloses drops from 9% to 1–2% (relative to fresh weight), hence they act as a storage pool in carbohydrate metabolism. There is also a drop in the sugar content in bananas during the post-climacteric stage.

Differences in various fruits can be remarkable. In oranges and grapefruits the acid content drops during ripening while the sugar level rises. In lemons, however, there is an increase in acids.

Decreases in arabinans, cellulose and other polysaccharides are found in pears during ripening. Cellulase enzyme activity has been confirmed in tomatoes.

Remarkable changes occur in the pectin fractions during ripening of many fruits (e. g., bananas, citrus fruits, strawberries, mangoes, cantaloupes and melons). The molecular weight of pectins decreases and there is a decrease in the degree of methylation. Insoluble protopectin is increasingly transformed into soluble forms. Protopectin is tightly associated with cellulose in the cell wall matrix. Its galacturonic acid residues are acetylated at OH-groups in positions 2 and 3 or are bound to polysaccharides as lignin (R^1 = H, CH_3, polysaccharide: arabinan, galactan and possibly cellulose; R^2 = H, CH_3CO, polysaccharide, lignin):



(18.43)

Soluble pectins bind polyphenols, quench their astringent effect and, thus, contribute to the mild taste of ripe fruits.

After prolonged storage there is a decrease in soluble pectins in apples. This drop is associated with a mealy, soft texture. Similar events occur in pears, but much more rapidly and with more extensive demethylation of pectin. Generally, the degree of pectin esterification drops from 85% to about 40% during ripening of pears, peaches and avocados. This drop is due to a remarkable increase in activities of polygalacturonases and pectin esterases. The rise in free galacturonic acid is negligible; therefore it appears that the release of uronic acid is associated with its simultaneous conversion through other reactions.

18.1.3.3.2 Proteins, Enzymes

During ripening of some fruits, although the total content of nitrogen is constant, there is an increase in protein content, an increase assigned primarily to increased biosynthesis of enzymes. For example, during ripening of fruit there is increased activity of hydrolases (amylases, cellulases, pectinolytic enzymes, glycolytic enzymes, enzymes involved in the citric acid cycle, transaminases, peroxidases and catalases). Proteinaceous enzyme inhibitors which inhibit the activities of amylases, peroxidases and catalases are found in unripe bananas and mangoes. The activities of these inhibitors appear to decrease with increasing ripeness.

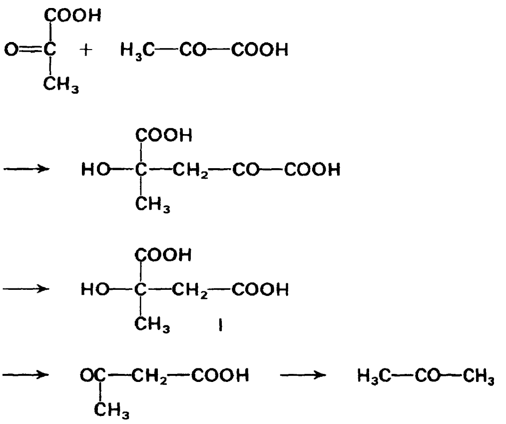
The ratios of NADH/NAD$^+$ or NADPH/NADP$^+$ pass through a maximum during ripening of fruit. For example, the values for mangoes are 0.32–0.67 in the unripe stage, 1.44–6.50 in the semiripe stage and 0.57–0.93 in the ripe stage. During ripening of fruit, shifts also occur in the amino acid and amine fractions. The shifts are not uniform and are affected by type and ripening stage of fruits.

18.1.3.3.3 Lipids

Little is known about changes in the lipid fraction. Shifts in composition and quantity have been found, especially in the phospholipid fraction.

18.1.3.3.4 Acids

There is a drop in acid content during ripening of fruits. Lemons, as already mentioned, are an exception. The proportion of various acids can change. In ripe apples malic acid is the major acid, while in young, unripe apples, quinic acid is dominant. In the various tissues of any single fruit, various acids can be dominant. For example, apple peels contain citramalic acid (I, cf. Formula 18.44) which is formed from pyruvic acid, and can produce acetone through acetoacetic acid. Acetone is formed abundantly during ripening:



$$\mathrm{O{=}C(COOH)CH_3} + \mathrm{H_3C{-}CO{-}COOH} \longrightarrow \mathrm{HO{-}C(COOH)(CH_3){-}CH_2{-}CO{-}COOH} \longrightarrow \underset{\mathrm{I}}{\mathrm{HO{-}C(COOH)(CH_3){-}CH_2{-}COOH}} \longrightarrow \mathrm{OC(CH_3){-}CH_2{-}COOH} \longrightarrow \mathrm{H_3C{-}CO{-}CH_3}$$

(18.44)

The synthesis of ascorbic acid is also of importance. It takes place in many fruits during ripening (cf. 18.1.2.7)

18.1.3.3.5 Pigments

The ripening of fruit is usually accompanied by a change in color. The transition of green to another color is due to the degradation of chlorophyll and the appearance of concealed pigments. Furthermore, the synthesis of other pigments plays a big role. For example, the lycopene content of the tomato increases greatly during ripening. The same applies to the carotenoid content of citrus fruits and mangoes. The formation of anthocyanin is frequently enhanced by light.

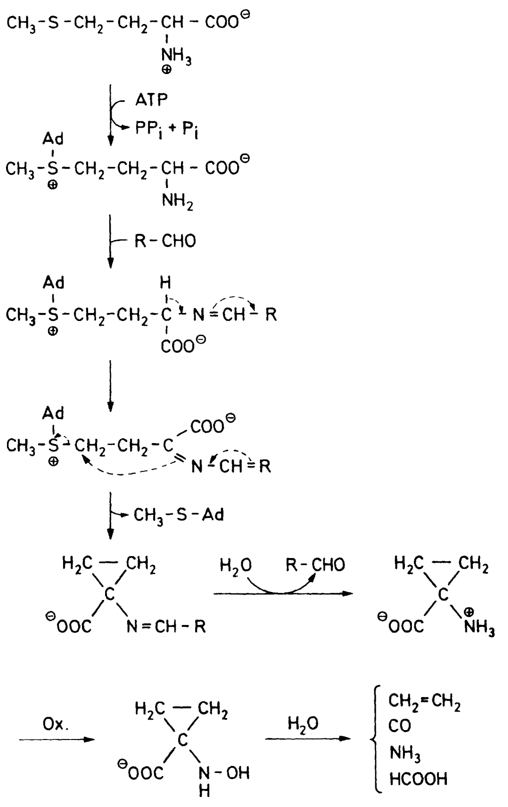
18.1.3.3.6 Aroma Compounds

The formation of typical aromas takes place during the ripening of fruit. In bananas, for example, noticeable amounts of volatile compounds are formed only 24 h after the climacteric stage has passed. The aroma build-up is affected by external factors such as temperature and day/night variations. Bananas, with a day/night rhythm of 30 °C/20 °C, produce about 60% more volatiles than those kept at a constant temperature of 30 °C. The synthesis of aroma substances is discussed in section 5.3.2.

18.1.4 Ripening as Influenced by Chemical Agents

18.1.4.1 Ethylene

Fruit ripening is coupled with ethylene biosynthesis:



(18.45)

Ethylene increases rapidly but differently in the case of climacteric fruits. The maximum values for some fruits are given in Table 18.35. However, nonclimacteric fruits produce only a little ethylene (Table 18.35). This gaseous compound increases membrane permeability and thereby probably accelerates metabolism and fruit ripening. With mango fruits, for example, it has been demonstrated that before the climacteric stage, ethylene stimulates oxidative and hydrolytic enzymes (catalase, peroxidase and amylase) and inactivates inhibitors of these enzymes.

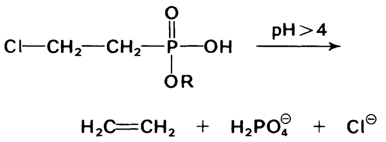
Table 18.35. Ethylene production in ripening fruits

	Fruit	Ethylene (μg/l)
Climacteric maximum	Avocado	500
	Banana	40
	Mango	3
	Pear	40
	Tomato	27
Nonclimacteric stationary state	Lemon	0.2–0.2
	Orange	0.1–0.3
	Pineapple	0.2–0.4

Climacteric and nonclimacteric fruits respond differently to external ethylene (Fig. 18.10). Depending on the ethylene level, the respiratory increase sets in earlier in unripe climacteric fruits, but its height is not influenced. In contrast, in nonclimacteric fruits there is an increase in respiration rate at each ripening stage which is clearly dependent on ethylene concentration.

The reaction pathway 18.45 is suggested for the biosynthesis of ethylene (R–CHO: pyridoxal phosphate; Ad: adenosine).

Ethylene and compounds capable of releasing ethylene under suitable conditions are utilized commercially for enhancing the ripening process. A number of such compounds are known, e.g., 2-chloroethylphosphonic acid (ethephon; R=H or CH_2–CH_2Cl) (Formula 18.46).



$$Cl{-}CH_2{-}CH_2{-}\underset{OR}{\overset{O}{\overset{\|}{P}}}{-}OH \xrightarrow{pH>4} H_2C{=}CH_2 + H_2PO_4^{\ominus} + Cl^{\ominus}$$

(18.46)

The use of ethylene before picking fruit (as with pineapples, figs, mangoes, melons, cantaloups and tomatoes) results in faster and more uniform ripening. Its utilization after harvesting accelerates ripening (e.g., with bananas, citrus fruits and mangoes). Ethylene can induce blossoming in the pineapple plant and facilitate detachment of stone fruits and olives. Vine defoliation can also be achieved.

The activity of propylene is only 1% of that of ethylene. Acetylene also accelerates ripening but only at substantially higher concentrations.

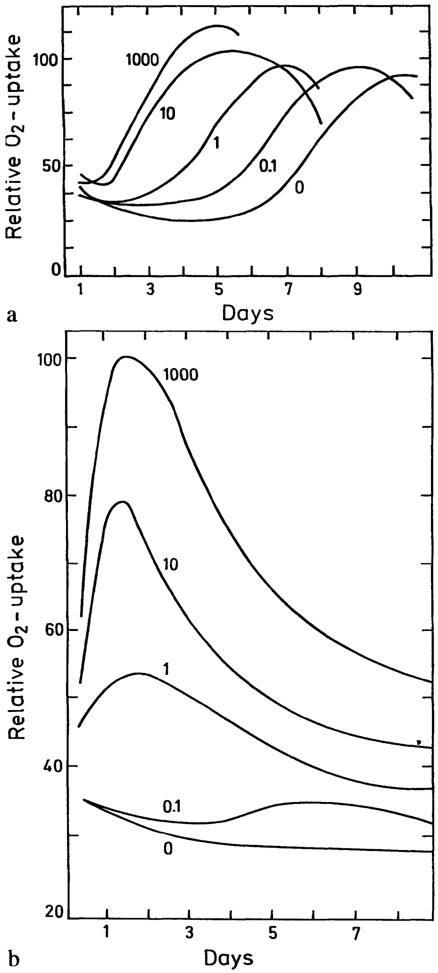


Fig. 18.10. The effect of ethylene on fruit respiration. (a) climacteric, (b) nonclimacteric. Numerals on the curves: ethylene in air, ppm (according to *Biale*, 1994)

18.1.4.2 Anti-Senescence Agents

In order to keep fruit fresh, the ripening is slowed down by cold storage (cf. 18.1.5) and/or with additives which inhibit the formation or action of ethylene.

18.1.4.2.1 Polyamines

The polyamines putrescine (butane-1,4-diamine), spermidine [N-(3-aminopropyl)butane-1,4-diamine] and spermine [N,N′-bis-(3-aminopropyl)-butane-1,4-diamine] belong to the group of naturally occurring anti-senescence agents. They increase during the early phase of growth of the fruit, when intensive cell division takes place, and, apart from exceptions, decrease during ripening. Studies have shown that the treatment of fruit with polyamines results in a slowing down of the ethylene production and respiration, which in turn has a positive effect on the firmness of the fruit flesh and on the color.

18.1.4.2.2 1-Methylcyclopropene (MCP)

As a result of structural similarities, MCP docks on to receptor proteins for ethylene, causing it to lose activity. The texture and color of apples and pears (sensitive varieties) do not change through months of cool storage. The sugar content also remains constant while the acid content increases. Gaseous MCP adsorbed on dextran is used for the treatment of fruit. The MCP is liberated by the addition of water. The concentrations applied are in the range 300–1000 ppb.

18.1.5 Storage of Fruits

18.1.5.1 Cold Storage

The suitability, duration and required conditions of fruit storage are dependent on variety and quality. Commonly used conditions are −1 °C to +2 °C at 80–90% relative humidity. The storage time varies from 4–8 months for apples, 2–6 months for pears, 2–3 months for grapes, 1–2 weeks for strawberries and raspberries, and 4–5 days for cherries. Efficient aeration is required during storage. Air circulation is often combined with purging to remove ethylene, the volatile promoter of fruit ripening. Weight losses occur during fruit storage due to moisture losses of 3–10%.

18.1.5.2 Storage in a Controlled (Modified) Atmosphere

This term is applied to an atmosphere which, in comparison to air, has a lowered oxygen con-

Table 18.36. Minimal O_2 and maximal CO_2 concentrations in the atmosphere during storage of fruits (temperature 0–5 °C)

Fruit	Minimal O_2 concentration (%)	Minimal CO_2 concentration (%)
Pear	1–2	2
Apple, kiwi Peach, plum	1–2	5
Pineapples	2	10
Sour cherry	2	15
Citrus fruits	5	10

centration and an increased CO_2 concentration. Common conditions for storage of many fruits are shown in Table 18.36. For each fruit variety it is important that optimal conditions for controlled atmosphere storage be maintained. For example, a high O_2 concentration accelerates ripening, while an overly low O_2 concentration results in high production of CO_2. An overly high concentration of CO_2 promotes glycolysis, which can cause off-flavors due to the formation of acetaldehyde and ethanol. Discoloration can also occur.

18.2 Fruit Products

The short shelf life of most fruits and the frequent need to store and spread out the surplus of a harvest for a prolonged period of time has brought about a number of processes which provide more durable and stable fruit products.

18.2.1 Dried Fruits

Like many other food products, moisture removal from fruits by a suitable drying process results in a product in which microbial growth is retarded and, with a suitable pretreatment, the enzymes present are largely inactivated. Fruit drying is probably the oldest procedure for preservation. It was originally performed in a rather primitive way (spreading the fruit in the hot air of a fireplace or hearth, kitchen stove or oven), thus providing dark "baked products". Solar drying is still a common process in southern and tropical countries for obtaining dried apple slices, apricots, peaches or pears or tropical fruits such as dates, figs or raisins. Predrying is often achieved in sunshine and additional drying by artifical heat in drying installations. The temperature in drying chambers, flat or tunnel dryers is between 75 °C (incoming air) and 65 °C (temperature of the exit air) at a relative humidity of 15–20%. Vacuum drying at about 60 °C is particularly gentle.

Carefully washed and trimmed fruits of suitable varieties are pretreated in various ways: *Pomme fruits* (apples, pears) are initially peeled mechanically and freed from the core and calix (seed compartment). Apples are then cut preferentially into 5–7 mm thick slices, and dried in rings (a yield of 10–20% of the unpeeled fresh weight). Sulfite treatment is used to prevent browning during processing and storage. The sulfurous acid prevents both enzymatic and nonenzymatic browning reactions, stabilizes vitamin C and prevents microbial contamination during storage of the end product. The utilization of dilute solutions of citric acid is also suitable for preventing browning. Whole or sliced pears are heated with steam to achieve a translucent appearance and then are dried at 60–65 °C. The yield is 13–14% of the fresh weight.

The *stone fruits* usually dried are plums/prunes, apricots and peaches. Plums are first dipped for 5–15 s into a hot, diluted solution of sodium hydroxide, or into 0.7% aqueous K-carbonate and then rinsed and dried at 70–75 °C or dried in the sun. Plum peels are often fissured to facilitate drying. In order to clean and to provide a black, glossy surface, dried plums are steamed additionally at 80–85 °C for a short time. The plum yield is 25–30% at a moisture content of not more than 19%. Apricots and peaches are treated alternately with cold and hot water, then are halved, the stone seed is removed and the fruit is dried in the sun or in drying installations at 65–70 °C. The yield, depending on fruit size, is 10–15%. SO_2 (sulfurous acid) treatment is common for apricots and peaches. Cherries play a less important role as dried fruit. To avoid substantial aroma losses, cherries are dried slowly and with a number of precautions.

Grapes are the most commonly dried *berry fruits*. Raisins are dark-colored, dried grapes which contain seeds, whereas sultana raisins are

Table 18.37. Composition of some dried fruits (g/100 g edible portion)

Fruit	Moisture	N-containing compounds ($N \times 6.25$)	Lipid	Available carbohydrates	Dietary fiber	Minerals	Vitamin C
Apricots	17.6	5.0	0.4	48	17.7	3.5	0.011
Dates	20.2	1.9	0.5	65	8.7	1.8	0.003
Figs	23.7	3.5	1.3	55	12.9	2.4	0–0.005
Peaches	24.0	3.0	0.6	53	12.8	3.0	0.017
Plums/prunes	24.0	2.3	0.6	47	17.8	2.1	0.004
Raisins	15.7	2.5	0.5	68	5.2	2.0	0.001

seedless, light-colored, dried grapes. Currants, with or without seeds, are dark and are much smaller in size than the other two raisin products. The surface treatment of raisins, with the exception of currants, involves the use of acetylated monoglycerides to prevent caking or sticking.

The compositions of some dried fruits are presented in Table 18.37. Dried fruits are exceptionally rich in calories and they supply significant amounts of minerals. Of the vitamins found in fruit, β-carotene and the B-vitamins remain intact. Vitamin C is lost to a great extent. Sulfite treatment destroys vitamin B_1. However, fruit color and vitamin C content are retained and stabilized.

18.2.2 Canned Fruits

Since the middle of the 19th century, heat sterilization in cans and glass jars has been the most important process for fruit preservation.

Undamaged, aroma-rich and not overripe fruits are suitable for heat sterilization. Aseptic canning is applicable only for fruit purées. Canned fruits used are primarily stone fruits, pears, pineapples and apples (usually apple purée). Strawberries and gooseberries are canned to a lesser extent.

Canned fruits are produced in a large volume by the food industry and also in individual households. Cherries are freed from stone seeds and stems, plums/prunes, apricots and peaches are halved and the stone seeds are removed, strawberry calix is removed, gooseberry and red currant stems are removed, apples and pears are peeled and sliced. Specialized equipment has been developed for these procedures.

With a few exceptions (raspberries and blackberries) all fruits are washed or rinsed. Apricots are readily peeled after alkali treatment at 65 °C. Fruits sterilized unpeeled, e. g., prunes or yellow plums, are first fissured to prevent later bursting. To avoid aroma loss and to prevent floating in the can, fruits which shrink considerably (such as cherries, yellow plums, strawberries and gooseberries) are dipped prior to canning into a hot 30% sugar solution and then covered with a sugar solution, with a sugar concentration approximately twice the desired final concentration in the can. Finally, the can is vacuum sealed at 77–95 °C for 4–6 min and, according to the fruit species, heat sterilized under the required conditions. For example, a 1 liter can of strawberries is sterilized in a boiling water bath at 100 °C for 18 min, while pears, peaches and apricots are heated at 100 °C for 22 min. Additions of ascorbic and citric acids for stabilization of color and calcium salts for the preservation of firm texture have been accepted as standard procedures for canned fruits consumed as desserts.

Canned fruits used for bakery products, confections or candies are produced like canned dessert fruits, however, the fruits are covered with water instead of sugar solutions.

18.2.3 Deep-Frozen Fruits

Fruits are frozen and stored either as an end product or for further processing. The choice of suitable varieties of fruit at an optimal ripening stage is very important. Pineapples, apples, apricots, grapefruit, strawberries and dark-colored cherries are highly suitable. Light-colored cherries, plums, grapes and many subtropical or tropical fruits are of low suitability.

Rapid chilling is important (air temperature $\leq -30\,°\text{C}$, freezing time about 3 h) to avoid microbial growth, large concentration shifts in fruit tissues, and formation of large ice crystals which damage tissue structure. A blanching step prior to freezing is commonly used only for few fruits, such as pears, and occasionally for apples, apricots and peaches. Some fruits are covered, prior to freezing, with a 30–50% sugar solution or with solid granulated sugar (1 part per 4–10 parts by weight) and are left to stand until the sap separates. In both instances oxygen is eliminated, enzymatic browning is prevented, and the texture and aroma of the fruit are better preserved. Addition of ascorbic acid or citric acid is also common.

Frozen fruit which is stored at -18 to 24 °C is stable for two to four years.

18.2.4 Rum Fruits, Fruits in Sugar Syrup, etc.

Rum fruits are produced by steeping the fruit in dilute spirits in the presence of sufficient sugar.

Fruits preserved in vinegar, mostly pears and plums, are prepared by poaching in wine vinegar sweetened with sugar and spiced with cinnamon and cloves.

Fruits in sugar syrup are prepared by treating raw or precooked fruits or fruit portions (may be precooked under a vacuum) with highly concentrated sucrose solutions which also contain starch syrup. The latter is added to enhance translucency, smoothness and tractability of the product. Candied lemon or orange peels are products of this kind.

Other varieties provide intermediary products processed further into fruit confections: glazed fruits (these are washed fruits treated with a sugar solution containing gum arabic and then subsequently dried at 30–35 °C) or candied fruits in which the dried, glazed fruit is also immersed in a concentrated sugar solution and then dried to form a candied hull. Another product is crystallized fruit in which the dried, glazed fruits are rolled over icing or granulated sugar (sucrose), then dried aditionally and, to achieve a shiny, glossy appearance, are exposed to steam for a short time.

18.2.5 Fruit Pulps and Slurries

Fruit pulp is not suitable for direct consumption. The pulp is in the form of slurried fresh fruit or pieces of fruit either split or whole, and, when necessary, stabilized by chemical preservatives. The minimum dry matter content of various pulps is 7–11%. For pulp production the fruit, which has been washed in special machines, is lightly steamed in steam conduits or precooking retorts.

The fruit slurry is an intermediary product, also not suitable for direct consumption. The production steps are similar to those for pulp. However, there is an additional step: slurrying and straining, i.e. passing the slurry through sieves. Both the pulp and the slurry can be stored frozen.

18.2.6 Marmalades, Jams and Jellies

18.2.6.1 Marmalades

Marmalade is a spreadable preparation made from pulp, slurry, juice, aqueous extracts or peels of citrus fruits and sugars. The product (1 kg) has to contain at least 200 g of citrus fruit (of which 75 g endocarp) and 60% by weight of soluble solids. The addition of fruit pectin and starch syrup are customary.

For the production of marmalade, the fresh fruits or intermediary products, such as fruit pulps or slurries, are boiled in an open kettle at atmospheric pressure (T up to 105 °C) or in a closed vacuum boiler at reduced pressure (T: 65–80 °C) with the addition of sugar (usually added in two batches). In general, the latter process is used industrially. The aroma substances are recovered from the vapor and returned in concentrated form before filling. The solids content and pH value are usually controlled automatically during boiling. Other ingredients (gelling agents, starch syrup and acids) are added before the thickening is completed by boiling. The end of boiling is determined by refractometer readings (the total boiling time is usually 15–30 min). The hot (70–75 °C) marmalade is then poured into appropriate containers.

18.2.6.2 Jams

Jams are produced similarly to marmalades but usually from one kind of fruit. They are thickened by boiling and constant stirring of the whole or sliced fresh or fresh stored raw material, or of fruit pulp. Ordinary jams are also made from fruit slurry. Boiling under a vacuum at 65–80 °C offers the advantage of preserving the aroma and color. The disadvantages are the absence of sucrose inversion and the low caramelization. These reactions produce the characteristic taste of jams boiled in an open kettle (T: 105 °C). Table 18.38 provides compositional data for some commercial jams. The optimal pH of 3.0 required for gelling is adjusted by the addition of lactic, citric or tartaric acid, if necessary.

18.2.6.3 Jellies

Jellies are gelatinous, spreadable preparations made from the juice or aqueous extract of fresh fruits by boiling down with sugar. The addition of fruit pectin (0.5% as calcium pectate) and tartaric acid or lactic acid (0.5%) is normal. In general, the water content is 42%, and the sugar content between 50% and 70%. The juice is boiled down in open kettles or in vacuum kettles with sugar (about half the weight of the fruit), pectin, if necessary, and the substances mentioned above. The scum is carefully skimmed off and the mixture is boiled further until a moisture content of about 42% is reached.

Table 18.38. Composition of various jams (average values in %)

Jam from	Moisture	Total sugar	Total acid[a]	Ash	Dietary fiber
Strawberries	35.0	58.7	0.89	0.23	0.80
Apricots	36.9	51.3	1.14	0.28	0.60
Cherries	36.6	57.3	1.26	0.28	0.50
Blackberries	34.2	58.0	0.37	0.24	1.20
Raspberries	35.9	54.6	1.03	0.23	1.20
Bilberries	35.1	55.8	0.60	0.22	0.37[b]
Plums/prunes	31.1	59.1	0.42	0.24	0.43[b]

[a] Sum of malic and citric acid.
[b] Pectin as calcium pectate.

18.2.7 Plum Sauce (Damson Cheese)

Plum/prune sauce is produced by thickening through boiling of fresh fruit pulps or fruit slurries. The use of dried plums is also common. Normally, the product has no added sugar, but sweetened products or products with other ingredients added are also produced. The soluble solids have to be at least 60% by weight.

18.2.8 Fruit Juices

Fruit juices are usually obtained directly from fruit by mechanical means, and also from juice concentrates (cf. 18.2.10) by dilution with water. The solid matter content is generally 5–20%. The juices are consumed as such or are used as intermediary products, e. g., for the production of syrups, jellies, lemonades, fruit juice liqueurs or fruit candies. Fruit juice production is regulated in most countries.

Juices from acidic fruits are usually sweetened by adding sucrose, glucose or fructose. Juices used for further processing usually contain chemical preservatives to inhibit fermentation. Some juices from berries and stone fruits, because of their high acid content, are not suitable for direct consumption. Addition of sugar and subsequent dilution with water provides fruit nectars or sweet musts (cf. 18.2.9). Since 1990, the per capita consumption of fruit juice and fruit nectar in Germany has been fairly constant at 40 l. In the case of fruit juices, the products presented in Table 18.39 are predominant.

Table 18.39. Per capita consumption of fruit juices in Germany (2004)

Product	Amount (l)
Apple juice	12.8
Orange juice	8.9
Multivitamin juice	3.8
Grape juice	1.3

Table 18.40. Composition of fruit juices and nectars (g/l)

	Total sugar	Volatile acid	Ash	Total acid[a]	Vitamin C
Apple juice	72–102	0.15–0.25	2.2–3.1	1.4	0–0.03
Grape juice	120–180	–	2.1–3.2	3.6–11.7	0.017–0.02
Blackcurrant nectar	95–145	–	2.25–3.2	9.15–12.75	0.2–0.56
Raspberry juice	2.7–69.6	–	4.1–5.2	–	0.12–0.49
Orange juice	60–110	0.13	2.2.–4.0	5–18	0.28–0.86
Lemon juice	7.7–40.8	–	3.0–4.3	42–83.3	0.37–0.63
Grapefruit juice	50–83	0.16	2.5–5.6	5–27	0.25–0.5

[a] Calculated as the sum of malic and citric acid (and tartaric acid in the case of grape juice.

Table 18.40 lists data on the composition of some juices and nectars. Multivitamin juices are produced from orange and apple juice with the addition of banana slurry, passion fruit, mango, pineapple and papaya as well as a mixture of vitamins C, E, B_1, folic acid, niacin and panthothenic acid.

Production of fruit juice involves the processing steps: fruit preparationn and the extraction, treatment and preservation of the juice.

18.2.8.1 Preparation of the Fruit

Preparation of the Fruit involves washing, rinsing and trimming, i. e. the faulty and unripe fruits are removed. The stone seeds and stalks, stems or calyx are then removed. Disintegration is accomplished mechanically in mills, thermally by heating (thermobreak at about 80 °C) or by freezing (less than −5 °C). The yield can be increased to 90% by enzymatic pectin degradation ("mash fermentation", particularly of stone fruits and of berries) or by applying procedures such as ultrasound or electropermeabilization. In the last mentioned process, the raw material is subjected to preliminary disintegration, the cells are then opened up by means of electrical impulses of high field strength, e. g., 2–5 kV/cm.

18.2.8.2 Juice Extraction

Separation of the juice is achieved using continuous or discontinuous presses or processes such as vacuum filtration or extraction.

Before pressing, the fruit tissue is digested with pectinolytic and cellulolytic enzymes at 50 °C to increase the yield. In this way, especially fruit with a soft texture can be directly converted into drinkable juices without the addition of water according to the scheme: preparation – washing – mashing – enzyme treatment – filtration – pasteurization – filling.

18.2.8.3 Juice Treatment

The juice treatment step involves fining and clarification, i. e. removal of turbidity, and stabilization to prevent additional turbidity. The former step commonly involves treatment with enzymes, mostly pectinolytic, and, if necessary, removal of starch and polyphenols using gelatin, alone or together with colloidal silicic acid or tannin, or polyvinylpyrrolidone. Finally, proteins are removed by adsorption on bentonite.

Clarification of juice is achieved by filtration through porous pads or layers of cellulose, asbestos or kieselguhr, or by centrifugation.

Since juice production provides juices which are well-saturated with air oxygen-sensitive products are deaerated. This is achieved by an evacuation step or by purging the juice with an inert gas such as N_2 or CO_2.

Fruit juices (with the exception of citrus juices) are produced as transparent, clarified products, although some turbid juices are available. In the latter case, measures are required to obtain a stable, turbid suspension. This is achieved with stone fruit juices by a short treatment with polygalacturonase preparations which have a low pectin esterase activity and which then partially degrade and, thus, stabilize the ingredients required for turbidity. Citrus juices (lemons, oranges, grapefruits) are heat-treated to inactivate the endogenous pectin esterase, which would otherwise provide pectic acid which can aggregate and flocculate in the presence of Ca^{2+} ions. However, since heat treatment damages fruit aroma, the use of polygalacturonase is preferred. This enzyme degrades the pectic acid to such an extent that flocculation does not occur in the presence of divalent cations.

18.2.8.4 Preservation

Finally, the fruit juice preservation step involves pasteurization, preservation by freezing, storage under an inert atmosphere, or concentration (cf. 18.2.10) and drying (cf. 18.2.12).

Pasteurization kills the microflora and inactivates the enzymes, particularly the phenol oxidases. Since a longer heating time is detrimental to the quality, a short, high-temperature heat treatment is the preferred process, using plate heat exchangers (clear juices 85–92 °C, 10–15 s; fruit slurries up to 105 °C and up to 30 s) with subsequent rapid cooling. The juice is stored in germ-free tanks. Filling operations for the retail market can lead to reinfection, hence a second pasteurization is required. It is achieved by filling preheated containers with the heated juice, or by heating the filled and sealed containers in chambers or tunnel pasteurizers.

Preservation by freezing generally involves transforming the juice or juice concentrate into an ice slurry (at -2.5 °C to -6.5 °C), then packing and cooling to the retail market storage temperature. The product is stable for 5–10 months in a temperature range of -18 °C to -23 °C.

Storage in an inert atmosphere makes use of the fact that filtered, sterilized juices are microbiologically stable at temperatures below 10 °C and in an atmosphere of more than 14.6 g CO_2/l. To attain such a concentration of CO_2, the filled storage tank has to be at a pressure of 0.59 MPa at 10 °C, or 0.47 MPa at 5 °C.

Fruit juices are poured into retail containers, i.e. glass bottles, synthetic polyethylene pouches, aluminum cans, or aluminum-lined cardboard containers.

18.2.8.5 Side Products

Pomace is the residue from the production of fruit juices. Citrus fruits and apple pomace are used for the recovery of pectins. Other fruit residues are used as animal feed, as organic fertilizer, or are incinerated.

18.2.9 Fruit Nectars

Fruit nectars are produced from fruit slurries or whole fruits by homogenization in the presence of sugar, water and, when necessary, citric and ascorbic acids. The fruit content (as fresh weight) is 25–50% and is regulated in most countries, as is the minimum total acid content. Apricots, pears, strawberries, peaches and sour cherries are suitable for nectar production. The fruits are washed, rinsed, disintegrated and heated to inactivate the enzymes present. The fruit mash is then treated with a suitable mixture of pectinolytic and cellulolytic enzymes. The treatment degrades protopectin and, thus, separates the tissue into its individual intact cells ("*maceration*").

High molecular weight and highly esterified pectin formed from protopectin provides the high viscosity and the required turbidity for the nectar. Finally, the disintegrated product is filtered hot, then saturated with the usual additives, homogenized and pasteurized.

Fruit products from citrus fruits (comminuted bases) are obtained by autoclaving (2–3 min at 0.3 MPa) and then straining the fruits through sieves, followed by homogenization. Fruit nectars also include juices or juice concentrates from berries or stone fruits, adjusted by addition of water and sugar.

18.2.10 Fruit Juice Concentrates

Fruit juice concentrates are chemically and microbiologically more stable than fruit juices and their storage and transport costs are lower. The solid content (dry matter) of the concentrates is 60–75%. Intermediary products, less stable concentrates with a dry matter content of 36–48%, are also produced. These semiconcentrates are pasteurized at 87 °C. Fruit juice concentration is achieved by evaporation, freezing, or by a process involving high pressure filtration. Initially, the pectin is degraded to avoid high viscosity and gel setting (undesired properties).

18.2.10.1 Evaporation

Concentration by evaporation is the preferred industrial process. Since the process leads to losses in volatile aroma constituents, it is combined with an aroma recovery step. The aroma of the juice is enriched 100 to 200 times by a counter-current distillation. This aroma is stored and recombined with the juice only at the dilution stage. In order to maintain quality, the residence time in evaporators is as short as possible. In a high-temperature, short-time heating installation, e. g., in a 3- and 4-fold stepwise gradient-type evaporator, the residence time is 3–8 min at an evaporating temperature of 100 °C in the first step and about 40 °C in the fourth step. The concentrate is then cooled to 10 °C. Recovery of the aroma is achieved by rectifying the condensate of the first evaporation stage. A short-time treatment of juices is also possible in thin-layer falling film evaporators. These are particularly suitable for concentrating highly viscous products such as fruit slurries.

18.2.10.2 Freeze Concentration

Concentration of juice by freezing is less economical than evaporation. Hence, it is utilized mostly for products containing sensitive aroma constituents, e. g., orange juice. The juice is cooled continuously below its freezing point in a scraper-type cooler. The ice crystals are separated from the resultant ice slurry by pressing or by centrifugation. The obtainable solid content of the end product is 40–50%. This content is a function of freezing temperature, as illustrated with apple juice in Fig. 18.11.

18.2.10.3 Membrane Filtration

Concentration of juice by filtration using semipermeable membranes and high pressure (0.1–1 MPa) is known as ultrafiltration. When the membrane is permeable for water and only to a limited extent for other small molecules ($M_r < 500$, e. g., salts, sugars, aroma compounds), the process is called reverse osmosis. Concentration of juice is possible only to about 25% dry matter content.

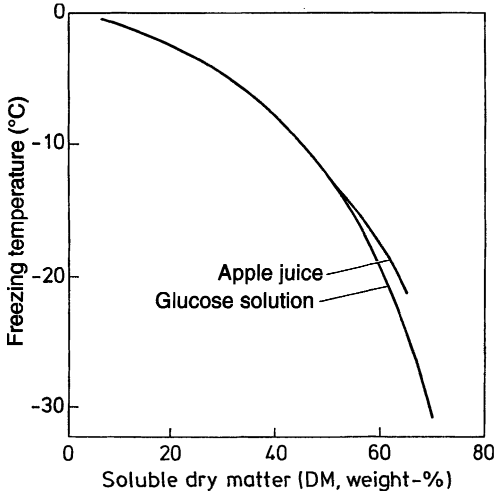


Fig. 18.11. Freezing temperature of apple juice and glucose solution as affected by soluble dry matter (DM) (according to *Schobinger*, 1978)

18.2.11 Fruit Syrups

Fruit syrups are thick, fluid preparations made by boiling one kind of fruit with an excess of sugar. They are sometimes prepared without heating by directly treating fresh fruit or fruit juice with sugar, occasionally also using small amounts of tartaric or lactic acids. Fruit syrups from citrus fruits often contain small amounts of peel aromas.

Fruit syrups are rapidly cooled to avoid aroma losses and caramelization of sugar. The boiling process partially inverts sucrose, preventing subsequent sucrose crystallization. Low-acid fruits are treated with tartaric or lactic acid. Boiling in closed kettles permits recovery of vaporized aroma compounds which can be added back to the end product. As in marmalade production, the boiling is occasionally done under vacuum (50 °C starting temperature, 65–70 °C final temperature) in order to retain the aroma. Syrup production by a cold process is particularly gentle. The raw juice flows over the granulated sucrose in the cold until the required sugar concentration has been achieved. Aroma-sensitive syrups which contain turbidity-causing substances, e. g., citrus fruit syrups, are made by adding sugar to the mother liquor with vigorous stirring. Fruit syrup can contain at most 68% of sugar (calculated as invert sugar) and has to contain at least 65% of soluble solids.

18.2.12 Fruit Powders

Fruit powders are produced by drying juices, juice concentrates or slurries. The hygroscopic powders contain less than 3–4% moisture. Addition of drying aids (such as glucose, maltose or starch syrup) in amounts greater than 50% of the dry matter can efficiently control clumping or caking due to the presence of fructose in the drying process. Freeze-drying, vacuum foam-drying (0.1–1 kPa, 40–60 °C) and foam-mat drying are suitable drying processes. In the last mentioned process, the material to be dried is foamed with foam stabilizers and inert gas and then dried. Spray drying is also applied. It has the disadvantage that often strong color and aroma changes occur.

18.3 Alcohol-Free Beverages

18.3.1 Fruit Juice Beverages

Fruits mostly provide only the taste in fruit juice beverages. These drinks are prepared from fruit juices or their mixtures or from fruit concentrates, with or without addition of sucrose or glucose, and are diluted with water or soda or mineral water. A minimum amount of fruit juice is stipulated: 30% of seed fruit juices or grape juice, 6% of citrus juice or citrus juice mixtures, and 10% of other juices or juice mixtures.

18.3.2 Lemonades, Cold and Hot Beverages

These drinks are prepared with or without the use of fruit juice or fruit extracts by the addition of natural fruit essences and sugar (sucrose or glucose), fruit acids and soda or mineral water. They are also consumed without added carbon dioxide, either cold or warmed. The drinks are usually colored. Lemonades made with the addition of fruit juices contain at least half the amount of fruit juice normally contained in fruit juice drinks. The sugar added to lemonades has to be at least 7% based on the finished beverage.

Tonic water is also considered a lemonade. It contains about 80 mg quinine/l to provide the characteristic bitter taste.

18.3.3 Caffeine-Containing Beverages

These are also considered as “lemonades” (particularly in Europe). The most popular are the cola drinks, which contain extracts from the cola nut (*Cola nitida*) or aromatic extracts from ginger, orange blossoms, carob and tonka beans or lime peels. Caffeine is often added (6.5–25 mg/100 ml). Phosphoric acid is sometimes used as an acidulant (70 mg/100 ml). The sugar content of cola drinks averages 10–11%. The deep-brown color of the drink is adjusted with caramel.

18.3.4 Other Pop Beverages

Some effervescent pop drinks are imitations of fruit juices and lemonade-type drinks, however, their sugar content is fully or partially replaced by artificial sweeteners and the natural essence of flavoring ingredients are replaced by artificial or artificially-enhanced essences. Coloring substances are usually added.

18.4 Analysis

As a result of the numerous raw materials and processes involved, the analysis of fruit products is difficult and tedious. Information on the following is important for an evaluation:

- Type, amount, and origin, if necessary, of the fruit and additives used (e. g., acids, sugar).
- Constituents that determine quality (e. g., aroma substances, vitamins).
- Method of processing.

Information of this type is provided by the quantitative analysis of various constituents, determination of species-specific compounds, and by the determination of abundance ratios of isotopes.

18.4.1 Various Constituents

Since the composition of the raw materials varies greatly, deviations from the standard can be recognized only by collective changes in the concentration of as many components as possible. For orange juice, Table 18.41 shows that when the guide values for certain components are exceeded or fallen short of, information is provided on the proportion of fruit, the use of expressed residues, acidification, sweetening, and microbiological spoilage.

Table 18.41. Guide values for orange juice

Quantity being measured/Component	Mean	Range of variation	Guide value[a]		Indicator[b]
Specific gravity at 20/20 °C	1.046	1.045–1.055	x	1.0450	1
Extract (°Brix)[c]	11.41	11.18–13.54	x	11.18	1
Soluble solids (g/L)	119.4	116.8–142.9	x	116.8	1
Titratable acids (pH 7.0) calc. as tartaric acid (g/L)	9.5	8.0–12	x	8.0	1
Ethanol (g/L)	––	––	o	3.0	3
Volatile acids calc. as acetic acid (g/L)	–	–	o	0.4	3
Lactic acid (g/L)	–	–	o	0.5	3
L(+)-Ascorbic acid (mg/L)	350	–	x	200	2
Peel oil (g/L)	–	–	o	0.3	7
Glucose (g/L)	28	20	x	22	1
Fructose (g/L)	30	22	x	24	1
Ratio of glucose to fructose	0.92	0.85–1.0	o	1.0	5
Sucrose (g/L)	33	47	o	45	5
Sucrose (% of total sugar)	–	–	o	50	5
Ash (g/L)	4.0	2.9–4.8	x	3.5	1
Sodium (mg/L)	14	–	o	30	1
Potassium (mg/L)	1900	1400–2300	x	1700	1
Calcium (mg/L)	80	60–120	o	110	1
Magnesium (mg/L)	100	70–150	x	90	1
Chloride (mg/L)	–	–	o	60	1
Nitrate (mg/L)	–	–	o	10	1
Phosphate (mg/L)	460	350–600	x	400	1
Sulfate (mg/L)	–	–	o	150	1
Citric acid (g/L)	9.4	7.6–11.5	x	8.0	4
Isocitric acid (mg/L)	90	65–130	x	70	4
Ratio of citric acid to isocitric acid[d]	105	80–130	o	130	4
L-Malic acid (g/L)	1.7	1.1–2.9	o	2.5	1
Prolin (mg/L)	800	450–1300	x	575	1
Formol value (0.1 mol/L NaOH per 100 mL)[e]	20	15–26	x	18	1
Flavonoid glycosides calc. as hesperidin (mg/L)	800	500–1000	o	1000	6
Water soluble pectins calc. as galacturonic acid anhydride (mg/L)	300	–	o	500	6

[a] Minimal (x) maximal (o) guide value.

[b] Indicator for: 1 fruit content, 2 heat or oxidation damage, 3 microbiological spoilage, 4 acidification, 5 sweetening, 6 extract of expressed residue, 7 as 6 but aromatized with peel oil.

[c] 1°Brix = 1 g of extract in 100 g of solution.

[d] cf. 18.1.2.4.

[e] Formol titration: after the addition of formaldehyde to a solution of the sample at pH 8–9, the free amino acids are determined by titration with sodium hydroxide solution.

Table 18.42. Phenolic compounds as indicator substances for the detection of adulteration of fruit products

Compound	Occurrence	Detection
Quercetin-3-rutinoside	Common, but not in strawberries	Elderberry juice in strawberry juice
Quercetin-3-O-(2″-O-α-L-rhamnosyl-6″-O-α-L-rhamnosyl)-β-D-glucoside	Red currants	Red currants in products from black currants
Naringin or naringenin	Grapefruits	Grapefruit juice in orange juice
Apigenin-6-C-β-D-glucopyranosyl-8-C-α-L-arabinopyranoside (schaftoside)	Figs	Fig juice in grape juice

18.4.2 Species-Specific Constituents

The occurrence of species-specific constituents is also analytically useful. The composition of the plant phenols of individual fruits can be analyzed quickly and very accurately by using HPLC. These data have shown that certain compounds are suitable indicators of adulteration (Table 18.42). These indicators must be fixed with great care. In fact, phloretin-2-glucoside (phloridzine) and isorhamnetinglucoside have been proposed as markers for apples and pears. Improvements in the analyses, however, showed that phloridzine and isorhamnetinglucoside widely occur in low concentrations in fruit, and the last mentioned glucoside also occurs in apples, among other fruit.

It must be guaranteed that the selected indicator substance is stable under the production conditions for the particular fruit product. Therefore, anthocyanins are generally not suitable. For fermented products, O-glycosides are not suitable because they are degraded by yeast enzymes. Suitable compounds are C-glycosidically bound flavonoids which are resistant to enzymatic hydrolysis and common chemical hydrolysis, e. g., schaftoside (cf. Table 18.42) can be detected even in wine and champagne when the must is adulterated with fig juice.

The analytical importance of amino acid (cf. 18.1.2.1.2), protein, enzyme (cf. 18.1.2.1.1), and carotinoid patterns (cf. 18.1.2.3.2) have already been mentioned.

Adulteration of orange juice by the addition of an aqueous extract of the pulp, which remains after pressing of the juice (pulp wash), is detected by the marker N,N-dimethylproline. The levels of this amino acid are higher in pulp wash than in juice.

18.4.3 Abundance Ratios of Isotopes

The content of the isotopes ^{2}H and ^{13}C is a criterion of the origin of the food or of individual constituents, e. g., sugar used to sweeten fruit juice. The method is based on the fact that isotopomeric molecules, e. g., $^{12}CO_2$ and $^{13}CO_2$, react at different rates in biochemical and chemical reactions (kinetic isotope effect). In general, the molecules with the heavier isotope react slower, so that this isotope is enriched in the products.

The resulting change in the abundance ratio is expressed as the δ-value, based on an international standard (Table 18.43).

$$\delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000[‰] \qquad (18.47)$$

$$R = \frac{C_1}{C_2} \qquad (18.48)$$

c_1/c_2: concentrations of heavy/light isotopes.

The $\delta(^{13}C)$ value, which is $-8 \pm 1‰$ for atmospheric CO_2, increases during CO_2 fixation as a function of the type of photosynthesis of the

Table 18.43. Abundance of important isotopes and international standards for their determination

Isotope	Rel. mean natural abundance [atom %]	International standard	
		Name	R[a]
^{1}H	99.9855	V-SMOW[b]	0.00015576
^{2}H	0.0145		
^{12}C	98.8920	PDB[c]	0.0112372
^{13}C	1.108		

[a] Abundance ratio (Formula 18.48).
[b] Vienna Standard Mean Ocean Water.
[c] Pee Dee Belemnite ($CaCO_3$ from the Pee Dee formation in South Carolina).

Table 18.44. Isotope discrimination in primary photosynthetic CO_2 binding

Plant group	CO_2 Acceptor	$\delta(^{13}C)$ value ‰	Foods
C_3-Plant	D-Ribulose-1,5-bis-phosphate carboxylase (RuPB-C)	−32 to −24	Wheat, rice, oats, rye, potatoes, barley, batata, soybean, orange, sugar beet, grapes
C_4-Plant	Phosphoenolpyruvate carboxylase (PEP-C)	−16 to −10	Corn, millet, sugar cane
CAM-Plant[a]	RuBP-C/REP-C	−30 to −12	Pineapples, vanilla, cactaceae, agave

[a] CAM: Crassulacean acid metabolism.

plant (Table 18.44). The discrimination in C_3-plants is the greatest and is caused by the kinetic isotope effect in the reaction catalyzed by ribulose-1,5-biphosphate carboxylase. It is considerably less in C_4-plants. CAM plants occupy an intermediate position (Table 18.44) because the C_3- or the C_4-path is taken depending on the growth conditions.

The large differences in the masses of ^1H_2O,$^2H^1HO$, and ^2H_2O result in considerable thermodynamic isotope effects on phase transitions. On evaporation, deuterium (^2H) correspondingly decreases in the volatile phase, so that surface-, ground-, and rain-water contains less ^2H than the oceans. The ^2H enrichment in the oceans is greatest at the equator and decreases with increasing latitude because the amount of water evaporating depends on the temperature.

The hydrogen of plant foods comes from precipitation and from the ground-water in that particular location. Therefore, plants of the same type of photosynthesis, which are cultivated at different places, differ in their $\delta(^2H)$ values. Kinetic isotope effects in plant metabolism, which due to the mass difference $^2H/^1H$ are much higher than in the case of $^{13}C/^{12}C$, also have an effect on the $\delta(^2H)$ values.

For isotope analysis, the sample is subjected to catalytic combustion to give CO_2 and H_2O. After drying, the $^{13}C/^{12}C$ ratio in CO_2 is determined by mass spectrometry. The $^2H/^1H$ ratio is determined in hydrogen, which is formed by reducing the water obtained from catalytic combustion. The $^2H/^1H$ ratio can change by $^2H/^1H$ exchange, e. g., as undergone by OH groups. Therefore, such groups are eliminated before combustion. For example, only the $\delta(^2H)$ values of the CH-skeleton in carbohydrates are determined after conversion to the nitrate ester.

Table 18.45. δ (^{13}C) and δ (^2H) values for orange juice and sugar of different origins

Food	δ (^{13}C)(‰)	δ (^2H)(‰)
Orange juice, freeze-dried	−25.6 ± 0.8	n.a.
Sucrose isolated from orange juice	−25.5 ± 2.5	−22 ± 10
Beet sugar	−25.6 ± 1.0	−135 ± 25
Cane sugar	−11.5 ± 0.5	−50 ± 20
Glucose-fructose syrup (corn)	−10.8 ± 0.9	−31

n.a.: not analyzed.

Sweetening orange juice with cane sugar or glucose-fructose syrup from corn starch lowers the $\delta(^{13}C)$ value of sugar, which is −25.5‰ in the native juice (Table 18.45). On the other hand, the addition of beet sugar (C_3-plant) can be recognized only via the $\delta(^2H)$ value. The addition of synthetic products from petrochemicals ($\delta(^{13}C)$: −27 ± 5‰) to foods from C_3-plants cannot be detected via the $\delta(^{13}C)$ value, but via the $\delta(^2H)$ value in many cases.

Apart from the global ^{13}C and ^2H contents of food constituents, the intramolecular distributions of these isotopes are typical of the origin and, therefore, of great analytical importance. They can be measured after chemical decomposition of the substance or with ^{13}C or ^2H NMR spectroscopy (example in 5.5.1.5).

18.5 References

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