20 Alcoholic Beverages

Alcoholic beverages are produced from sugar-containing liquids by alcoholic fermentation. Sugars, fermentable by yeasts, are either present as such or are generated from the raw material by processing, i. e. by hydrolytic cleavage of starches and dextrins, yielding simple sugars. The most important alcoholic beverages are beer, wine and brandy. Beer and wine were known to early civilizations and were produced by a well-developed industry. The distillation process for liquor production was introduced much later. The nutritional energy value of ethanol is high (29 kJ/g or 7 kcal/g).
Figure 20.1 illustrates the *Embden–Meyerhoff–Parnas* scheme of alcoholic fermentation and glycolysis. For related details about the reactions and enzymes involved, the reader is referred to a textbook of biochemistry.

20.1 Beer

20.1.1 Foreword

Beer making or brewing involves the use of germinated barley (malt), hops, yeast and water. In addition to malt from barley, other starch- and/or sugar-containing raw materials have a role, e. g., other kinds of malt such as wheat, unmalted cereals called adjuncts (barley, wheat, corn, rice), starch flour, starch degradation products and fermentable sugars. The use of additional raw materials may necessitate in part the use of microbial enzyme preparations.
Beer owes its invigorating and intoxicating properties to ethanol; its aroma, flavor and bitter taste to hops, kiln-dried products and aroma constituents formed during fermentation; its nutritional value to the content of unfermented solubilized extracts (carbohydrates, protein); and, lastly, its refreshing effect to carbon dioxide, a major constituent. Data on beer production and consumption are given in Table 20.1 and a schematic representation of the production of beer is given in Fig. 20.2.

20.1.2 Raw Materials

20.1.2.1 Barley

Barley is the most important of the raw materials used for beer production. Different cultivars of the spring barley (*Hordeum vulgare convar. distichon*) with exceptionally suitable properties are used as brewing and malting barley in Germany. In addition, six-row winter barley has an increasing role. Barley of high brewing value provides ample quantities of extract from the resultant malt, and has a high starch but moderate protein (9–10%) content, a high degree of germination (at least 95% of kernels), high germination vigor and good swelling ability. Sensory assay (hand appraisal) should also be included in the evaluation of a barley.

20.1.2.2 Other Starch- and Sugar-Containing Raw Materials

20.1.2.2.1 Wheat Malt

Wheat malt is mixed with barley malt in a ratio of 40:60 in the production of top fermented beer.

20.1.2.2.2 Adjuncts

In addition to barley malt, supplementary sources of starch are used in the form of unmalted cereals (adjuncts) in order to dilute the mash by 15–50%. The adjuncts are barley, wheat, corn and rice (cracked rice) in the form of whole meal, grits, flakes or flour.

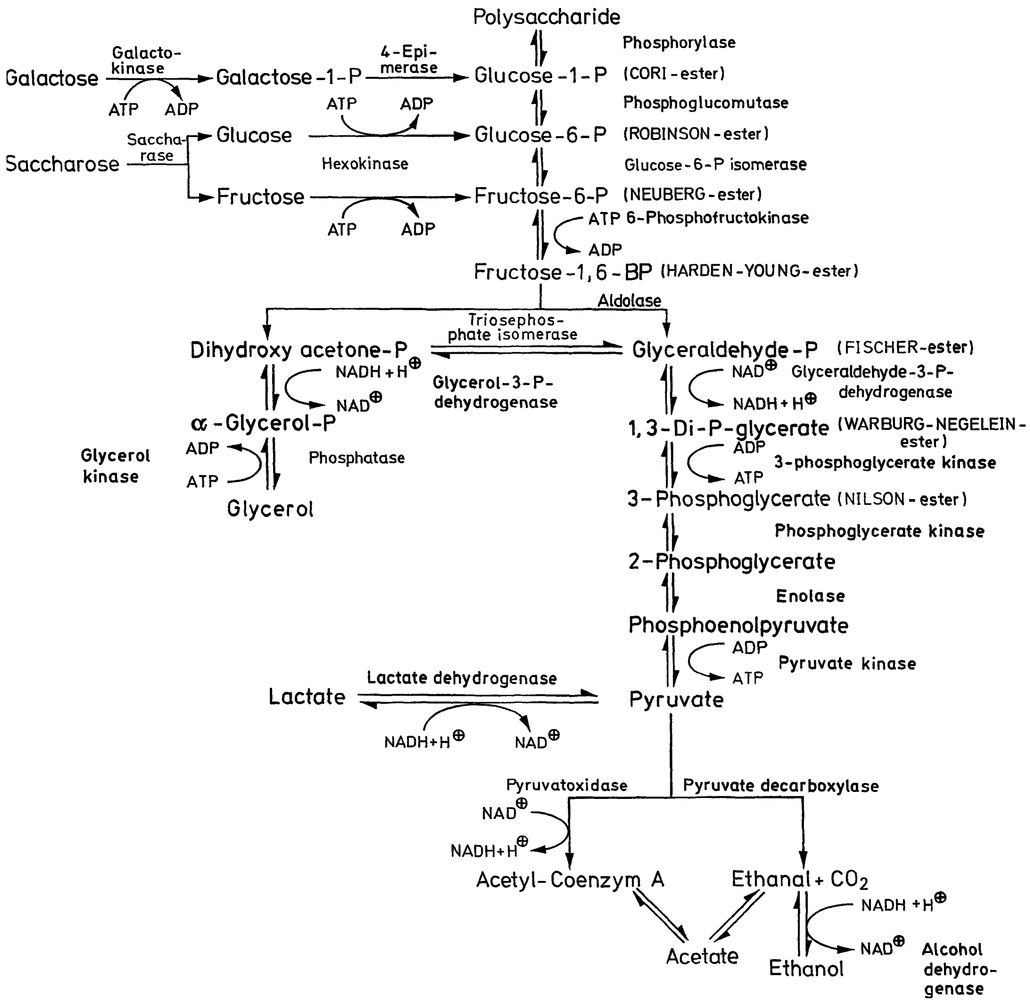


Fig. 20.1. *Embden–Meyerhoff–Parnas*-scheme of glycolysis and alcoholic fermentation

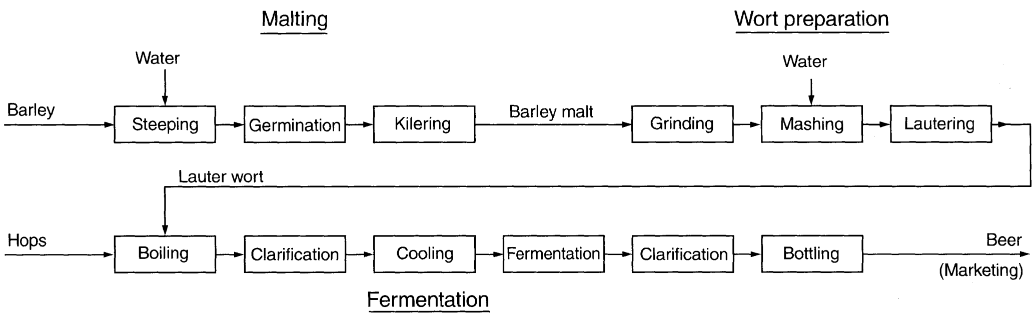


Fig. 20.2. Production of beer

Table 20.1. Production and consumption of beer in 1980, 1997 and 2004

Country	Production (10^6 hl)			Consumption (l/capita)		
	1980	1997	2004	1980	1997	2004
Belgium	14.3	14.0	15.4	131	101	93
Denmark	8.1	9.2	8.4	131	117	90
Germany	92.3[a]	114.8	106.0	146[a]	131	116
Finland	2.8	4.8	4.6	54	67	84
France	21.7	19.5	18.1	57		33
Greece	4.1[b]	3.9	4.4	41[b]	39	
Ireland	6.0	8.1	8.0	122	124	108
Italy	8.6	11.5	13.7	17	25	30
Luxembourg	0.7	0.5	0.4	116	115	
Holland	15.7	24.7	25.1	86	86	78
Austria	7.6	9.4	8.9	102	113	109
Portugal	3.6	6.6	7.3	35	64	62
Sweden	3.7	4.9	4.0	47	62	52
Spain	20.0	24.9	30.6	54	67	
United Kingdom	64.8	59.1	58.0	118	104	101
Czech Rep.			18.5			161

[a] Without GDR.
[b] 1990.

Adjuncts are low in enzyme activity, hence their use may necessitate the addition of microbial enzyme preparations with α-amylase and proteinase activities.
Unmalted barley contains about three times more β-glucans than malted barley. In order to decrease the viscosity of unmalted barley extract to values similar to those of malted barley, β-glucans must be degraded with the enzyme β-glucanase, which is present in microbial enzyme preparations.

20.1.2.2.3 Syrups, Extract Powders

Since adjunct processing may result in undesirable changes, extracts from enzyme- or acid-treated barley, wheat or corn have recently been introduced in the form of syrup or powder. The use of syrup from barley to as much as 45% of the total mash is possible.

20.1.2.2.4 Malt Extracts, Wort Concentrates

For production of hop-free malt extracts or hopped wort concentrates, the usual worts are evaporated in vacuum or concentrated by freeze drying. Such concentrates are diluted prior to use. The content of bitter substances and the tendency to produce cloudiness or turbidity are decreased in such concentrates, since tannins and proteins are removed during the evaporation step.

20.1.2.2.5 Brewing Sugars

Sucrose, invert sugar and starch-sugar are introduced at the stage of hopping or before the beer is bottled.

20.1.2.3 Hops

20.1.2.3.1 General Outline

Hops are a very important and indispensable ingredient in beer production. They act as a clarifier, since they precipitate the proteins in wort, change the wort character to give a specific aroma and bitter taste and, together with ethanol and carbon dioxide, their active antibiotic properties contribute to the stability of beer. Lastly, the pectin content of hops enhances the foam-building ability of beer. The hop (*Humulus lupulus*) is a tall,

Table 20.2. Production of hops in 2006 (1000 t)

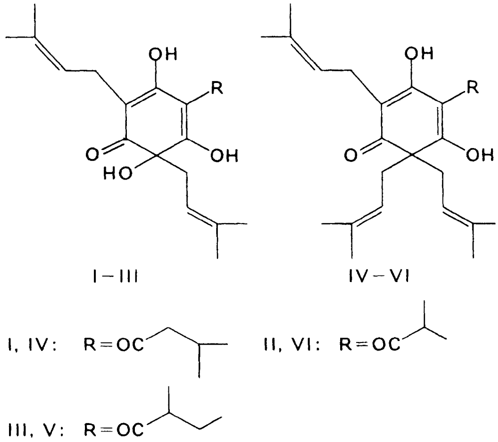
Continent	Hops	Country	Hops
World	129	Germany	34
		USA	26
Africa	23	Ethiopia	23
America, Central	–	China	22
America, North	26	Czech Rep.	5
America, South		Poland	3
and Caribbean	–	UK	2
Asia	25	Korea	2
Europe	53	Slovenia	2
Oceania	2	Spain	1
		Australia	1
		France	1
		Albania	1
		$\sum$ (%)[a]	98

[a] World production = 100 %.

hardy, perennial climbing vine. The flowers of the female plants, though lacking pollination, grow well and cluster into a conical blossom which has large thin scales or bracts. This cone, when ripe, is harvested and used commercially. The plant is propagated vegetatively by planting cuttings from fleshy roots. The hop cones are picked in August or September and are dried and pressed into bales. The lupulin gland in the upper and lower portion of bracts contains, in addition to essential oils, bitter constituents. Data on hop production are given in Table 20.2.

20.1.2.3.2 Composition

Table 20.3 presents data on the composition of hops. The constituents of utmost importance are the bitter substances. In fresh hops they occur mostly in the form of α-acids (cf. Formula 20.1): humulon (I), cohumulon (II), adhumulon (III); and in the form of β-acids: lupulon (IV), colupulon (V) and adlupulon (VI). These compounds are susceptible to changes during drying, storage and processing of hops. The changes usually involve isomerization, oxidation and/or polymerization. As a consequence, a great number of secondary products are found.



(20.1)

The quality and intensity of the bitter taste derived from these secondary products are different. Evaluation of hops is therefore based on a determination of composition of individual α- and β-acids, rather than of the total content of bitter substances. As seen in Table 20.4, the composition varies greatly with hop origin. During the boiling of hops, humulons isomerize into isohumulons (cis-compounds, VII; trans-compounds, VIII; cf. Formula 20.2), which are more soluble and bitter than the initial compounds. The isohumulons can be further transformed into humulinic acids (IX,X), which have only about 30% of the bitterness of isohumulons.

Hulupons (XI) and luputrions (XII) are the secondary products of the lupulons. They possess an exceptionally pleasant and mild bitter taste which is much less bitter than the compounds from which they are derived. Hence the bitter taste of beer is primarily due to compounds of the humulon fraction.

Table 20.3. Composition of hops

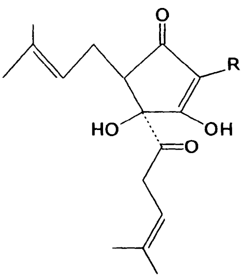
Constituent	Content (%)[a]	Constituent	Content (%)[a]
Bitter compounds	18.3	Crude fiber	15.0
Essential oil	0.5	Ash	8.5
Polyphenols	3.5	N-free extractable mater	
Crude protein	20.0		34.0

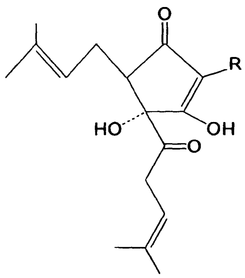
[a] As % dry matter; moisture content approx. 11%.

Table 20.4. Content of humulons and lupulons in hops from various sources (values in %)

Hops	α-Acids			β-Acids		
	humulon	cohumulon	adhumulon	lupulon	colupulon	adlupulon
Japan	46	41	13	21	68	11
America	54	34	12	32	57	11
Hallertau	59	27	14	45	43	12
Northern Brewer	64	24	12	46	43	11
Saaz	67	21	12	51	37	12

Table 20.5 shows the odorants of dried hops. The occurrence of undecatriene and -tetraene, which have a balsam-like, aromatic and pine-like odor, is remarkable. These hydrocarbons, and particularly myrcene and linalool belong to the compounds which produce the characteristic odor of hops.


VII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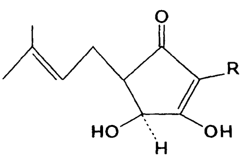
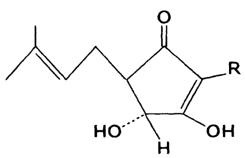
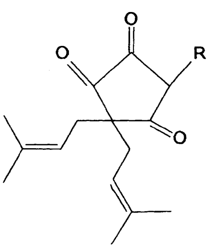
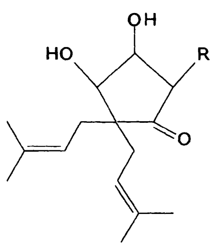

IX


X


XI


XII

(20.2)

Table 20.5. Potent odorants in hops

Compound	Concentration (mg/kg solids)
Myrcene	3200
R-Linalool	68
Butyric acid	28
Hexanoic acid	21
Pentanoic acid	20
Nonanal	3.6
2-Methylpropionic acid	2.4
3-Methylbutyric acid	2.3
2-Methylbutyric acid	1.5
Hexanal	1.5
4-Vinylguaiacol	1.5
2-Methylbutyric acid methylester	0.15
(E,Z)-1,3,5-Undecatriene	0.076
(E,Z,E)-1,3,5,9-Undecatetraene	0.045
(Z)-3-Hexenal	0.029
1,3,5,8-Undecatetraene[a]	0.024
Isobutyric acid ethylester	0.023
1-Octen-3-one	0.022
2-Methylbutyric acid propylester	0.0018

[a] Steriochemistry unknown.

20.1.2.3.3 Processing

Freshly harvested hops are dried in a hop kiln in a stream of warm air (30–65 °C) to 8–10% moisture, followed by a readjustment of moisture content to 11–12%.

In addition to hop cones, which are prone to quality loss even under proper storage conditions, processed products from hops are acceptable and utilized.

Hop powder (water content 3–8%) is obtained by drying and grinding the cones, which makes the active aroma ingredients more extractable. Prior to grinding, part of the inert material is separated and thus lupulin-enriched concentrates are obtained.

Hops are extracted with a mixture of water and an organic solvent (e. g., alcohol, diethylether), giving extracts of varying compositions. Recently, a hops extraction process using supercritical carbon dioxide has become important.

Isomerized extracts, in which humulon has been converted into isohumulon by heat treatment, are suitable for a cold hopping procedure. In traditional beer hopping this conversion is achieved by boiling the wort for a long time. Isomerized extracts are used in the main fermentation or at a later step in brewing.

Boiling of hops results in the loss of a large portion of oil constituents with the steam. The addition of hops shortly before the end of the boiling process or the use of hop resins or concentrates may greatly enhance the hop aroma of the product. Phenolic constituents in hops contribute to protein coagulation during wort boiling. A part of protein-tannin complexes formed may precipitate at low temperatures after long storage, resulting in turbidity in the beer.

20.1.2.4 Brewing Water

The water used for wort preparation in a brewery has a great influence on beer quality and character. The salt constituents of water can change the pH of the mash and wort. Bicarbonate ions cause a pH increase, while Ca^{2+} and Mg^{2+} ions cause a pH decrease. Heating of water which contains bicarbonates increases the alkalinity according to the equation:

$$HCO_3^{\ominus} + H^{\oplus} \rightleftharpoons CO_2 + H_2O \qquad (20.3)$$

in which the equilibrium is shifted to the left since, during heating, the CO_2 component escapes as a gas. Ca and Mg ions react with secondary phosphates in wort to form insoluble tertiary phosphates, releasing protons which add to the acidity of the water:

$$3Ca^{2\oplus} + 2HPO_4^{2\ominus} \rightleftharpoons Ca_3(PO_4)_2 + 2H^{\oplus} \qquad (20.4)$$

Magnesium sulfate in high concentrations imparts an unpleasant bitter taste to beer. Manganese and iron salts induce turbidity, discoloration and taste deterioration. Concentrations of NaCl or nitrate (>300 mg/l) which are too high interfere with fermentation. During fermentation, nitrate is reduced to nitrite, which is toxic for yeast.

The unique character of different kinds of beer (Pilsen, Dortmund, Munich, Burton-on-Trent), without doubt, can historically be ascribed to the brewing water used in those places, with residual alkalinity playing the major role. Water, low in soluble bicarbonates of calcium, magnesium, sodium or potassium, and soluble carbonates and hydroxides, is suitable for strongly-hopped light beers, such as Pilsener, while alkaline water is suitable for dark beers, such as those from Munich.

Preparation of brewing water is mainly directed to the removal of carbonates. Precipitation by heating with lime is customary. Furthermore, when lime water is used without heating, water softening occurs. Removal of excess salt by ion-exchange resins is also advantageous. Today any water can be treated to match the requirement of a desired type of beer.

20.1.2.5 Brewing Yeasts

Brewing yeasts are exclusively strains of *Saccharomyces*. Two types are recognized: top fermenting yeasts for temperatures $>10\,°C$, and bottom fermenting yeasts used down to 0°C. The top fermenting yeasts, e. g., *Saccharomyces cerevisiae Hansen*, rise to the surface during fermentation in the form of large budding ("sprouting") associations. They ferment raffinose only partially since they lack the enzyme melibiase. The bottom fermenting yeasts, e. g., *Saccharomyces carlsbergensis Hansen*, settle to the bottom during fermentation and completely ferment all sugars including raffinose. There are yeasts with high fermentation ability which remain suspended for a long time, giving a high fermentation rate. Yeasts with low fermentation ability flocculate early and settle to the bottom (super-flocculent yeasts) and hence are unable to continue active fermentation. Pure cultures of many yeast strains currently in use are derived from a single yeast cell and are used as "starter yeast" in plant operations. After the main fermentation, a part of the yeast is harvested for use in freshly-prepared worts, until the yeast becomes useless due to contamination or degeneration. In this way, it is possible to continuously select suitable yeast strains for a defined goal.

20.1.3 Malt Preparation

The cereals are soaked (steeped) in water and then allowed to germinate. The product, green malt, is dried and mildly roasted into a more or less dark and aroma-rich kiln-dried malt. During processing, the rootlets are removed from the malt. The loss due to malting is 11–13% of the dry weight. Prior to use, the malt is stored for 4–6 weeks.

20.1.3.1 Steeping

Cereal kernels are steeped in water to raise their moisture content to induce germination. The water content is 42–44% for light and 44–46% for dark malt. Usually the steeping water is alternately added and removed. Barley is first steeped for only 4–6 h at 12–15 °C water temperature so that the water content is adjusted to ca. 30%. In the following dry period, which lasts 18–20 h, the grains swell and enzymatic processes start rapidly. In the second wet steeping at ca. 18 °C, a water content of 38% is obtained in 2 h. Good aeration is needed in all phases to remove the CO_2 produced by respiration. The normal steeping temperature is 12–24 °C. Alkali treatment (CaO, NaOH) of steeping water serves to reduce microbial contamination and to remove undesirable polyphenols from the hulls.

20.1.3.2 Germination

When the cereals reach the desired moisture content (after ca. 26 h) and germination is started, they are allowed to germinate in germinator chests or less often in drums. The removal of CO_2 and heat is achieved by blowing in moist air (500 m^3/t). The sprouts appear at 16–18 °C in 16–20 h. The water content of barley is first increased to ca. 41% by spraying and then in steps to 47% to further support germination. The growth of the rootlet continues up to 1.5 times the grain length. At the end of the process which on the whole lasts ca. 40–50 h, the temperature is reduced to 11–13 °C. The law in some countries allows the addition of growth substances to accelerate germination, e. g., gibberellic acid.

20.1.3.3 Kilning

The germinated cereals, termed green malt, contain 43–47% moisture. They are dried in a kiln to give a storable malt with a water content from 2.5% (dark) to 4.5% (lager).
Light malt requires fast drying so that the *Maillard* reaction does not get a look-in. The process is carried out in high-performance kilns at a temperature which is raised from 50 to 65 °C. The barley heats up and germination stops above 40 °C at a water content which is reduced to 20%. However, the activities of hydrolases (endopeptidases, α-amylases) still increase, as desired. The final drying is carried out at 82–85 °C, leading to unavoidable enzyme losses.
In the production of dark malt, the moisture is withdrawn so slowly that the material temperature is higher than with light malt. Although this results in an inhibition of germination, there is an extension of the period in which the activities of the hydrolases increase. The degradation of proteins and carbohydrates to precursors of the *Maillard* reaction is correspondingly extensive. Finally, the malt is rapidly dried at 100 to 105 °C, the *Maillard* reaction providing intensive color and aroma substances.

20.1.3.4 Continuous Processes

Several kinds of installations have been developed which provide continuous steeping, germination and, occasionally, also kilning, offering substantial savings in time. Steeping in this case is performed as a single washing followed by water spraying and continuous transferring to the germination stage. The process conditions are regulated by means of forced air. In some installations the malt is moved for different stages, while in others it remains in the same container from steeping to kilning.

20.1.3.5 Special Malts

Special malts are prepared for many purposes. Dark caramelized malt is held briefly at 60–80 °C to saccharify its starch and is then roasted at 150–180 °C for the desired degree of color. Such color-rich malt is free of diastase enzyme activity, is a good foam builder, and is mostly used for aromatizing malt beers and strong bock beers. Light caramelized malt is made in a similar way, but is treated at lower temperatures after the saccharification step. This preserves the enzyme activities. It is lightly colored and when used gives beer an increased foaming capacity and full-bodied properties. Colored malt is obtained by roasting the kiln-dried malt at 190–220 °C, omitting the prior saccharification step. It can be used to intensify the color of dark beers.

20.1.4 Wort Preparation

The coarsely ground malt is dispersed in water. During this time, the malt enzymes hydrolyze starch and other ingredients. A clear fermentable solution, the so-called wort, is obtained by filtration. When boiled with added hops, the wort takes on the typical beer flavors.

20.1.4.1 Ground Malt

Malt is disintegrated by passing it through several grinding rolls and sifters. The ground products, hull, middlings and flour, are then combined in the desired proportions. By using finely ground meal, the extraction yield increases, but problems arise in wort filtration. Wet milling is commonly preferred for better filtration as it yields a higher proportion of intact hulls. In addition, it provides the desired high extraction yield. For wet milling the water content of the malt is adjusted to 25–30%. It is then ground by a set of rollers and processed immediately into wort.
Continuous wet meal steepers have been developed to guarantee a defined steeping time and, thus, to prevent the malt grains from becoming slippery and gelatinized by overly long steepage.

20.1.4.2 Mashing

In the mashing step, the malt meal is made into a paste with brewing water (heatable mixing vessel) and partially degraded and solubilized with malt enzymes.
For 100 kg of malt, 4–5 hl of water for light beers and 3–3.5 hl for dark beers are needed. This amount of water is divided into a major portion for production of the mash, and into one or several post-mashing rinses used to wash out extract from the hulls. The course of pH and temperature during mashing are of utmost importance for determining wort composition and, hence, the type and quality of beer. The optimum activity of malt α-amylases is from 70–75 °C at pH 5.6–5.8, and of malt β-amylases from 60–65 °C at pH 5.4–5.6, while that of malt endopeptidases is from 50–60 °C at pH 5.0–5.2. Hence, wort with a pH near 6 will not, without prior pH adjustment, provide optimal conditions for the action of enzymes. The methods used for temperature control in mashing are of two types: decoction and infusion. In the decoction method, the initial temperature of the total mash is raised by removing an aliquot of mash, heating this to boiling and then returning it to the main mash in the mash tun. In general one-, two- or three-mash return procedures are used commercially. The latter is used exclusively for dark beer brewing; the two-mash return for light beer; and the one-mash return procedure for brewing all types of beer. The three-mash return procedure will be briefly described as an example: The crushed malt is mixed in the mash tun with water at 37 °C; the first aliquot is drawn, heated to boiling and returned to the mash tun. In this way the total mash temperature is raised to 52 °C. Two repetitions raise the total mash temperature stepwise to 64 and then to 75 °C. The mashing process is completed at a terminal mash temperature of 74–78 °C.
In the case of poorly “solubilized” malt in which the starch-containing membranes have not ruptured, enzymatic degradation and the extract yield can be improved by stopping briefly at 47–50 °C before further temperature increase. This delays

enzyme inactivation. On the other hand, when a low alcohol beer is desired, the malt mashed at 37 °C is drained into boiling water, increasing the temperature to 70 °C and resulting in extensive enzyme inactivation.
In infusion mashing, used mostly in England for brewing top fermented beer, the terminal mashing temperature is achieved not by stepwise increases, but by live steam injection or addition of hot water. As in the decoction method, the temperature program used can vary greatly.

20.1.4.3 Lautering

The separation of wort from hulls and insoluble residues of the grain is done by a classical procedure in a lauter tun, a vessel with a slotted false bottom. The hull and other residues form a ca. 35 cm deep layer in the bottom which acts as a filter through which the extract, or wort, is strained. The initial turbid liquid (turbid wort) with 16–20% extract is pumped back to the tun. Finally, to obtain more wort, the spent grains are rinsed or sparged 3 to 4 times with water.
Modern installations for lautering use strain masters or discontinuous or continuous mash filters. The draff, the lautering residue, is used for animal feed.

20.1.4.4 Wort Boiling and Hopping

Wort boiling with hops or hop products is done in a brew kettle (hop kettle) in which the initial and subsequent worts from the lautering step are collected. Addition of hops is adjusted according to the type and quality of beer desired. The quantity (in hop cones/hectoliter) for light lager beer is 130–150 g; for Dortmund-type beer, 180–220 g; for Pilsener beer, 250–400 g; for dark Munich beer, 130–170 g; and for malt beer and dark bock beer, 50–90 g. The critical factor is the content of bitter substances in the hops selected. The utilization of the bitter substances (α-acids) is only 30–35%.
Boiling for 70 to 120 min concentrates the wort, coagulates protein ("break forming"), solubilizes hop ingredients and converts the bitter components to their isoforms and, lastly, inactivates enzymes. The hot wort is then chilled, filtered, aerated and, finally, "pitched" with yeast.
In modern processes, the classical brew kettle is replaced by a whirlpool kettle with external cooker. Shorter boiling times and a better quality of beer are achieved with this system. Moreover, separation from the spent hops can be conducted in the same vessel.
Processes that use pressure boiling (high-temperature wort boiling up to 150 °C) can produce beer with an unpleasant cooked taste.

20.1.4.5 Continuous Processes

Efforts are being made to introduce continuous processes via heat exchangers and to save energy and make the process environmentally friendly with heat recovery from the exhaust steam.
Wort treatment, i. e., removal of the trub formed during boiling (protein-polyphenol complexes, cf. 18.1.2.5.8), is generally conducted in whirlpool vats (possibly combined with wort drying) or via continuous centrifuges. After cooling to the pitching temperature (6–8 °C), the cooling trub obtained is separated by filtration or centrifugation.

20.1.5 Fermentation

20.1.5.1 Bottom Fermentation

Bottom fermentation involves a primary and a secondary step. In the primary fermentation step, the cooled wort with about 6.5–18% dry mass extracted from malt ("stemwort") is pumped into fermenting tanks, located in fermentation cellars cooled to 5–6 °C. The tanks are made of plastic-lined concrete, enamelcoated steel, aluminum or V_2A steel. The wort is inoculated ("pitched") with yeast in the form of a thick yeast slurry of *Saccharomyces Carlsbergensis* (0.5–1 l/hl) and fermented at 8–14 °C until more than 90% of the fermentable extract has been converted. The primary fermentation is completed in 7–8 days, at which point the yeast "breaks", i. e., flocculates and settles to the bottom. The beer is transferred to large clean

tanks. With a wort extract content of 12%, 4% of ethanol is produced during fermentation.
The young "green" beer is stored for 1–2 months in tanks at 0–1 °C for secondary fermentation. The beer is clarified by settling of the yeast and separation of protein-polyphenol complexes (cf. 18.1.2.5.8). The yeast multiplies attaining 4 to 5 times the original quantity and is harvested after fermentation. It is used several times until it is no longer biologically pure or it loses fermenting power.

20.1.5.2 Top Fermentation

Primary fermentation proceeds in fermentation tanks, but at higher temperatures (18–24 °C) than bottom fermentation, and requires a total time of ca. 3 days. The yeast builds a solid cap at the top of the tank. It is skimmed off into individual fractions (hops flock, yeast flock, post-flock). The secondary fermentation is a very slow process and may continue in tanks or bottles. Top fermentation is used mostly in England and Belgium, while in Germany it is used in the production of "Kölsch", "Altbier" and "Weiss" beer, a light tart ale made from wheat.

20.1.5.3 Continuous Processes, Rapid Methods

Several continuous processing methods provide accelerated fermentation. They make use of thermophilic yeasts, higher fermentation temperatures and more intensive wort aeration.

20.1.6 Bottling

After ageing, beer is filtered through cotton filter pads and some silicates, often having been preclarified through a kieselguhr pad or by centrifugation. Then, with the aid of a special cask/keg filling apparatus, it is foamlessly filled into transportable casks or metal cisterns. In addition to impregnated oakwood casks, specially-lined iron, aluminum or V_2A steel containers are also acceptable. Bottle filling proceeds from a "bottle tank" in a fully automated process. Tin-plated or aluminum cans are also used.
Pasteurization gives the beer biological stability for overseas export. To avoid cloudiness due to protein precipitation and changes in flavor, the beer is heated to 60–70 °C in a water bath or by steam. The beer is often pasteurized at 62 °C for 20 min. For sterile filling the beer is heated to 70 °C for 30 s or is passed through microfilters (with pore size less than the size of bacteria) and then poured into sterilized bottles or cans.
Temperature fluctuations during storage and transport must be avoided if beer quality is to be preserved.

20.1.7 Composition

20.1.7.1 Ethanol

The ethanol content, which has a very important influence on the aroma, is 1.0–1.5% by weight for a low fermented extract-rich beer, 1.5–2.0% for a weak or thin beer, 3.5–4.5% for a full beer, and 4.8–5.5% for a strong beer. Higher alcohols, such as 2-methylbutanol, 3-methylbutanol, methylpropanol and 2-phenylethanol, are also present in very small quantities.

20.1.7.2 Extract

The nonalcoholic constituents of beer vary within a wide range from 2–3% for plain beers to 8–10% for strong beers. These constituents are the beer solids and consist of to 80% carbohydrate, mostly dextrins. It is possible to calculate the solids content of the original wort before fermentation from the solids content (E, weight %) and alcohol content (A, weight %) of the beer product. The calculation is based on the fermentation equation: 2 parts by weight of sugar equal 1 part by weight of alcohol. The initial solids content of wort, which actually represents a measure of malt utilization, is designated as "stemwort" (St) and can be calculated by the formula:

$$\mathrm{St} = \frac{100\ (\mathrm{E} + 2.0665\ \mathrm{A})}{100 + 1.0665\ \mathrm{A}} \tag{20.5}$$

Thus, for example, if the solids content (E) of a beer is 3% (w/v) and the alcohol content (A) is 5.0% (v/v), then the solids content of the wort before fermentation was 12.6% (w/v). The stemwort content in Germany is 2–5.5% for plain beers, 7–8% for draft beers, 11–14% for full beers and above 16% for strong beers.

20.1.7.3 Acids

Carbon dioxide is responsible to a substantial extent for the refreshing value and stability of beer. CO_2 is 0.36–0.44% in bottom fermented beers, while in Weiss beer the CO_2 content is up to 0.6–0.7%. A CO_2 content below 0.2% gives flat and dull beers. Apart from small amounts of lactic, acetic, formic, and succinic acids, beer contains 9,10,13- and 9,12,13-trihydroxyoctadecenoic acid. In fact, 9.9 ± 2.1 mg/l were found in five types of beer and 9(S), 12(S), 13(S)-trihydroxy-10(E)-octadecenoic acid was the main compound and accounted for 50–55% of the 16 stereoisomers. The pH of beer is between 4.7 (dark, strong beer) and 4.1 (Weiss beer).

20.1.7.4 Nitrogen Compounds

The N-compounds in beer (0.15–0.75%) originate primarily from proteins in the raw materials and from yeast. They consist mainly of proteins plus high molecular weight protein degradation products; both being responsible for cloudiness in beer during cold storage. The free amino acids found in malt are also present in beer. It appears that glutamic acid contributes to beer taste. The presence of volatile amines has also been confirmed.

20.1.7.5 Carbohydrates

The carbohydrate content is approximately 3–5%, while in some strong beers or malt beers it may be considerably higher. Pentosans are also present in addition to dextrins, mono- and oligosaccharides (maltotriose, maltose, etc.). Glycerol normally is 0.2–0.3% of beer.

20.1.7.6 Minerals

Minerals make up 0.3–0.4% of beer and consist mostly of potassium and phosphate. Calcium, magnesium, iron, chloride, sulfate and silicates are also present.

20.1.7.7 Vitamins

Vitamins of the B-group (vitamins B_1 and B_2, nicotinic acid, pyridoxine and pantothenic acid) are present in various beers, often in significant amounts.

20.1.7.8 Aroma Substances

The odorants, e. g., for Pilsener beer are shown in Table 20.6. The aroma is reproduced by a suitable mixture of these substances dissolved in water, the pH of which is adjusted to 4.3 with carbonic acid. This emphasizes the fact that the key odorants of this type of beer can be analytically identified. (R)-Linalool and ethyl-4-methylpentanoate are derived from hops and pass into the beer on boiling the wort.

The odor- and taste-active substances essentially determine the type of beer. The bitter taste of Pilsener beers is produced by relatively high concentrations of isohumulons, and humulenes (including oxidation products), while larger amounts of furaneol are responsible for the caramel note of dark beers.

In the production of alcohol-free beer, the concentrations of important aroma substances drop (Table 20.7).

20.1.7.9 Foam Builders

The foam building properties of beer are due to proteins, polysaccharides and bitter constituents. The β-glucans stabilize the foam through their ability to increase viscosity. Addition of semisynthetic polysaccharides, e. g., propyleneglycol alginate (40 g/hectoliter), to beer provides a very stable foam although the addition is judged as unfavorable.

Table 20.6. Odorants in Pilsener Bier

Compound	Concentration (mg/l)	Aroma value[a]
Ethanol	4080	1639
(E)-β-Damascenone	0.0023	575
(R)-Linalool	0.045	321
Acetaldehyde	5.1	204
Ethyl butanoate	0.198	198
Ethyl-2-methylpropanoate	0.0032	160
Ethyl-4-methylpentanoate	0.00028	93
Dimethylsulfide	0.059	59
3-Methylbutanol	49.6	50
2-Methylbutanol	14.4	45
Ethylhexanoate	0.205	41
4-Hydroxy-2(or 5)-ethyl-5(or 2)-methyl-3(2H)-furanone	0.019	17
2-Phenylethanol	15.1	15
4-Hydroxy-2,5-dimethyl-3(2H)-furanone	0.312	13
Diethoxyethane	0.050	10
3-Methylbutanal	0.004	10
3-Methyl-2-buten-1-thiol	0.00001	8
3-(Methylthio)propanol	0.991	4
3-Hydroxy-4,5-dimethyl-2(5H)-furanone	0.001	3
Butyric acid	1.8	2
Ethyloctanoate	0.160	2
3-Methylbutyric acid	0.855	1
4-Vinyl-2-methoxyphenol	0.137	1

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

Table 20.7. Odorants in lager beer and alcohol-free beer

Compound	Lager beer (mg/l)	Alcohol-free beer (mg/l)
3-Methylbutanol	49.6	6.7
2-Phenylethanol	17.5	2.3
Ethyl hexanoate	0.15	0.01
Ethyl butanoate	0.06	0.01
4-Hydroxy-2,5-dimethyl-3(2H)-furanone (HD3F)	0.35	0.19
4-Vinylguaiacol	0.52	0.13

Lysophosphatidyl cholines (LPC), which occur in cereal as amylose inclusion compounds (starch lipids: cf. 15.2.5), reduce the foam stability. The temperature management during the mashing process regulates the LPC concentration because it determines the activity ratio of α-amylase, which contributes to the release of LPC from amylose, to phospholipase B, which catalyzes the degradation of LPC. Temperatures above 65 °C favor the more stable α-amylase, increasing the LPC concentration.

20.1.8 Kinds of Beer

There is a distinction between top and bottom fermented beers.

20.1.8.1 Top Fermented Beers

Selected examples of top fermented beers from Germany are: Berlin weiss beer, brewed from a wort having 7–8% solids from barley and wheat malts and inoculated at fermentation with yeast and lactic acid bacteria; Bavarian weiss beer brewed from weakly-smoked barley malt with a little wheat malt and fermented only with yeast; Graetzer beer made from wheat malt with a smoky flavor and with a stemwort content of

7–8%; malt beer (caramel beer), a dark, sweet and slightly hopflavored full beer; the bitter beers such as those from Cologne or Duesseldorf (Altbier) which are strongly hop-flavored full beers; top fermented plain beers (Jungbier or Frischbier) with a low stemwort content and often artificially sweetened; Braunschweig's mumme, an unfermented, non-hop flavored malt extract, hence not a true beer or a beer-like beverage. English beers have a stemwort content up to 11–13%. Stout is a very darkly colored and alcohol-rich beer made from concentrated boiled wort (up to 25% stemwort; alcohol content >6.5%). Milder varieties of stout are known as Porter beer.

Pale ale is strongly hopped light beer, whereas mild ale is mildly hopped dark beer. Incorporation of ginger root essence into these beers yields ginger-flavored ale.

Top fermented beers from Belgium, which are stored for a longer time, are called Lambic and Faro beers.

20.1.8.2 Bottom Fermented Beers

These beers show a significantly increased storage stability and are brewed as light, mildly colored or dark beers.

Pilsener beer, an example of a light colored beer, is typically hop flavored, containing 11.8–12.7% stemwort. In contrast, Dortmunder-type beer is made from a more concentrated wort which is fermented longer and thereby has a higher alcohol content. Lager beer (North German Lager) is similar to Dortmunder in hop flavoring, while the stemwort content is close to a Pilsener beer. Munich beers are dark, lightly hop flavored and contain 0.5–2% colored malt and often a little caramel malt. They taste sweet, have a typical malt aromatic flavor, and are fermented with a stemwort content of 11–14%. Beers with a high content of extract are designated as export beers. Traditional dark beers and currently produced special light beers, are the bock beers (Salvator, Animator, etc.). They are also strong beers with more than 16% stemwort. The dark Nuernberg and Kulmbacher beers are even higher in colored malt extracts and thereby are darker than Munich beers. An example of mildly colored beer is the Maerzen beer (averaging 13.8% stemwort). It is produced from malt of Munich in which the use of colored malt is omitted.

20.1.8.3 Diet Beers

Diet beers exhibit a high degree of fermentation and contain almost no carbohydrates, which are a burden for diabetics. They are produced by special fermentation processes and contain a relatively high alcohol content. Subsequently, the alcohol level is frequently reduced to values typical of normal beer.

20.1.8.4 Alcohol-Free Beers

In the production of alcohol-free beers, the alcohol content of normal beer (top or bottom fermented, light or dark) is largely removed (≤0.5% by volume) by reverse osmosis (cf. 18.2.10.3) or distillation under vacuum at ca. 40 °C. The influence on the aroma is presented in 20.1.7.8.

20.1.8.5 Export Beers

These originate from widely different kinds of beer. They are mostly pasteurized and additionally treated with flocculating or adsorption agents (tannin, bentonite) or with proteolytic enzyme preparations to remove most of the proteins. The proteolytic enzymes split the large protein molecules into soluble products. Such beers are free of cloudiness or turbidity (chill-proofed beers) even after prolonged transport and cold storage.

20.1.9 Beer Flavor and Beer Defects

The taste and odor profile of a beer, including possible aroma defects, can be described in detail with the help of 44 terms grouped into 14 general terms, as shown in Fig. 20.3. Apart from a great variety of terms for odor notes, the terms bitter, salty, metallic, and alkaline are used only for taste and the terms sour, sweet, "body" etc. are applied to both taste as well as odor.

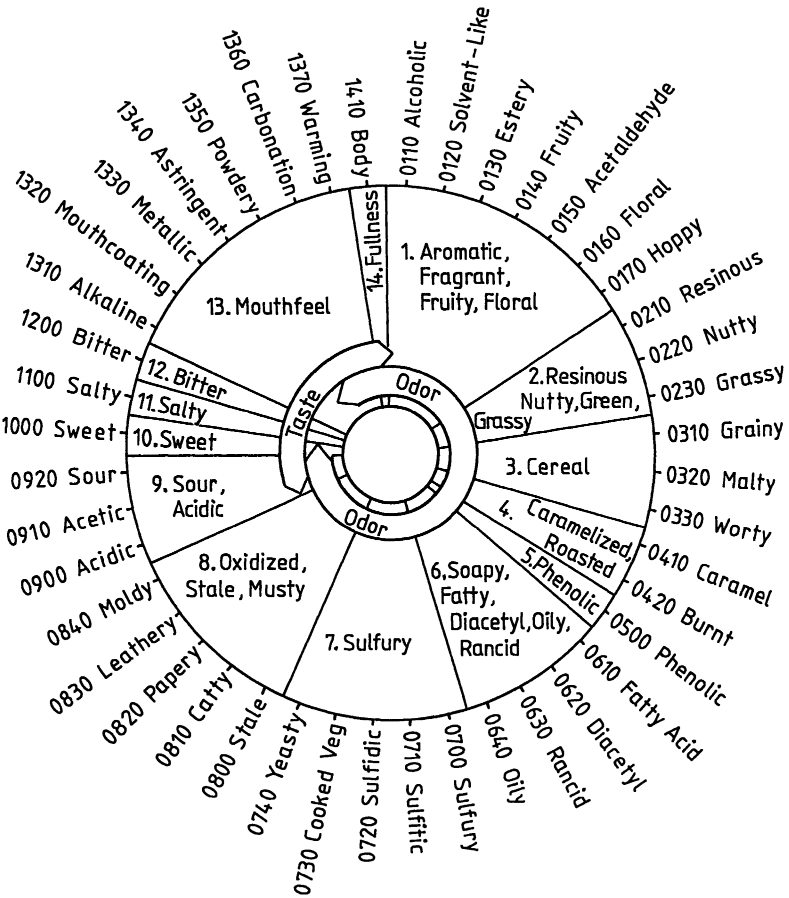


Fig. 20.3. Terminology for the description of odor and taste notes of beer (*American Society of Brewing Chemists*, according to *Meilgaard*, 1982)

Nine of the terms given in Fig. 20.3 describe the most important odor and taste characteristics of a good beer (Table 20.8). They are also suitable for the differentiation of different types of beer (Table 20.8).

Foaming is an important criterion of the taste of beer. A distinction is made between foam volume (produced by the content of carbon dioxide), foam density, and especially foam stability (caused by protein degradation products, bitter hop compounds, and pentosans). Lower fatty acids that are present in beer bouquet act as defoamers.

Beer defects detract from the odor and taste and are caused by improper production and storage. An example of a taste defect is the harsh, hard, bitter taste produced by the oxidation of polyphenols and some hop constituents. A flat taste, as already mentioned, comes from a low content of carbon dioxide. Diacetyl and ethanal in concentrations greater than 0.13 mg/l and 25 mg/l respectively, produce a taste defect. Acceleration of fermentation caused, e. g., by intensive stirring of the wort, raises the content of diacetyl and higher alcohols in the beer and lowers the content of esters and acids. On the whole, the aroma is negatively influenced. Higher concentrations of ethanal can arise, e. g., at higher fermentation temperatures and higher yeast concentrations.

Beer is very sensitive to light and oxidation. The "light" taste is due to the formation of 3-methyl-

Table 20.8. Main characteristics of the odor and taste of various types of beer

Flavor group	Intensity[a]					
	Munich	Pilsner	Pale ale	US lager	Stout[b]	Lambic
Bitterness	3–6	6–10	5–8	2–4	6–10	3–6
Alcoholic flavor	2–4	3–4	3–4	3–5	3–5	3–6
Carbonation	3–4	3–4	1–3	4	3–4	3–5
Hop character	2–6	6–10	5–8	0.5–4	6–10	3–6
Caramel flavor	4–8	0.5–2	3–5	0.5–1	6–100	1–3
Fruity/estery flavor	1–2	1–1.5	1–2	2–3	2–3	3–5
Sweetness	2–3	1–2	1–2	2–3	1–2	1–2
Acidity	1–2	1–2	1–2	1–2	2–3	3–20
Cabbage-like	1–2	1–3	0.2–0.8	1–3	0.2–0.8	1–10

[a] Semiquantitative values on the basis of aroma values.
[b] Top fermented English strong beer with a stemwort content of up to 25%.

2-buten-l-thiol (cf. Table 5.5). This substance becomes unpleasantly noticeable at concentrations higher than 0.3 μg/l. It is one of the characteristic aroma substances below this concentration. Enzymatic peroxidation of lipids contained in the wort and nonenzymatic secondary reactions during wort boiling give rise to the aroma defects listed as No. 8 in Fig. 20.3.

A sweetish off-flavor formed during storage of beer is caused by an increase in 3-methylbutanal, methional, phenylacetaldehyde, ethyl methylpropanoate and ethyl 2-methylbutanoate.

The addition of ascorbic acid or glucose oxidase/catalase (cf. 2.7.2.1.1) is recommended to overcome color and flavor defects caused by oxidation. Therefore, low-oxygen bottling is of great importance. Bottled beer should not contain more than 1 mg O_2/l.

Unwanted carbonyl compounds, which can produce an off-flavor in stored beer, are bound by sulfite derived from yeast metabolism. Yeast reduces the sulfate present in the wort to sulfite and sulfide, which is then consumed in the biosynthesis of sulfur-containing amino acids. If the growth of yeast comes to a standstill, excess sulfite is eliminated, increasing the stability of the beer to oxidative processes.

The very potent aroma substance 3-methyl-3-mercaptobutyl formate (cf. 5.3.2.5) can produce an off-aroma called "catty" (0810 in Fig. 20.3). The concentration of phenylacetaldehyde can also increase to such an extent on the storage of beer that it becomes noticeable in the aroma.

On storage, beer can become cloudy and form a sediment. Proteins and polypeptides make up 40–75% of the turbidity-causing solids. They become insoluble due to the formation of intermolecular disulfide bonds, complex formation with polyphenols, or reactions with heavy metals ions (Cu, Fe, Sn). Other components of the sediment are carbohydrates (2–25%), mainly α- and β-glucans. For measures used to prevent cloudiness, see 20.1.8.5. Undesirable microorganisms, e. g., thermophilic lactic acid bacteria, acetic acid bacteria (*Acetobacter, Gluconobacter*) and yeasts, can cause disturbances and defects in various process steps (mashing, fermentation, finished product).

20.2 Wine

20.2.1 Foreword

Wine is a beverage obtained by full or partial alcoholic fermentation of fresh, crushed grapes or grape juice (must). The woody vine grape has thrived in the Mediterranean region since ancient times and Italy, France and Spain are still among the leading wine-producing countries in the world. Other major producers are USA, Argentina, Chile, Germany and South Africa. Table 20.9 provides data on wine production and consumption in some countries. An overview of the individual process steps in wine production is presented in Fig. 20.4.

Table 20.9. Wine production 1999 and 2006 (1000 t), vineyard area (1993) and wine consumption (l/capita)

Continent	Production 1999	2006	Vineyard area (1993)			
World	27,944	27,772	82.81			
Africa	1005	1174	3.47			
America, North, Central	2217	2282	7.93			
America, South	2077	3046				
Asia	1250	1908	13.85			
Europe	20,593	17,850	56.86			
Oceania	802	1512	0.7			
Country	**Production**		**Vineyard area (1993)**	**Consumption**		
	1999	2006		(1971)	(1993)	(1997)
France	5806	5349	9.42	107	64	54
Italy	6265	4712	9.81	111	61	60
Spain	3298	3644	13.7	60	39	38
USA	2045	2232	3.25	5	6	–
Argentina	1255	1540	2.05	85	48	–
Germany	1229	891	1.06	18	23	23
South Africa	878	1013	–	–	–	–
Australia	679	1410	0.63	–	–	–
Portugal	742		3.7	91	55	53
Romania	650		2.51	23	55	–
China		1400				
Chile		977				
$\sum$(%)[a]	82					

[a] World production = 100%.

20.2.2 Grape Cultivars

Among the cultivated species of *Vitis*, the most important is the grapevine *Vitis vinifera*, L. ssp. *vinifera* in its many forms; more than 8000 cultivars are known. The size, shape and color of the grapes vary: there are round, elongated, large or small grape clusters. Grapes are either wine-type grapes, for white or red wine making, or table grapes, which are even grown in greenhouses in some northern countries. The cultivars are different in sugar content and aroma. Table 20.10 provides information about the major grape cultivars of Germany, with some of their characteristics. Table 20.11 shows the share of the major cultivars in vine growing areas. Table 20.12 gives data on the grape cultivars of some other countries. The European *V. vinifera* and the American vines (*V. labrusca*) have been crossed in order to produce pest-resistant forms (hybrids, "direct producers"), giving plants with pest resistance and good quality must production, although the hybrids still leave much to be desired. The wines are considered rather ordinary, with less character and a more obtrusive flavor than the parent plants. Grape cultivars providing top quality white wines are:

- *Riesling* – native to Germany; a hardy cultivar grown in the Pfalz (Rhine Palatinate) and along the Mosel (Moselle), Rhine and Nahe rivers.
- *Traminer* – cultivated extensively in Alsace, Baden and Pfalz, and in Austria.
- *Rulaender* (grey burgundy, Pinot gris) – from Alsace and Burgundy regions in the Kaiserstuhl district, and from Hungary.
- *Kerner* – an early ripening cultivar, which comes close to the balance of Riesling.

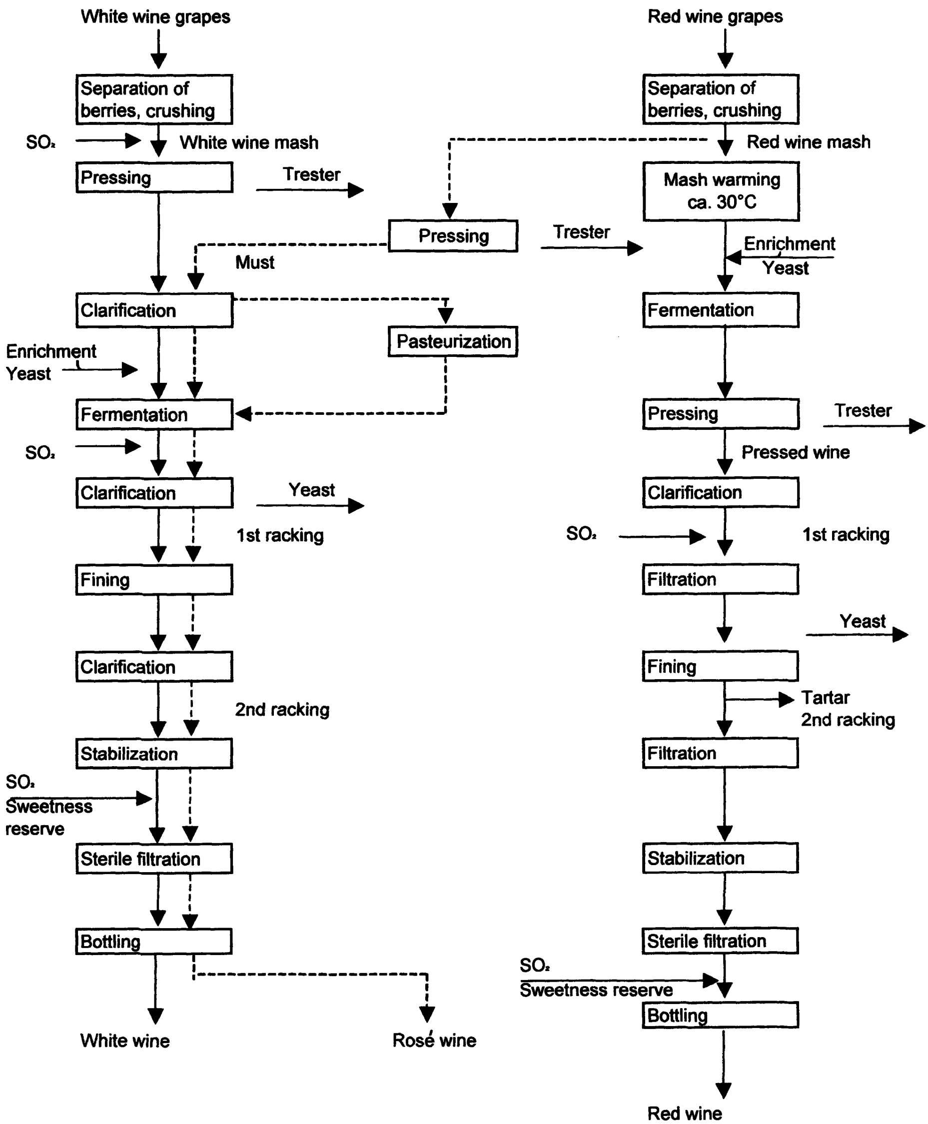


Fig. 20.4. Production of wine

- *Semillon Blanc* – together with Sauvignon and sometimes with Muscatel, provides Sauternes from the Bordeaux region.
- *Sauvignon* – used for Sauternes, and processed into its own types of wine, such as in the Loire region.
- *White Burgundy* (Pinot blanc) – yields the white wines from Burgundy (Chablis, Meursault, Puligny-Montrachet).
- *Chardonnay* – related to white burgundy, cultivated for example in Champagne.
- *Auxerrois* – also related to white burgundy.

Grape cultivars providing good white wines are:

- *Muscatel* and *Muscat-Ottonel* – cultivars with an exceptionally rich bouquet.
- *Furmint* – the grape cultivar of Hungarian Tokay wines.

Table 20.10. Important German grape cultivars

Cultivar	Wine type[a]	Acid[b]	Must weight[c]	Maturation characteristics[d]	Yield[e]	Comments about wine[f]
White wine cultivars						
Auxerrois		2	2	4	3	A vivacious wine with distinquished bouquet
Bacchus	M	2	2	3	3	Flowery with a muscat note fragrance
Burgundy, white	S	3	2	4		A full-bodied wine, pleasantly aromatic and more neutral as Rulaender
Ehrenfelser	R	2	2	5	2	Fruity, mildly acidic, a Riesling-like wine
Elbling, white	S	3	1	6	3	A light wine, devoid of rounded body and bouquet
Faber	M		2	2	3	A refined, refreshing and fruity flavored wine
Gutedel, white	M	1	1	3	3	Light wine, pleasing and captivating, mildly aromatic
Huxelrebe	T	2	2	2	3	A mellow wine with muscat-like bouquet
Kerner	R	2	2	4	2	A refreshing wine with a fine Riesling-like bouquet
Morio-Muscat	B	2	1	3	3	A wine with strong captivating muscat aroma
Mueller-Thurgau	M	2	1	2	3	Mild and refreshing wine with fine muscat flavor
Muscatel-yellow	B	2	2	5	1–2	A superior wine with a strong muscat-like aroma
Muscat-Ottonel	B	2	2		2	A pleasing wine with a strong refined muscat bouquet
Nobling	S	2	2	2	2	A full-bodied wine with a fruity flavor and fine bouquet
Optima	A	2	3	2	2	A refined, captivating wine with a fragrant aroma
Ortega	B	2	3	1	1	A wine with refined peach-like aroma
Perle	T	1	2	3	3	A mellow wine with flowery bouquet
Riesling, white	R	3	1	5	2	A superior refreshing and pleasing wine, with a fruity and flowery flavor
Rulaender (grey burgundy)	T	2	2	3	3	A body-rich wine with burning and passionate perception, and a pleasing bouquet
Scheurebe	T	3	2	4	3	A strong fruity flavored body-rich wine with a bouquet reminiscent of black currants
Siegerrebe	B	1	3	1	1	A wine with highly intensive refined bouquet
Sylvaner, green	S	2	1	4	3	A mellow pleasing wine with a delicately fruity flavor
Traminer, reddish (Clevner)	T	2	2	4	1	A wine with an exceptionally strong persisting bouquet

Table 20.10. (continued)

Cultivar	Wine type[a]	Acid[b]	Must weight[c]	Maturation characteristics[d]	Yield[e]	Comments about wine[f]
Red wine cultivars						
Burgundy, blue, late		2–3	2	4	2–3	Full-bodied, strongly flavored with a rounded bouquet, dark red mellow wine
Heroldrebe						A superior neutral wine with a tannin-like astringency
Limberger, blue		2	2	5	2	Characteristically fruity, a somewhat herbaceous, tarty and finely astringent bluish-red wine
Muellerrebe (black riesling)		2	2	4	2	Reminiscent of late Burgundy, but of lower quality
Portuguese, blue		2	1–2	1	3	A neutral mellow bluish-red wine with a bouquet deficiency
Trollinger, blue		2	2		3	A mellow refreshing light wine with a pungent flavor and light-red in color

[a] Quality German wines are classified as table wines (Tafelwein, Oechsle degrees less than 60), quality wines (with all the required characteristics of the growing region and an Oechsle degree of at least 60) and the special high quality wines (Oechsle degrees at least 73). The latter are denoted according to increasing quality as Kabinett, Spaetlese, Auslese, Beerenauslese and for the top quality as Trockenbeerenauslese. In addition to the rating, the label might carry a designation as Eiswein (ice-wine, see text).
R: Riesling group of wine (superior, fruity wine with distinct acidity)
S: Sylvaner group (neutral wine devoid of a distinct bouquet)
M: Mueller-Thurgau group (light, flowery with discrete bouquet)
T: Traminer group (wine with a fine bouquet)
B: Bouquet group of wine (wine with strong and aromatic bouquet)
A: Auslese group of wines (fullbodied great wines).
[b] 1: Low (approx. 50 g/l), 2: medium (approx. 5–10 g/l), and 3: high acidity (10–15 g/l).
[c] 1: 60–70 Oechsle degrees, 2: 70–85 °C, and 3: >85 Oechsle degrees.
[d] 1: Very early maturing (beginning–middle of September), 2: early (middle–end of September, 3: early-medium (end of September, beginning of October), 4: medium late (beginning–middle of October), 5: late (middle–end of October), and 6: very late maturing cultivar (end of October beginning of November).
[e] 1: Low (60 hl/ha), 2: average (60–80 hl/ha), and 3: high yielding cultivar (≥90 hl/ha).
[f] The wine organoleptic quality description has its own wine dictionary. Terms classify and refer to wine (1) aroma or bouquet, (2) body, (3) sweetness and acids, (4) variety or cultivar, (5) age and (6) wine taste harmony (i. e. to which extent are the constituents of wine agreeably blended or related).

- *Sylvaner* – grown in Pfalz, Rheinhessen and Franken regions of Germany.
- *Mueller-Thurgau* – grown widely in east Switzerland and in Germany; it is a cross between Riesling and Sylvaner.
- *Gutedel* (Chasselas, Fendant, Dorin) – often found in Baden, Alsace, West Switzerland, and France.
- *Scheurebe* – a favored cultivar in Germany, obtained by crossing Sylvaner and Riesling.
- *Morio-Muscat*, a cultivar of exceptional bouquet.
- *Veltliner* – of significance in Austria, as is
- *Zierfandler*.

Grape cultivars providing top quality red wines are:

- *Pinot Noir* – the famous red vine cultivated in the Cote d'Or region of Burgundy, and also in Germany along the river Ahr and in Baden.

Table 20.11. Cultivation of important grape cultivars in Germany

Grape cultivar	Vineyard area in ha, 2005	
White grape cultivars	64,500	(63.2%)
Riesling	20,794	(20.4%)
Müller-Thurgau	14,346	(14.1%)
Silvaner	5383	(6.3%)
Kerner	4253	(4.2%)
Grey burgundy (Rulaender)	4211	(4.1%)
White burgundy	3335	(3.3%)
Bacchus	2205	(2.2%)
Scheurebe	1864	(1.8%)
Gutedel	1129	(1.1%)
Chardonnay	1018	(1.0%)
Other	5962	(9.2%)
Red grape cultivars	37,537	(36.8%)
Blue late burgundy	11,660	(11.4%)
Dornfelder	8259	(8.1%)
Blue Portuguese	4818	(4.7%)
Blue trollinger	2543	(2.5%)
Black riesling	2459	(2.4%)
Regent	2158	(2.1%)
Lemberger	1612	(1.6%)
Other	4028	(10.7%)

- *Cabernet-Sauvignon*,
- *Cabernet-Franc*, and
- *Merlot* – are cultivated together and provide the famous red wines of the Bordeaux region.

Other red grape cultivars are:

- *Gamay* – from the southern part of Burgundy and from Beaujolais and Maconnais.
- *Pinot Meunier* – black Riesling; of importance in Champagne, Wuerttemberg and Baden.
- *Portuguese* – found in Pfalz, Rheinhessen, and Wuerttemberg.
- *Trollinger* (Vernatsch) – cultivated in south Tyrol and in Wuerttemberg.
- *Limberger* – found in Wuerttemberg and Austria.
- *Blue Aramon* – the cultivar which provides the wines from Midi, France.
- *Rossary* – widely cultivated in south Tyrol.

Grape vine cultivation requires an average annual temperature of 10–12 °C. The average monthly temperature from April to October should not fall below 15 °C. The northern limit for cultivating the grape vine is close to 50 °C latitude. The permissible altitude for cultivation is dependent on the climate (plains in Italy, Spain and Portugal; sunny slopes of Germany; up to 13,000 m on Mt. Aetna in Sicily; up to 2700 m in the Himalayas). Soil cultivability and quality and weather are of decisive importance.

20.2.3 Grape Must

20.2.3.1 Growth and Harvest

After blooming and fruit formation, the grape berry continues to grow until the middle or the end of August, but remains green and hard. The acid content is high, while the sugar content is low. As ripening proceeds, the berry color changes to yellow-green or blue-red. The sugar content rises abruptly, while both the acid and water contents drop (Fig. 20.5).

The harvest (picking the berry clusters from the vines) is performed as nearly as possible when the grape is fully ripe, about the middle of September until the end of November, or it may be delayed until the grapes are overripe. In the USA and Europe, machines are being increasingly used for this very laborious harvesting, e. g., grape harvesters. However, they cannot sort the grapes according to the degree of ripeness. Terms which relate to the time of harvest include "vorlese", early harvest, "normallese", normal harvest, and "spaetlese", late harvest. The latter term, when applied to German wines, identifies excellent, top quality wines. Particularly well-developed grapes of the best cultivars from selected locations are picked separately and processed into a wine called "Auslese". When the grapes are left on the vine stock, they become overripe and dry – this provides the raisins or dried berries for "Beerenauslese", "Trockenbeerenauslese", or "Ausbruch" wine (fortified wine). In some districts, such as Tyrol and Trentino, the grapes are spread on straw or on reed mats to obtain shrivelled berries – this provides the so-called straw wines, Grapes that are botrytised (a state of "dry rot" caused by the mold *Botrytis cynerea*, the noble rot) have a high sugar content and a must of superior quality, consequently also producing a superior, fortified wine. Frozen grapes left on the vine stock (harvested at −6 °C to −8 °C and pressed in the frozen state) provide

Table 20.12. Major grape cultivars of selected countries

Country	Grape cultivar	Comments about cultivation area and quality
France	*White wine cultivars*	
	Aligote	Bourgogne, a “vin ordinaire”, modest quality wine
	Chardonnay	Cultivated in Champagne and Bourgogne area (Chablis, Montrachet, Pouilly), a very good quality wine
	Chemin blanc	Cultivated in regions of Tourraine, Anjou and Loire
	Folle blanche	Wine used for brandy production in Cognac and Armagnac
	Grenach blanc	Midi
	Melon blanc (Muscadet)	Mellow refreshing wine with a slight muscat bouquet
	Muscadelle	Cultivated in Bordeaux and Charente regions, 5–10% blended into Sauternes and Graves wines
	Pinot blanc	Cultivated in Alsace, Champagne, Loire and Cote d’Or
	Pinot gris	Alsace wine
	Roussane (Rouselle)	Cultivated in Rhone region, a full-bodied, pleasing fragrancy wine
	Sauvignon	Wine of Bordeaux, Loire and Cher regions, a full-bodied fragrant wine, with Semillon used for production of Sauternes wine
	Semillon blanc	As Sauvignon, used for production of Sauternes wine
	Red wine cultivars	
	Cabernet Franc	Spread in Bordeaux and Loire regions, a superior, strong pleasing wine, with Cabernet Sauvignon and Merlot is an ingredient of Bordeaux wines
	Cabernet Sauvignon	As Cabernet Franc, aroma rich, a superior quality wine
	Carignan	Grown in Rhone, Midi and Provence regions
	Cot (Malbec)	Bordeaux, one of the best grape cultivars
	Cinsaut	Grown in Southern France
	Grenach noir	Grown in Southern France
	Gamay noir	Beaujolais, Maconnais; fruity pleasant, refreshing wine
	Merlot	A Bordeaux wine, full-bodied, rich and mellow; as Cabernet Franc and Cabernet Sauvignon is an ingredient of Bordeaux wines
	Petit Verdot	Grown in Bordeaux region, component of Bordeaux wines
	Pinot noir	Bourgogne, and wine of Cote d’Or
	Syrah	Grown in Southern France
Italy	*White wine cultivars*	
	Malvasia, bianca	An important cultivar across Italy
	Mascato, bianco	Grown mostly in Northern Italy, a wine of Asti region
	Trebbiano	Widely grown across Italy
	Vermentino	Grown along Italian riviera, a very good white wine
	Weissterlaner	Wine of South Tyrol
	Red wine cultivars	
	Aleatico	Widely grown in Italy
	Barbera	One of the most important cultivars
	Freisa	Grown in Piemont and Vercelli regions, one of the best Italian cultivars
	Gross-Vernatsch (Trollinger)	The wine of Bolzano, Trento and Como
	Lagrein	Grown in South Tyrol
	Merlot	
	Nebbiolo	A prefered cultivar of Piemont and Lombardy regions
	Pinot Nero	Grown in Northern Italy with Rome as Southern limit
	San Giovese	Spread from Toscana till Latium; major constituent of Chianti wine

Table 20.12. (continued)

Country	Grape cultivar	Comments about cultivation area and quality
Austria	*White wine cultivars*	
	Mueller-Thurgau	
	Muscat-Ottonel	
	Neuburger	A pronounced cultivar bouquet, pleasantly acidic
	Rheinriesling	
	Rotgipfler	Fruity, aroma rich, full-bodied; together with Zierfandler an ingredient of Gumpoldskirchner wines
	Sylvaner	
	Traminer	
	Veltiliner, green	A pleasant pleasing bouquet refreshing wine
	Veltiner, red	Fruity wine with a fine bouquet
	Veltliner, (early red, Malvasier)	
	Welschriesling	A mellow wine with fine bouquet
	Zierfandler, red	A wine with burning and passionate perception, fragrant aromatic, with a cultivar specific bouquet
	Red wine cultivars	
	Burgundy, blue, late	
	Blaufraenkisch (Limberger)	
	Portuguese, blue	
	Sankt Laurent	A strong wine, dark red colored, with a fine Bordeaux-like bouquet
Switzerland	*White wine cultivars*	
	Gutedel (Chasselas, Fendant, Dorin)	A major Swiss grape cultivar
	Marsanne Blanche (Hermitage)	A mellow wine with a refined bouquet
	Riesling	
	Mueller-Thurgau	Major cultivar of Eastern Switzerland
	Red wine cultivars	
	Burgundy, blue	
	Gamay	Grown in Western Switzerland
	Merlot	The wine of Tessin (Ticino)
Hungary	*White wine cultivars*	
	Furmint, yellow	Used for Tokay wine production
	Red wine cultivars	
	Kadarka	The most important Hungarian red wine cultivar

ice-must which, because of freezing, is enriched in sugar and acid and, as such, is a source of high quality wines (ice-wines).

20.2.3.2 Must Production and Treatment

The grape clusters cut from vine stocks using grape shears are cleaned of rotten and dried berries and then, as fast as possible, separated from the stems. This is done in a roller crusher which consists of two fluted horizontal rolls by which the berries are crushed without breaking the seeds or grinding the stems. The latter are separated out by a stemmer. The crushed grapes are then subjected to pressing to release their juice, the must. The mechanical and partly continuously operated presses are basket-type screw-presses (extruder-like tapered screw), hydraulic or pneumatic presses. The free-running must is collected prior to pressing (first run) and, after mild pressing, the major portion (pressed-must)

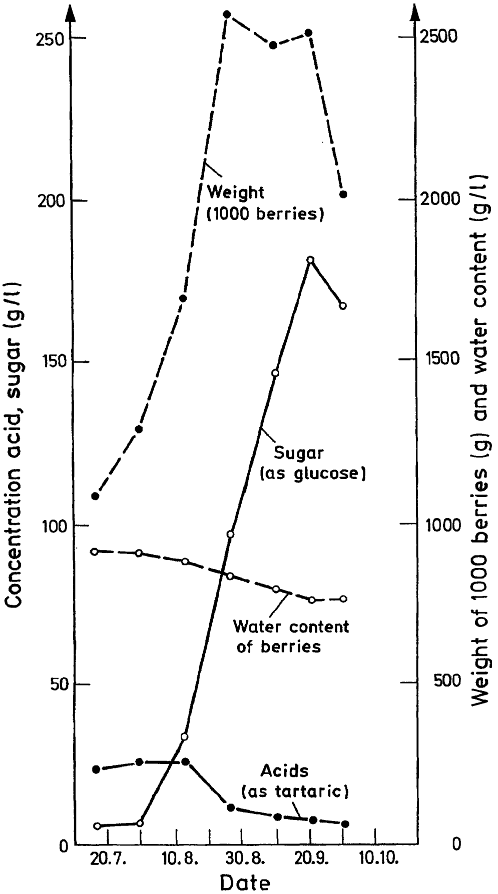


Fig. 20.5. Sylvaner wine grape ripening with measurement of the content of acid (as tartaric), sugar (as glucose), weight of 1000 berries and water content of the berries

is produced. The remaining grape skins and seeds (pomace) are loosened or shaken-up and pressed again. This provides the second or post-extract. In red wine making the crushed berries (the mash) are fermented without prior removal of the pomace, i. e. the must is fermented together with the skin. This is done in order to extract the red pigments localized in the skin, which are released only during fermentation. When blue grapes are processed in the same manner as white ones, or blends of blue and white grapes are combined and then processed, pink wines are obtained. They are designated as rosé wines. In red wine making the extraction of red pigments is sometimes facilitated by raising the temperature to 50 °C prior to fermentation of the mash, or to 30 °C after the main fermentation, followed by a short additional fermentation.

The left over stems, skins and seeds provide the pomace. It is used as feed or fertilizer, or is fermented to provide pomace wine. This is consumed as a homemade drink and is not marketed. Pomace brandy is obtained by distillation of fermented pomace. The average must yield is 75 l/100 kg grapes. Of this, 60% is free juice (must), 30% press-must and 10% must from the second pressing.

The fresh, sweet must can be treated with sulfur dioxide (50 mg SO_2/l) to suppress oxidative discoloration and the growth of undesirable microorganisms. In order to remove undesirable odors or off-tastes, the must is treated with activated charcoal and, when necessary, is clarified by separators or filters. In general, sulfurization before fermentation is dispensed with if the material is faultless and pure culture yeast is used. If required, the must is pasteurized by a short heat treatment (87 °C/2 min).

The addition of sugar to and deacidification of must will be discussed in 20.2.5.4.

20.2.3.3 Must Composition

Table 20.13 provides data on the average composition of grape musts. For the quality assessment of grape must, its relative density at 20 °C is decisive. This is measured with a special aerometer (must balance). The must weight M, expressed in Oechsle degrees, is directly read off.

$$\mathrm{M}\,[^\circ\mathrm{Oe}] = (\mathrm{D} - 1) \times 10^3 \qquad (20.6)$$

Accordingly, a must with D = 1.080, has an M of 80 °Oe. In Germany, the quality levels for

Table 20.13. Average composition of grape must

Constituent	Content (g/l)
Water	780–850
Sugar (as glucose)	120–250
Acids (as tartaric acid)	6–14
N-Compounds	0.5–1
Minerals	2.5–3.5

Table 20.14. Quality levels and natural minimum alcohol content of German wines

Quality level	Minimum alcohol content[a]	
	Zone A[b]	Zone B[b]
Table wine	5.0	6.0
Country wine	5.5	6.5
Quality wine	7.0[c]	8.0
Quality wine with vintage		
- Cabinet	9.5[d]	10.0
- "Spaetlese"	10.0	11.4
- "Auslese"	11.1	13.4
- "Beerenauslese"	15.3	17.5
- Ice wine	15.3	17.5
- "Trockenbeeren"	21.5	21.5

[a] in % vol.
[b] Vine growing areas: Germany without Baden (Zone A), Baden (Zone B).
[c] Partly 6.0.
[d] Partly 9.0.

wine are traditionally defined through the must weight, e. g., (°Oe): Cabinet (70–73), "Spaetlese" (85–90), "Auslese" (92–100), "Beerenauslese" (120). Internationally, the natural alcohol content is a characteristic feature of quality. The corresponding values for German wine are presented in Table 20.14.

Since the density of the must is primarily dependent on the sugar content c, it can be estimated using the following equation:

$$c[\%] = (0.25 \times ^\circ \mathrm{Oe}) - 3 \qquad (20.7)$$

Hence, a must of 100 °Oe contains about 22% sugar.

20.2.3.3.1 Carbohydrates

Ripe grapes contain equal amounts of glucose and fructose, while fructose predominates in overripe or botrytised berries.

In addition L-arabinose (ca. 1 g/l), rhamnose (up to ca. 400 mg/l), galactose (up to ca. 200 mg/l), D-ribose (ca. 100 mg/l), D-xylose (ca. 100 mg/l) and mannose (up to ca. 50 mg/l) are present. Saccharose (ca. 10 g/l) is detectable only if the saccharase is inhibited during pressing. Other oligosaccharides present are: raffinose (up to ca. 200 mg/l), maltose (ca. 20 mg/l), melezitose (ca. 100 mg/l) and stachyose (ca. 150 mg/l). Pectins (0.12–0.15%) and small amounts of pentosans are present.

20.2.3.3.2 Acids

The major acids of must are L-tartaric and L-malic acids. Succinic, citric and some other acids are minor constituents. In a good vintage, tartaric acid is 65–70% of the titratable acidity, but in years when unripe grapes are fermented, its content is only 35–40% and malic acid predominates. The good vintage year of 1911, for example, yielded grapes with 3.1 g/l malic acid and 6.4 g/l tartaric acid; in the inferior vintage year of 1912, on the other hand, malic acid was 10.7 g/l and tartaric acid 6.0 g/l.

20.2.3.3.3 Nitrogen Compounds

Proteins, which include various enzymes, peptides and amino acids, are present in low amounts (cf. 18.1.2.1)

20.2.3.3.4 Lipids

The lipid content of must is about 0.01 g/l.

20.2.3.3.5 Phenolic Compounds

Tannins occur primarily in stems, skin and seeds. In a carefully prepared white must, the tannin content is no more than 0.2 g/l. In contrast, red wines contain high levels of tannin, 1–2.5 g/l or even higher. In white grapes, quercetin, its 3-rhamnoside quercitrin and carotinoids contribute to the color. The main part of the color pigments of European red-wine vines are free (unesterified) anthocyanidin-3-glucosides with malvidin-3-glucoside (40–90% of the anthocyans) as the dominating compound. Apart from the 3-monoglucosides, anthocyanidin-3,5-diglucosides also occur on crossing with American cultivars (hybrids).

β-Glucosidases, which come from yeast, hydrolyze the free anthocyanidin glucosides to

the instable aglycones during fermentation. Of special analytical interest are the anthocyan glucosides which are not attacked by the hydrolases and can easily be separated by RP-HPLC. These glucosides occur as side products and are acylated with acetic acid, p-cumaric acid or caffeic acid. The spectrum of the pigments depends on the grape cultivar, e. g., Cabernet Sauvignon contains about three times as much malvidin-3-acetylglucoside as malvidin-3-cumarylglucoside. However, the acylated anthocyans also decrease with time due to oxidation and condensation reactions. Consequently, their detection in wines that are more than 2–3 years old becomes increasingly difficult.
Cyanidin-3-glucoside is a suitable indicator of cherry wines which have been added to a wine to intensify the red color.

20.2.3.3.6 Minerals

Must contains predominantly potassium, followed by calcium, magnesium, sodium and iron. Important anions are phosphate, sulfate, silicate and chloride.

20.2.3.3.7 Aroma Substances

The must aroma substances will be discussed together with wine aroma substances (cf. 20.2.6.9).

20.2.4 Fermentation

Wine fermentation may occur spontaneously due to the presence of various desirable wine yeasts and wild yeasts found on the surface of grapes. Fermentation can also be conducted after must pasteurization by inoculation of the must with a pure culture of a selected strain of wine yeast. Wild yeasts include *Saccharomyces apiculatus* and *exiguus*, while the pure selected yeasts are derived from *Saccharomyces cerevisiae var. ellipsoides* or *pastorianus*. The pure wine yeast possesses various desirable fermentation properties. High fermenting strains are used to give high alcohol wines (up to 145 g/l) and those which are resistant to tannin and high alcohol levels are used in red wine fermentation. Other types of yeast are "sulfite yeast" with little sensitivity to sulfurous acid (sulfur dioxide solutions), "cold fermentation yeasts", which are active at low temperatures and, finally, special yeasts for sparkling wines, which are able to form a dense, coarse-grained cloudiness that is readily removed from the wine. The desired yeasts (5–10 g of dried yeast per hectoliter of must) are added to must held in fermenters (vats made of oak, or chromiumnickel steel tanks lined with glass, enamel or plastic). The must is then fermented slowly for up to 21 days below 20 °C for white wines or 20–24 °C for red wines. The course of fermentation is influenced by sulfurous acid: 100 mg/l SO_2 delay the start of fermentation by 3 days, 200 mg/l SO_2 by 3 weeks.
As a safeguard against air (discoloration), bacterial spoilage (acetic acid bacteria) and also to retain carbon dioxide, the liquid loss in the fermenter is compensated for by topping up with the same wine. After the end of main (primary) fermentation, which lasts 5–7 days, the sugar has been largely converted to alcohol while the protein, pectin and tannins, along with tartrate and cell debris, settle with the yeast cells at the bottom of the fermenter. This sediment is called bottom mud, dregs or lees.
Partial precipitation of tartaric acid as cream of tartar (mixture of K hydrogentartrate and Ca tartrate) is affected by temperature, alcohol content and pH (Fig. 20.6). The crystallization of tartar can be retarded by the addition of metatartaric acid (up to 100 m/l), obtained by heating tartaric acid above the melting point. The addition is carried out directly before bottling. A tartar stability of 6–9 months is achieved. After this period, the metatartaric acid is slowly converted to tartaric acid. The unfermented residual sugar (residual sweetness) may be retained when necessary, if the secondary fermentation is suppressed by addition of sulfurous acid. Fermentation stops at an ethanol concentration of 12–15% (v/v), depending on the type of yeast.
The young wine, which is drunk with the yeast in some regions of Germany and Austria ("Federweisser" or "Sauser"), is usually withdrawn from the fermentation tank via clarifying separators after the primary fermentation. Red wine mash is fermented at somewhat higher temperatures by using various procedures, often in closed

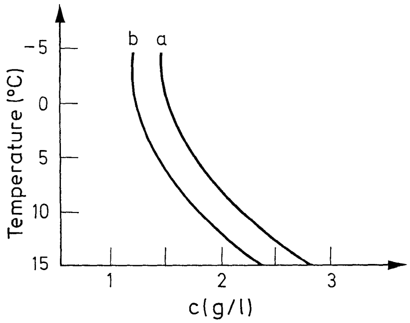


Fig. 20.6. The effect of temperature and ethanol concentration on cream of tartar solubility in wine. (a) 8 vol-%, (b) 12 vol-%. (according to *Vogt*, 1974)

double-walled enamellined tanks. The wine initially drawn off is the better quality free-run wine, followed by the pressed wine, an astringent and dry fraction ("*press-wine*"). The young wine should not stay on the pomace longer than necessary to extract the pigments, otherwise it will become tannin-enriched and hence harsh and astringent. In industrial production the extraction of the red pigments is not done by fermentation of the mash but by heat treatment of the mash (cf. 20.2.3.2).

The fermentation residue or pomace is processed into yeast-pressed wine or yeastbrandy, into wine oil (for brandy essence) and into tartaric acid. The left-over pomace is used as a feed or fertilizer. Pomace wine, obtained by fermenting a sugar solution containing the dispersed pressed-out pomace, is made only into a household drink and is not marketed.

20.2.5 Cellar Operations After Fermentation; Storage

The following cellar operations develop a particular character in the wine and give it stability and durability.

20.2.5.1 Racking, Storing and Aging

Racking of young wine is required to get rid of the sediment. The wine is drawn-off or decanted into large sulfur-treated vats, with or without aeration. The time for racking is determined by the cellar master's experience. The wine racking is repeated as required. Racking should be carried but as early as possible. When necessary, 5–10% of unfermented sterile grape must is blended with the young wine to round-off and sweeten its flavor.

The objective of wine aging/storage is to further build up the aroma and flavor constituents. Aging requires various lengths of time. In general the wine is removed from vats after 3–9 months and poured into bottles in which aging continues. Duration of aging and storability differ and depend on wine quality. The great Burgundy and Bordeaux wines require at least 4–8 years in order to develop while for an average German wine, maximum development is achieved well within 5–7 years. Only great quality wines endure aging lasting 10–12 years or more without quality loss. Changes induced during wine maturation are not yet well understood. Reactions between wine ingredients, such as ethanol, acids and carbonyl compounds, which form the typical aroma components of wine, are covered in 20.2.6.9.

20.2.5.2 Sulfur Treatment

Crushed grapes (mash) or must are treated with sulfur immediately after grape crushing to preserve the constituents that are sensitive to oxidation, prevent enzymatic browning via phenol oxidation and suppress the growth of undesirable microorganisms (acetic acid bacteria, wild yeast, molds). Sulfur treatment of wines prior to the first racking serves the same purpose: wine stabilization (cf. 8.12.6). Futhermore, a very important effect is the suppression of undesirable aroma notes ("air", "oxidation", "ageing", "sherry" notes) by the binding of carbonyl compounds, especially of ethanal, as hydroxysulfonic acids. Sulfur treatment is achieved by the addition of sulfites, an aqueous solution of sulfurous acid or by adding liquid SO_2. The maximum quantities are stipulated by law. Only a part of the added sulfurous acid remains as free acid. A portion is oxidized to sulfate, while another binds to sugars and carbonyl compounds. The rapid oxidation of sulfurous acid can be partially reversed by the addition of L-ascorbic acid. Use of the right amount of SO_2 is important for fermentation, aging and stability and hence for the quality of the wine. Efforts are made to achieve 30–50 mg of free SO_2/l of finished wine.

20.2.5.3 Clarification and Stabilization

Suitable measures should not only eliminate any turbidity present, but also prevent its formation during storage (fining).
Turbidity-causing solids are mostly proteins as well as oxidized and condensed polyphenols. Furthermore, multivalent metal ions can cause discoloration and sediments. Wine clarification is usually achieved by precipitation reactions, filtration or centrifugation. In blue-fining the excess metal ions which are responsible for metal-induced cloudiness (iron, copper and zinc) are precipitated by precisely calculated amounts of potassium ferrocyanide. In this process, soluble Berlin blue is formed first,

$$KFe(CN)_6 + FePO_4 \rightarrow KFe_4 \cdot Fe(CN)_6 + K_3PO_4 \qquad (20.8)$$

which is then converted to insoluble Berlin blue.

$$3KFe_4(CN)_6 + 3FePO_4 \rightarrow Fe_4 \cdot Fe(CN)_6 + K_3PO_4 \qquad (20.9)$$

The blue turbidity formed helps to eliminate the persistent protein turbidity (grayish and black casse). The treated wine is tested for excess cyanoferrate and for free cyanide to be on the safe side. In other fining procedures, edible gelatin, isinglass (beluga dried bladder gelatin) combined with casein, egg albumen, tannin, iron-free bentonite, kaoline, agar-agar and purified or activated charcoals are added to the wine. This results in adsorption or precipitation of the substances causing cloudiness and unpleasant taste, the interaction products all being quick-settling coagulums. Phenolic compounds are removed from wine by polyvinylpyrrolidone (detanninizing) and undesirable sulfur compounds by cupric sulfate.
The clarification by filtering involves pads of asbestos, cellulose, infusorial earth, and filter aids such as Hyflo Super Cel and Filter Cel. The filters are built either as sheet filters or as washable filter presses. Sterile filtration has achieved great importance for the stability of wine and sweet must. Sterilizing filters made of asbestos or membrane sheets retain not only yeast cells, but also the much smaller spores of fungi and even bacteria. Sterilizing filters are also suitable for stopping fermentation and thus retaining a desired level of unfermented sugar (residual sweetness) at a selected stage of fermentation.
Suitable measures to prevent crystalline sediments in the bottle are, e. g., cooling the wine for a few days to 0–4 °C, addition of metatartaric acid (cf. 20.2.4), and reducing the concentrations of potassium, calcium, and tartaric acid by electrodialysis. Excessive concentrations of calcium produced by deacidification measures (cf. 20.2.5.4) can also result in additional crystal sedimentation (calcium tartrate, calcium mucate, and calcium oxalate). The elimination of excess calcium with D-tartaric acid is recommended as a counter-measure.

20.2.5.4 Amelioration

Must and wine amelioration is required when unfavorable weather in some years results in grapes with an excess of acids and a low sugar content. Such grapes would provide a must which could not be processed directly into a drinkable, palatable wine. The ameliorated wine should contain neither more alcohol nor less acid than the wine of the same type and origin from a good vintage year. The usual procedures involved are the addition of sugar, deacidification and wine blending.
The addition of sugar (*enrichment*), for which regulations exist in most countries, can be carried out before or during fermentation. Sucrose (dry sweetening) or grape must concentrates are added. To improve the quality, the *sweetness reserves* of the wine can be raised by the addition of grape must. The fermentation of this must is prevented by cold sterile storage, short-time heating (87 °C) or impregnation with CO_2 (15 g/l, pressure tank). The bouquet (aroma) is not improved. Poor or inferior wine is not improved by amelioration. Deacidification is achieved primarily by adding calcium carbonate, which may give either a precipitate of calcium tartrate or a mixture of calcium tartrate and calcium malate. Un-

sulfured wines which still have an excessively high acid content can be subjected to biological acid degradation (malolactic fermentation). In this process, lactic acid bacteria (e. g., *Leuconostoc oenos*) convert L-malic acid (10 g) to lactic acid (6.7 g):

$$\begin{aligned} &HOOC{-}CHOH{-}CH_2{-}COOH \\ &\rightarrow HOOC{-}CHOH{-}CH_3 + CO_2 \end{aligned} \qquad (20.10)$$

In addition, the residual sugar, aldehydes and pyruvate are degraded so that less SO_2 is required in a subsequent sulfur treatment step. The multiplication of the lactic acid bacteria is promoted by increasing the temperature to 20 °C and stirring up the yeast settlings.

Wine blending is a suitable way of rectifying defects, refreshing old wines, deepening the color of red wines (table wines) and enhancing the bouquet or readjusting the low acid content, thus producing a uniform quality wine for the market.

Tartaric or citric acid can be added to low-acid wines from southern European countries. The addition of gypsum or phosphate treatment to enhance the color of red wines, which is used in the case of certain southern wines (e. g., Malaga, Marsala) is based on the increase in the color yield caused by lowering the pH with $CaSO_4$ or $CaHPO_4$.

20.2.6 Composition

The chemical composition of wine varies over a wide range. It is influenced by environmental factors, such as climate, weather and soil, as well as by cultivar and by storage and handling of the grapes, must and wine.

Within the scope of wine analysis, wine extract, alcohol, sugar, acids, ash, tannins, color pigments, nitrogen compounds and bouquet-forming substances are important. Hence, the value and quality of a wine is assessed through the content of ethanol, extract, sugar, glycerol, acids and bouquet substances. With the large number of quality-determining constituents, the evaluation and classification of wine are possible only by a combination of chemical analysis and sensory testing.

20.2.6.1 Extract

The extract includes all the components of wine mentioned above, except the volatile, distillable ones. Many of the extract components are present in must and are described in that section; others are typical fermentation and degradation products. The extract content of 85% of all German white wines is about 20–30 g/l (average about 22 g/l), while the extract content of red wines is somewhat higher – German “Auslese” wines contain about 60 g/l; other sweet wines, 30–40 g/l.

Since the sugar content can be manipulated, the “sugar-free extract” (extract in g/l minus reducing sugar in g/l plus 1 g/l for arabinose, which is also detected in the reductometric determination, but is not fermentable) is of greater importance for an evaluation of quality.

20.2.6.2 Carbohydrates

Carbohydrates (0.03–0.5%) present in fully fermented wines are small amounts of the hexoses glucose and fructose and of nonfermentable pentoses. Incompletely fermented wines contain higher concentrations of both hexoses, but substantially more of the slower fermenting fructose. The average ratio of glucose to fructose in the residual sugar of wine is 0.58:1, but it varies to a great extent. The pentose sugars which are present in fermented wines consist of 0.05–0.13% arabinose, 0.02–0.04% rhamnose, and xylose in trace amounts.

20.2.6.3 Ethanol

The ethanol content of wine varies over a wide range. It serves as a quality feature (cf. 20.2.3.3). An alcohol level above 144 g/l indicates addition of ethanol.

The extent to which ethanol is derived from added sugar in fermentation can be determined by the NMR spectroscopic measurement of the ratio of the hydrogen isotopes ^1H to ^2H. The method is based on the fact that the plant-specific $^2H/^1H$ ratio (R value, cf. 18.4.3) of the sugar also appears in ethanol: about 2.24 (corn sugar), about 2.70 (beet sugar), about 2.45 (wine). The detection limit is 6–8 °C Oe for a wine of unknown origin and it falls to 2–3° Oe (corresponding to ca. 0.5% v/v of ethanol) when the age, origin and grape cultivar are known.

20.2.6.4 Other Alcohols

Methanol occurs in wines at a very low level (38–200 mg/l), but much more is present in the fermentation of pomace as a product of pectin hydrolysis. Brandy distilled from pomace often contains 1–2% methanol. Higher alcohols in wine are propyl, butyl and amyl alcohols which, together, constitute 99% of the wine fusel oil. Hexyl, heptyl and nonyl alcohol and other alcohols including 2-phenylethanol (up to 150 mg/l) are present in small amounts. The average butylene glycol (2,3-butanediol) content is 0.4–0.7 g/l and is derived from diacetyl by yeast fermentation. Glycerol, 6–10 g/l, originates from sugars and gives wine its body and round taste. Added glycerol can be revealed by the determination of the glycerol factor (GF):

$$GF = \frac{\text{Glycerol}\,(g/l) \times 100}{\text{Alcohol}\,(g/l)} \tag{20.11}$$

The natural variation range of GF in wines, as long as they have not been produced from noble rot material, lies between 8 and 10. Values above 12 indicate an additive. Low amounts of additive cannot be safely detected using the GF. More suitable is then the use of GC-MS to test the wine for the by-products of the technical synthesis of glycerol, e. g. 3-methoxypropanediol or cyclic diglycerols. Sorbitol is found in very low amounts. D-Mannitol is not present in healthy wines, but is present in spoiled, bacteria-infected wines at levels up to 35 g/l.

20.2.6.5 Acids

The pH of grape wine is between 2.8 and 3.8. Titratable acidity in German wines is between 4 and 9 g/l (expressed as tartaric acid). Acid degradation and cream of tartar precipitation decrease the acid content of ripe wines. Red wines generally contain less acids than white wines. The wines from Mediterranean countries and often high-grade wines ("Beerenauslese", "Trockenbeerenauslese") are low in acid content. Wine acids from grapes are tartaric, malic and citric acids and acids from fermentation and acid degradation are succinic, carbonic (carbon dioxide) and lactic acids and low amounts of some volatile acids. The presence of acetic and propionic acids as well as an anomalous amount of lactic acid is an indication of diseased wine.

Botrytis cinerea can form gluconic acid in concentrations of up to 2 g/l of must. Therefore, this acid is found in the corresponding wines.

20.2.6.6 Phenolic Compounds

Red wines contain phenols in considerably higher concentrations than white wines (Table 20.15). Exceptions are gentisic and ferulic acid, but relatively high concentrations of the last mentioned compound are characteristic of Riesling.

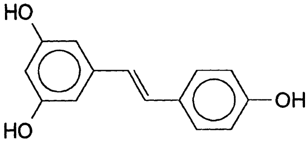
In the maturation of red wine, tanning agents polymerize (proanthocyanidins, cf. 18.1.2.5.2) in two ways and become insoluble, reducing the astringent taste. Acidcatalyzed polymerization proceeds via the carbocation shown in Formula 18.21. In addition, proanthocyanidins are cross-linked by acetaldehyde, which is formed

Table 20.15. Phenols in white and red wine[a]

Compound	White wine	Red wine
Gentisic acid	0.15–1.07	0.44–0.046
Vanillic acid	0.09–0.38	2.3–3.7
Ferulic acid	0.05–4.40	0.05–2.9
p-Coumaric acid	1.57–3.20	2.6–4.5
Caffeic acid	1.50–5.20	3.15–13
Gallic acid	0.50–2.80	13–30
cis-Reservatol	<0.10	0.27–0.88
trans-Reservatrol[b]	<0.25	0.71–2.5
cis-Polydatin[c]		0.02–0.68
trans-Polydatin[c]		0.02–0.98
(+)-Catechin	3.8–4.20	60–213
(−)-Epicatechin	1.7–3.8	25–82
Quercetin		0.5–2.6

[a] Concentration in mg/l.
[b] trans-3,4′,5-trihydroxystilbene (cf. Formula 20.12).
[c] cis-or trans-3,4′,5-trihydroxystilbene-3-β-D-glucoside.

by the slight oxidation of ethanol that occurs on storage of red wine.



(20.12)

20.2.6.7 Nitrogen Compounds

The nitrogen compounds in must precipitate to a smaller extent by binding to tannins during grape crushing and mashing, while most (70–80%) of them are metabolized by the growing yeast during fermentation. Free amino acids, especially proline (about 200–800 mg/l) are the major nitogen compounds which remain in wine. Tryptophan, which is present in must in concentrations of 1–30 mg/l, and acetaldehyde, which is provided by yeast, are precursors of 1-methyl-1,2,3,4-tetrahydro-β-carbolin-3-carboxylic acid (MTCA). In fact, 0–18 mg/l of MTCA have been detected in wine. Its formation (cf. Formula 20.13) is inhibited by SO_2, which traps the precursors. On distillation, MTCA apparently remains in the residue because only traces, if at all, are present in brandy and whiskey. However, MTCA is not restricted to fermented products like wine, beer and soy sauce as the precursors are widely found, e. g., in milk, cheese and smoked foods.

20.2.6.8 Minerals

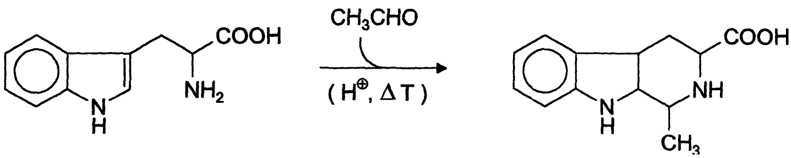
The mineral content of wine is lower than that of the must since a part of the minerals is primarily removed by precipitation as salts of tartaric acid. The ash content of wines is about 1.8–2.5 g/l, while that of must is 3–5 g/l. The average composition of ash in %, is: K_2O, 40; MgO, 6; CaO, 4; Na_2O, 2; Al_2O_3, 1; CO_2; 18; P_2O, 16; SO_3, 10; Cl, 2; SiO_2, 1.

The iron (as Fe_2O_3) content of wine is 5.7–13.4 mg/l, but it can rise to much higher levels (20–30 mg/l) through improper processing of grapes.

20.2.6.9 Aroma Substances

Most of the volatiles in wine, more than 800 compounds, with a total concentration of 0.8–1.2 g/l, has been identified. For the wines Gewürztraminer and Scheurebe, it has been found that the compounds listed in Tables 20.16 are so odor active that they can produce the aroma in each case. This could be confirmed for Gewürztraminer in a model experiment. A synthetic mixture of odor and taste compounds in the concentrations given in Table 20.16 and 20.17 reproduced the aroma and the taste of Gewürztraminer.

The two cis-rose oxides and 4-mercapto-4-methylpentan-2-one, which has an exceptionally low odor threshold (cf. 5.3.2.5), have been identified as the cultivar-specific odorants in Gewürztraminer and Scheurebe. In addition, ethyloctanoate, ethylhexanoate, 3-methylbutylacetate, ethylisobutanoate, linalool, (E)-β-damascenone and wine lactone (cf. structure in 5.2.5) exhibit high but different aroma values in the two types of wine. Other typical odorants are listed in Table 20.18. Some red wines, e. g. from Shiraz grapes contain the bicyclic terpene (−)-rotundone, the key aroma compound of pepper (cf. 22.1.1.2.1). Its concentration is high (up to 145 ng/l) in samples showing an intense “peppery” aroma note. Ethanol is essential for the aroma of wine. Since the odor thresholds of many volatiles increase in the presence of ethanol, e. g., those of ethyl-2- and -3-methylbutanoate increase by a factor of 100 (Table 20.19), it influences the bouquet of wine. Correspondingly, the intensity of the fruity note increased in an aroma model for Gewürztraminer when the alcohol content was lowered. The odorants partly originate from the grape (primary aroma) and are partly formed on



(20.13)

Table 20.16. Odorants in Gewürztraminer and Scheurebe

Aroma substance	Concentration (mg/l)	
	Gewürztraminer[a]	Scheurebe[b]
Acetaldehyde	1.86	1.97
3-Methylbutylacetate	2.9	1.45
Ethylhexanoate	0.49	0.28
(2S,4R)-Rosenoxide	0.015	0.003
(2R,4S)-Rosenoxide	0.006	
Ethyloctanoate	0.63	0.27
(E)-β-Damascenone	0.00083	0.00098
Geraniol	0.221	0.038
3-Hydroxy-4,5-dimethyl-2(5H)-furanone (HD2F)	0.0054	0.0033
(3S,3aS,7aR)-Tetrahydro-3,6-dimethyl-2(3)-benzofuranone (wine lactone)	0.0001	0.0001
Ethanol	90,000	90,000
Ethylisobutanoate	0.150	0.480
Ethylbutanoate	0.210	0.184
Linalool	0.175	0.307
Ethylacetate	63.5	22.5
1,1-Diethoxyethane	0.375	n.a.
Diacetyl	0.150	0.180
Ethyl-2-methylbutanoate	0.0044	0.0045
Ethyl-3-methylbutanoate	0.0036	0.0027
2-Methylpropanol	52	108
3-Methylbutanol	128	109
Dimethyltrisulfide	0.00025	0.00009
4-Mercapto-4-methyl-pentan-2-one	<0.00001	0.0004
(3-Methylthio)-1-propanol (Methionol)	1.415	1.040
Hexanoic acid	3.23	2.47
2-Phenylethanol	18	21.6
trans-Ethylcinnamate	0.002	0.023
Eugenol	0.0054	0.0005
(Z)-6-Dodecenoic acid-γ-lactone	0.00027	0.00014
Vanillin	0.045	n.a.
Sulfur dioxide	7.3	30

[a] Gewürztraminer, dry, year 1992.
[b] Scheurebe, Cabinet semi-dry, year 1993.
n.a., not analyzed.

Table 20.17. Taste substances in Gewürztraminer and Scheurebe

Compound/Ion	Concentration (mg/l)	
	Gewürztraminer[a]	Scheurebe[b]
Group I: sour, astringent		
Acetic acid	280	255
Tartaric acid	1575	1260
Citric acid	875	594
Malic acid	377	4790
Lactic acid	1680	980
Succinic acid	590	480
Oxalic acid	100	<50
γ-Aminobutyric acid	21	23
Group II: sweet		
D-Glucose	870	13,040
D-Fructose	575	13,500
Proline	760	320
Group III: salty		
Chloride	20	135
Phosphate	270	245
Sulfite	35	120
Potassium	1240	1100
Calcium	32	231
Magnesium	55	81
Glutamic acid	54	18
Group IV: bitter		
Lysine	27	16

[a,b] cf. Table 20.16

Table 20.18. Cultivar-specific aroma substances of wine

Compound	Cultivar
Ethyl cinnamate	Muscatel wines
β-Ionone	
Linalool	
Geraniol	
Nerol	
β-Damascenone	Riesling, Chardonnay
cis-Rose oxide	Gewürztraminer
2-*sec*-Butyl-3-methoxypyrazine	Sauvignon
2-Isobutyl-3-methoxypyrazine	
4-Mercapto-4-methylpentan-2-one	Scheurebe

fermentation (secondary aroma). A large part of the grapes used is neutral in aroma (e. g., white Burgundy, Silvaner, Chardonnay). However, there are also aroma-rich grapes, e. g., Muscatel, Gewürztraminer, Morio-Muskat and Sauvignon.

Table 20.19. Odor thresholds of the odorants of wine in water (I) and in 10% (w/w) ethanol (II)

Compound	Threshold value (μg/l)	
	I	II
Acetaldehyde	10	500
Ethylacetate	7500	7500
Ethyl-2-methylbutanoate	0.06	1
Ethyl-3-methylbutanoate	0.03	3
3-Methylbutylacetate	3	30
Ethylhexanoate	0.5	5
Ethyloctanoate	0.1	2
Acetic acid	22,000	200,000
cis-Rose oxide	0.1	0.2
4-Mercapto-4-methylpentan-2-one	0.0001	0.0006
Wine lactone	0.008	0.01
(E)-β-Damascenone	0.001	0.05
Linalool	1.5	15
Geraniol	7.5	30

Table 20.20. Esters in wine with sensory relevance

Compound	White wine (mg/l)	Red wine (mg/l)
Ethyl acetate	0.15–150	9–257
Ethyl propanoate	0–0.9	0–20
Ethyl pentanoate	1.3	5–10
Ethyl hexanoate	0.03–1.3	0–3.4
Ethyl octanoate	0.05–2.3	0.2–3.8
Ethyl decanoate	0–2.1	0–0.3
Hexylacetate	0–3.6	0–4.8
2-Phenylethyl acetate	0–18.5	0.02–8
3-Methylbutyl acetate	0.03–0.5	0–23
Ethyl lactate	0.17–378	12–382

The concentration ranges of esters found in a larger number of white and red wines are presented in Table 20.20. The high variability of the ester fraction has an effect on the intensity of fruity notes in the aroma profile.

The content and composition of the ester fraction is greatly influenced by fermentation conditions. The higher the temperature and the lower the pH during fermentation, the lower the ester concentration (Table 20.21).

Terpenes mainly contribute to the aroma of Muscatel wines and, to a smaller extent, other wines. In the must, however, these terpenes are still largely present as odorless glycosides, di- and polyols (cf. 5.3.2.4). Using Gewürztraminer as an example, Table 20.22 shows that terpenes as well as esters and alcohols increase rapidly on fermentation. In addition, the monoterpenes also increase on aging of the wine in stainless steel tanks. On the one hand, terpene glycosides are hydrolyzed by must glycosidases, and on the other, the nonenzymatic hydrolysis of these precursors are promoted by heat treatment of the must and the low pH.

In addition a broad pattern of aroma-active monoterpenes (e. g., nerol oxide, hotrienol) is formed by cyclization and dehydration reactions of di- and polyhydroxylated monoterpenes (examples, cf. 5.3.2.4), e. g., the cis-rose oxides can be formed by the cyclization of 3,7-dimethylocta-6-en-1,5-diol.

Wine extracts the quercus lactone (structure cf. 5.3.2.3) on storage in oak barrels. The difference in aroma compared with maturation in steel tanks also results from oxidative processes, which cause an increase in aldehydes in oak bar-

Table 20.21. Effect of fermentation conditions on formation of higher alcohols and esters

Temperature (°C)	pH	Higher alcohols total (mg/l)	Fatty acid esters total (mg/l)
20	3.4	201	10.8
20	2.9	180	9.9
30	3.4	188	7.8
30	2.9	148	5.4

Table 20.22. Concentration changes in odorants in the production of Gewürztraminer[a]

Odorants	Concentration (mg/1)		
	I	II	III
Ethyl-2-methyl-butanoate	<0.0001	0.0023	0.0026
Ethyl hexanoate	0.0035	0.465	0.345
cis-Rose oxide	0.0011	0.0053	0.011
Linalool	0.0026	0.029	0.043
Geraniol	0.0087	0.035	0.045
3-Methylbutanol	0.440	64.0	61.0
(E)-β-Damascenone	0.00003	0.0063	0.0017

[a] I, pressed juice; II, after malolactic fermentation (cf. 20.2.5.4); III, after aging in a steel tank.

Table 20.23. Aging of Gewürztraminer in a steel stank (I) and in an oak barrel (II) – changes in the concentrations of important aroma substances[a]

Compounds	Concentration (mg/l)	
	I	II
Acetaldehyde	1.86	4.32
3-Methylbutanal	<0.001	0.051
3-Methylbutylacetate	2.9	0.450
Methional	<0.0005	0.0099
β-Damascenone	0.00084	0.0028
Guaiacol	0.0036	0.056
Vanillin	0.045	0.335
Quercus lactone	n.a.	0.134

[a] Storage 14 months; n.a. not analyzed.

rels, as shown in Table 20.23 for Gewürztraminer. β-Damascenone and vanillin also increase.

The aroma substances formed on storage of bottles include 1,1,6-trimethyl-1,2-dihydro-naphthalene (TDN). After longer storage, it exceeds the aroma threshold (ca. 20 μg/l water) and contributes a kerosine-like aroma note to the aroma profile in particular of old Riesling wines. In Riesling wines from southern European countries, this aroma substance can increase to such an extent on aging that they acquire a very unpleasant taste after even a short storage time (kerosine/petrol note, Table 20.24). As a result of the intensive sunshine and high temperatures, the precursor carotinoids are formed in relative high concentrations and are then degraded to TDN in this cultivar.

The monoterpene pattern can be used to differentiate cultivars. For example, a clear distinction can be made between wines from the grape cultivar "White Riesling" and wines from other grape cultivars which are also sold as "Riesling". As shown in Fig. 20.7, the monoterpene concentrations (especially of linalool, hotrienol, α-terpineol, and 3,7-dimethylocta-1,5-*trans*-dien-3,7-diol) in "White Riesling" are considerably higher than in the other "Riesling" wines.

Methoxypyrazines (Table 20.18) in concentrations of 10–20 ng/l are characteristic of Sauvignon wines. They are exceptionally odor active (cf. 5.3.1.7) and produce a paprika note in the odor profile.

20.2.7 Spoilage

As with beer, defects in wine are reflected in appearance, odor and taste and, if not controlled, result in complete spoilage. A full explanation of all defects is beyond the scope of this book; hence only a general outline will be provided.

Of importance is browning due to oxidative reactions of phenolic compounds which, in red wine, may result in complete flocculation of the color pigments. This oxidative darkening process is as much chemical as enzymatic (polyphenoloxidases). Sulfurous acid is the preferred agent to prevent browning. Once the wine is affected by browning, it may be lightened by treatment with activated charcoal. The charcoal treatment can also remove other defects, such as the taste of mash or rotten grapes. Iron-induced turbidity (white or greyish casse) appears as a white, greyish-white or greyish haze or cloudiness and consists mostly of ferric phosphate ($FePO_4$). It is formed by the oxidation of ferrous compounds in wine. Proteins, tannins or pectins can participate in the build-up of such cloudiness (black casse). The so-called copper casse or turbidity is based on the formation of Cu_2S and other compounds with monovalent copper. It originates from the Cu^{2+} ions present in wine and their reduction in the presence of excess SO_2. Other taste defects compiled in Table 20.24 can be divided into:

- those produced by the cultivar (e. g., strawberry note, fox note)
- those produced in fermentation by other microbial processes (e. g., "boeckser", mousy note, medicine note)
- those formed during wine storage and aging in wood barrels or by contamination (e. g., cork note, musty note, kerosine note, untypical aging note).

A medicine note is detected when the phenols listed in Table 20.24 are formed in excessively high concentrations on the degradation of ferulic and p-coumaric acid. This aroma defect has been observed especially in the cultivar "Kerner" when the grapes were exposed to intensive sunlight.

The "untypical aging note" (Table 20.24) is produced by stress during ripening of the berries. Dryness, low nitrogen uptake with a high yield can result in the formation of the unwanted odorant 2-aminoacetophenone during fermentation.

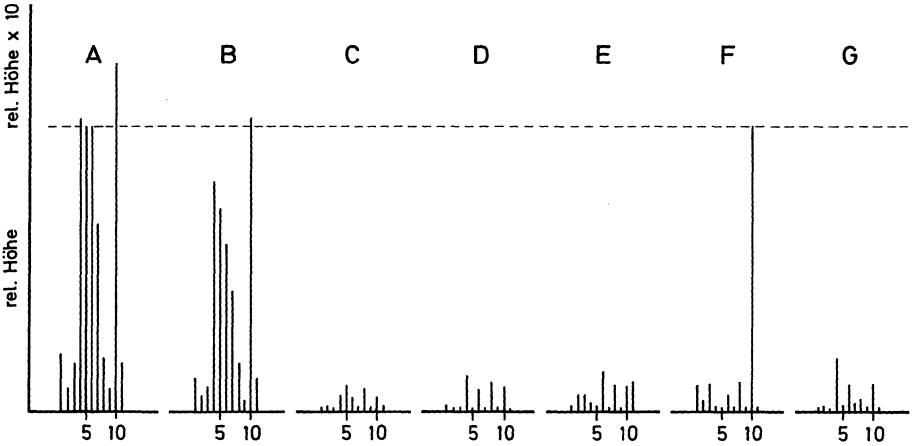


Fig. 20.7. Monoterpenes in wines from the grape cultivar "White Riesling" and in wines from other grape cultivars which are also sold as "Riesling" (according to *Rapp* et al., 1985). A: White Riesling (Rheinpfalz), B: White Riesling (France), C: Welschriesling (Austria), D: Welschriesling (Italy), E: Laski Rizling (Yugoslavia), F: Hunter Valley Riesling (Australia), G: Emerald Riesling (USA). Monoterpenes: **1** *trans*-furan linalool oxide, **2** *cis*-furan linalool oxide, **3** neroloxide, **4** linalool, **5** hotrienol, **6** α-terpineol, **7** not identified, **8** *trans*-pyran linalool oxide, **9** *cis*-pyran linalool oxide, **10** 3,7-dimethylocta-1,5-*trans*-dien-3,7-diol, **11** 3,7-dimethyl-1-octen-3,7-diol

Table 20.24. Aroma defects in wine

Aroma defect	Key aroma substances	Cause
Mousy note	2-Ethyl-3,4,5,6-tetrahydropyridine, 2-acetyl-3,4,5,6-tetrahydropyridine, 2-acetyl-1,2,5,6-tetrahydropyridine	Lactic acid bacteria in combination with yeasts of the genus *Brettanomyces*
Strawberry note	4-Hydroxy-2,5-dimethyl-3(2H)-furanone (HD3F): >1500 µg/l	Characteristic of the cultivar
Medicine note	4-Vinylphenol + 4-vinylguaiacol: >800 µg/l	Climate, microbiological processes
Medicinal, woody, smoky, horse sweat	4-Ethylphenol + 4-ethylguaiacol: >400 µg/l	Climate, microbiological processes
Kerosine/petrol note	1,1,6-Trimethyl-1,2-dihydro-naphthaline (TDN): >300 µg/l	Southern climate, excessively high carotinoid concentration in Riesling
"Boeckser"	Hydrogen sulfide	Fermentation
Cork taste/musty note	2,4,6-Trichloroanisole, geosmin, 2-methylisoborneol, 1-octen-3-one, 4,5-dichloroguaiacol, chlorovanillin	Contamination during wine storage
Untypical aging note (naphthaline note, fox note, hybrid note)	2-Aminoacetophenone: >0.5 µg/l	Stress reaction of the vine

The so-called "boeckser" is caused by the smell of hydrogen sulfide. The very unpleasant, rotten and yeasty "boeckser" (= mercaptan) odor is most objectionable and lingers for a long time. It is due to ethylthiol, which can be removed by activated charcoal. The volatile sulfur compounds originate from sulfite which is reduced to H_2S by yeast, later reacting with ethanol to form ethylthiol. Additional wine taste defects are the odd and disagreeable cork tastes which is due to the formation of the odorants listed in Table 20.24 and 2,4,6-trichloroanisole. Above concentrations of 15–20 ng/l, it contributes to the cork flavor of wine. Geosmin, 1-octen-3-one, 4,5-di-chloroguaiacol and chlorovanillin may cause musty off-flavors.

Additional yeast spoilage is induced by species of the genera *Candida* (*Mycoderma*), *Pischia* and *Hansenula* (*Willia*). Other microorganisms are involved in the formation of viscous, moldy and ropy wine flavor defects. Bacterial spoilage may involve acetic acid and lactic acid bacteria. In this case vinegar or lactic acid souring is detectable. It has usually been associated with mannitol fermentation which may result in considerable amounts of mannitol.

Sorbic acid can be converted to 2-ethoxy-3,5-hexadiene by heterofermentative lactic acid bacteria. In concentrations of 0.1 m/l, this compound produces a "geranium" note.

A "mousy" taint is occasionally detected in fruit and berry wines and, less often, in grape wines. It is thought that the tetrahydropyridines given in Table 20.24, which have been also identified as important flavor compounds of toasted bread (cf. 15.4.3.3.2), contribute to the "mousy" taint. These compounds might be formed by microorganisms in wine.

Likewise, red wines, particularly color-deficient wines, show a microbiologically-induced change reflected in a substantial increase in volatile acids and the degradation of tartaric acid and glycerol. The bitter taste of red wines is caused by bacteria, mold and yeast. The bitter taste is usually a result of glycerol conversion to divinyl glycol. Cloudiness of red wines appears to be due either to bacterial or yeast spoilage or to physical reasons alone, such as the precipitation of cream of tartar. The latter occurs frequently and mostly in bottled wines. Cream of tartar precipitates as a result of oversaturation of the salt solution, as appears to be the case with protein-tannin interaction products. With oversaturation, they sediment as a fine greyish-yellow haze. Cloudiness caused by mucic acid salts also occurs.

20.2.8 Liqueur Wines

In contrast to wine, liqueur wines (older term "dessert wines") are not exclusively made from fresh or mashed grapes or grape must. The alcohol content is at least 15% by volume and at most 22% by volume. The production proceeds according to two different processes, which are partly also combined:

- *Concentrated liqueur wines* are produced by the fermentation of concentrated grape juices which are very rich in sugar (e. g., from dry grapes) or by the addition of concentrated grape juice to wine.
- *Mixed liqueur wines* (e. g., Sherry/Malaga, Port wine/Madeira, Samos, Marsala) are produced from partly fermented must with the addition of alcohol or mixed thickened must. The addition of alcohol stops the fermentation.

The extract, alcohol and sugar contents of dessert wines are given in Table 20.25.

At least 2–5 years are needed to make dessert wines. In the production of sherry the wine is stored in partially filled butts, i. e. in the presence of excess air. Flor yeasts develop on the wine surface in the form of a continuous film or wine cover (sherry yeast). The typical sherry flavor is derived from the aerobic conditions of maturation. During this time the concentrations of the following compounds increase at the expense of alcohol and volatile acids: ethanal, acetals, esters, sotolon (cf. 5.3.1.3) and 2,3-butylene glycol. In port wine production the wine is drawn off to casks before the end of fermentation and is fortified with wine distillates. The fortifying procedure is repeated several times ("multiple addition") until the desired alcohol content is reached. Sotolon is the key aroma substance of Port wine. Its odor threshold in this wine is 19 μg/l. Its concentration increases linearly during storage. Port stored for one year and for 60 years contained 5 and 958 μg/l sotolon respectively.

20.2.9 Sparkling Wine

Experience has shown that carbon dioxide imparts a refreshing, prickling and lively character to wine (as already mentioned for young wines). Hence, the production of a refined form of wine, enriched with carbon dioxide (sparkling wine) was developed and used in the early 18th Century, originally in the Champagne region of France ("Champagne" wine).

Table 20.25. Composition of liqueur wines

	Extract (g/l)	Alcohol (g/l)	Sugar (g/l)	Glycerol (g/l)	Tritratable acid (g/l)[a]
Malaga	159.2	143.4	135.8	5.0	5.3
Portwine	67.6	166.5	47.0	2.8	4.5
Madeira	129.0	149.5	107.5		
Marsala	81.0	150.4	52.2	6.2	5.9
Samos	119.0	152.0	82.0	7.5	6.8
Tokay essence	257.5	84.4	225.3	4.1	6.5
Rheingauer top quality	140.6	107.7	99.4	14.3	10.2
Pfaelzer (Palatinate) top quality	171.6	86.7	121.3	10.5	11.6
Sauternes top quality	127.8	101.2	82.7		0.3

[a] Expressed as tartaric acid.

20.2.9.1 Bottle Fermentation ("*Méthode Champenoise*")

In the production of sparkling wine, young wines from suitable regions are used since fermentation of their grape juice in casks provides the special, fresh, fruity bouquet ("cuvé") desired. Blending of wines ("coupage") from different localities, often with older wines, is aimed at obtaining a uniform end-product. In this way clarified wine is then converted into an effervescent beverage by subjecting it to a second fermentation. Sugar is added (about 20–25 g/l) to wine, together with a pure yeast culture, for the purpose of attaining the desired final alcohol content (85–108 g/l) and carbon dioxide pressure (4.5 bar at 20 °C). Special yeasts are selected which, in addition to being good fermenters and insensitive to carbonic acid, sediment as a firm, grainy precipitate ("depot") after fermentation is complete.

The wine is bottled ("tirage") in such a way as to leave a small headspace of air and is then corked with a natural or plastic cork or, very often, with "crown" caps. The cork is finally and firmly secured with an iron clamp ("agrafe"). The bottles are stacked in cellars at normal temperatures (9–12 °C). The fermentation lasts several months while the build-up of carbonation may go on longer, perhaps for up to 3–5 years. During this time, the carbon dioxide pressure within the bottle rises considerably. The sparkling wines are classified in France depending on the pressure: "grand mousseux", high pressure (4.5–5 bar); "mousseux", intermediate pressure (4–4.5 bar) and "cremant", low pressure (below 4 bar).

At this stage the sparkling wine is ready for yeast removal (disgorging). The bottles are restacked upside-down. Then the contents are repeatedly shaken until the yeast is loosened and settles on the cork. After 6–8 weeks the bottles are placed upright and the cork is removed using disgorging pliers. Simultaneously, the yeast is pushed out by the pressure from within the bottle. In order to simplify this production step, which is considered the most difficult step, the neck of the bottle is frozen to about −20 °C and the yeast is forced out as an "ice" plug. Because of this time-consuming, costly procedure, the loss of wine, and other problems inherent in clearing the bottle of its yeast deposit, a "transfer system" has been introduced. The raw wine which has fermented in the bottle is emptied into a tank. The measured wine is filtered from the tank under pressure into a shipping/export bottle. The sparkling, yeast-free wine ("vin brut", dry wine) is then, depending on the market demand, supplemented with "liqueur" (dosage), quite commonly a plain solution of candy in wine. The bottle, with a headspace volume of 15 ml, is then corked and the cork is wired down. For further build-up of CO_2, the finished sparkling wine needs to be stored for an additional 3–6 months.

20.2.9.2 Tank Fermentation Process ("*Produit en Cuve Close*")

With the aim of simplifying the costly and time-consuming classical process, much of the sparkling wine production is now based on fermentation of wine in pressurized steel tanks instead of in bottles. The carbon dioxide-saturated wine is clarified and filtered and then chilled thoroughly and bottled. Fermentation is carried out at a pressure of about 7 bar over a 3 to 4 week period.

20.2.9.3 Carbonation Process

The carbonation of wine ("vin mousseux gacéifié") involves artificial saturation of wine with carbon dioxide, instead of the natural CO_2 developed during fermentation. Thus, the process is identical to the production of carbonated mineral water. The second fermentation, sugar addition and disgorging are omitted. However, sweetening with liqueur, corking and cork wiring are all retained. Perl wine is also a wine with artificially added carbon dioxide, which has a pressure limited to 2.5 bar, in comparison with "sekt".

20.2.9.4 Various Types of Sparkling Wines

Champagne is obtained by the classical bottle fermentation of wine from the French grape which grows in the region of Champagne. Sparkling wines produced in this region are the only ones that may be sold under the name of "Champagne". German sparkling wines are called "Schaumwein" and are commonly sold as "Sekt"; such Italian wines are "Spumante"; while in Spain and Portugal they are "Espumante".
According to the residual sugar content (g/l), sekt is classified as extra brut (0–6), brut (0–15), extra dry (12–20), dry (17–35), semi-dry (35–50) or mild (>50). Sparkling wine for diabetics is sweetened with sorbitol. Sparkling wines are also made from fruit and berry wines (apple, pear, white and red currant, bilberry). The process is that described above for carbonation.

20.2.10 Wine-Like Beverages

Compositions of some typical wine-like products are given in Table 20.26.

Table 20.26. Composition of some wine-like beverages[a]

Beverage	Alcohol	Extract	Acids[b]	Sugar	Minerals
Apple cider	58.4	23.4	3.8^{+}	1.7	2.8
Cidre	51.0	29.7	2.8^{+}	10.4	2.6
Pear wine	49.3	53.7	6.5^{+}	9.0	4.1
Red currant cider	62.1	39.8	18.6*	1.8	4.0
Gooseberry cider	96.3	78.6	7.5*	55.8	1.8
Sour cherry cider	101.4	62.7	11.7*	3.8	3.61
Malt wine	70.6	24.5	4.6^{+}	4.9	1.36
Malton sherry	123.0	115.2	8.1^{+}	55.9	2.3
Mead	51.4	242.4	3.9^{+}	208.0	1.34
Sake	121.2	28.6	5.7^{+}	5.5	1.0

[a] Results are given in g/l.
[b] Acids are calculated as malic ($^{+}$) or citric acid (*).

20.2.10.1 Fruit Wines

For the production of fruit wine, pressed juice (fruit must) is made from apples, pears, cherries, plums, peaches, red currants, gooseberries, bilberries, cranberries, raspberries, hip berries and rhubarb. In general, the process used is the same as that for making wine from grapes. Apple and pear mash are first pressed and the pressed juice (must) is fermented, while berry mash is fermented directly in order to extract the color pigments. Natural fermentation is suppressed by inoculation with pure, cultured yeast (cold-fermenting yeast). The vigor of the fermentation of berry musts, which are nitrogen deficient, is increased by addition of small amounts of ammonium salts (fermentation salts). Lactic acid (3 g/l) is added to acid-deficient musts, such as that from pears, in order to achieve a clear ferment and, often, sucrose solutions are added to berry and fruit musts to alleviate acidity. The yield and quality of pome fruit must is improved by mixing 9 parts of fruit residue with 1 part of water and adding sucrose to raise the density of the must to 55 Oechsle degrees.
Fruit wines are produced industrially in many countries, e. g., apple wine, which is called cider in France, the UK and the USA, and pear

wine, known as "poiré" in France. In Germany fruit wine is made along the Mosel river, around Frankfurt and in the state of Baden-Wuerttemberg. It is a popular beverage and is commonly called "plain must".

20.2.10.2 Malt Wine; Mead

Malt wine is made from fermented malt extract (the hot water extract of whole meal malt). Malton wine is made in the same way, except that sucrose is added at 1.8-times the amount of malt in order to increase the sugar and alcohol content of the wine. The wort is then soured by the action of lactic acid bacteria (0.6–0.8% lactic acid, final concentration). The acid fermentation is stopped by heating the wort to 78 °C and, after inoculation with a pure yeast culture, the wort is fermented to an alcohol content of 10–13%. The beverage thus formed has the character of a dessert wine, but is different because of its high content of lactic acid and its malt extract flavor. Mead is an alcoholic liquor made of fermented honey, malt and spices, or just of honey and water (not more than 21 water per kg of honey). Since early times, mead has been widely consumed in Europe and, even today, it is enjoyed the most of all the wine beverages in eastern and northern Europe.

20.2.10.3 Other Products

Other wine-like products include palm and agave wines ("Pulque"), maple and tamarind (Indian date) wines, and sake, the Japanese alcoholic drink made from fermented rice, which resembles sherry and is enjoyed as a warm drink.

20.2.11 Wine-Containing Beverages

Wine-containing beverages are made with wine, liquor wines or sparkling wines and, hence, they are alcoholic beverages.

20.2.11.1 Vermouth

Vermouth was first produced in the late 18th century in Italy (Vermouth di Torino, Vino Vermouth) and later in Hungary, France, Slovenia and Germany. For the production of vermouth, wormwood (*Artemisia absynthium*) is extracted with the fermenting must or with wine, or it is made from a concentrate of plant extracts added to wine. Other herbs or spices are additionally used, such as seeds, bark, leaves or roots, as is the case with thyme, gentian or calamus, the sweet flag plant.

20.2.11.2 Aromatic Wines

These wines are similar to vermouth aperitif wines. They are flavored by different herbs and spices. Ginger-flavored wine is an example of this type of wine.

20.3 Spirits

20.3.1 Foreword

Spirits or liquors are alcoholic beverages in which the high alcohol concentration is achieved by distillation of a fermented sugar-containing liquid. Examples are distilled wines (brandies), liqueurs, punch extracts and alcohol-containing mixed drinks. Table 20.27 compares the alcohol consumption with respect to spirits, wine and beer in selected countries.

20.3.2 Liquor

The term liquor includes all liquids, even pure alcohol, which are obtained by fermentation followed by distillation. Some types of liquors contain flavorings.

20.3.2.1 Production

Liquors are produced by removing alcohol from an alcohol-containing liquid by distillation. Such liquids may already contain the alcohol, or alcohol is produced by the fermentation of a sugar-containing mash. The mash may include fermentable forms of sugars (D-glucose, D-fructose, D-mannose and D-galactose), or those forms are prepared by prior hydrolysis of di-

Table 20.27. Alcohol consumption with respect to the type of drink in l per inhabitant in 2003

Country	Spirits	Wine	Beer	Total
Luxembourg	1.6	6.7	4.3	12.6
Hungary	3.5	3.9	4.0	11.4
Czech Rep.	3.8	1.0	6.2	11.0
Ireland	2.0	2.7	6.1	10.8
Germany[a]	1.0	2.6	5.6	10.1
Spain	2.4	3.2	4.4	10.0
UK	1.8	2.2	5.6	9.6
Denmark	1.1	3.5	4.9	9.5
France	2.4	4.9	2.0	9.3
Austria	1.4	3.2	4.7	9.3
Switzerland	1.6	4.1	3.3	9.0
Slowakia	3.5	1.2	3.8	8.5
Lettland	6.1	0.5	1.5	8.1
Greece	1.6	3.4	2.7	7.7
Sweden	0.9	1.7	2.3	4.9

[a] In 2004.

and oligosaccharides (sucrose, lactose, raffinose, gentianose, melecitose, etc.) or polysaccharides. The main raw materials are:

- alcohol-containing liquids (wine, beer, fruit wines, fermented milk);
- sugar-containing sources, such as sugar cane and beet, molasses, fruit and fruit products, fruit pomace, whey, palm extract and sugar-rich parts of tropical plants;
- starch- and inulin-containing raw materials (fruit, cereal, potato, topinambur, sweet potato, cassava, tapioca or chicory).

Saccharification of the starch-containing material is achieved with malt (green malt or kiln-dried malt), or by microbial amylases e. g., from the molds Aspergillus niger and A. oryzae. Fermentation is achieved with *Saccharomyces cerevisiae*, which converts sucrose and hexoses (glucose, galactose, mannose, fructose). Other substrates can be fermented, e. g., with *Saccharomyces uvarum* (raffinose), *Kluyveromyces fragilis* (lactose), and *Kluyveromyces marxianus* (inulin). Distillation is performed in various ways, depending on the source and desired end-product. For the distillation of rum, arrack, fruit brandies and cereals, and brandy from wine, the apparatus is often a relatively simple still, used in such a way as to obtain a distillate which contains several other products of fermentation besides ethanol, or which contains the aroma substances of the starting raw material. These aroma substances are alcohols, esters, aldehydes, acids, essential oils and hydrogen cyanide. Repeated distillation is needed to obtain an alcohol-enriched distillate. In the production of pure or absolute alcohol the aim is the opposite: the final product being free from materials other than ethanol.

20.3.2.2 Alcohol Production

Alcohol used for drinks is made primarily from potatoes, cereals and molasses. Distiller's yeast, especially the top fermenting culture (cf. 20.3.2.1), is used for fermentation. Since the fermentation proceeds in an unsterilized mash and at elevated temperatures and since the growth of yeast occurs in mash acidified with lactic or sulfuric acid (pH 2.5–5.5), the yeast must be highly fermentative, tolerant of elevated temperatures ($\leq 43\,°C$) and resistant to acids and alcohol. In addition to saccharification by malt which contains mainly β-amylase, high-activity microbial α-amylases are also used. Molasses does not require saccharification. The saccharified mash is cooled to 30 °C and then inoculated with a yeast starter which has been cultured on a sulfuric or lactic acid medium of the mash or directly with distiller's yeast. After 48 h of fermentation, the ethanol present at 6–10% by volume in the mash is distilled off along with the other volatile constituents. This step and the following rectification of the crude alcohol are achieved by continuous processes.

To facilitate the removal of the fusel oils, the crude alcohol is diluted to 15% by volume prior to rectification. The head product obtained from the rectification column consists nearly of pure ethanol (96.6% by volume) which is used for production of alcohol-fortified beverages. Large amounts of acetaldehyde, methanol and low boiling esters are present in the first runnings of the distillate, while the last runnings contain primarily fusel oil, other high alcohols, furfural and esters. These runnings combined with other intermediate fractions provide technical alcohol. The fusel oil, obtained in amounts of 0.1–0.5 l per 100 l alcohol, is used for technical purposes, while the distillation residue (the wash or stillage) is frequently used as animal feed. The yield of alcohol from 100 kg of mash starch is 62–64 l, i. e. about 89% of the theoretical value.

Technical alcohol is denatured or embittered to prevent its use for other than technical purposes, e. g., for drinking. Burning alcohol is denatured by addition of a mixture of methylethylketone and pyridine and alcohol for industrial use with other solvents, such as petroleum ether, camphor, diethyl ether or dyes.

20.3.2.3 Liquor from Wine, Fruit, Cereals and Sugar Cane

These beverages have a distinct taste and odor and contain at least 38% ethanol by volume. They are called natural, genuine or true liquors. The distillate resulting from a single distillation has a low alcohol content and often contains the specific odor and taste components of the starting material (harsh raw grain or harsh raw juniper liquor-gin). In the production of liquor, the ultimate aim is to collect most of the desirable, specific fragrance and aroma substances (esters, essential oils) or to develop them (hydrogen cyanide, fermentation products, yeast oil) by using suitable mashing, fermentation and distillation processes. The freshly distilled liquor has a hard, burning taste and unpleasant odor. It is improved by aging, which gives it a new, desirable aroma and flavor. Therefore, aging of liquor is of the utmost importance.

20.3.2.3.1 Wine Liquor (Brandy)

Brandy is distilled wine which contains at least 38% by volume of alcohol. Brandy to which alcohol is added is designated as a brandy blend or adulterated brandy.

The term "cognac" is restricted to brandy made in France in the region of Charente. The brandy produced in southern France, called Armagnac, is close in quality to cognac. Brandy production originated in France. Fermented grape juices (must) are distilled in very simple copper-pot stills on an open fire, often without prior removal of the yeast. The primary distillate (sectionnement) with a harsh, unpleasant odor is refined by repeated distillations ("repasse"). Brandy production soon spread to other countries (Germany, Russia, Spain, Hungary, the USA, Australia) and today brandy is frequently distilled by a continuous process and its production has become a large-scale industry. In Germany imported wines serve as starting material and are increasingly obtained from raw distillates. Distilled wine is a wine without residual sugar, to which a non-rectfied wine distillate with maximum 86 per cent by volume of alcohol has been added. It contains 18–24% (v/v) of alcohol and max. 1.5 g/l of volatile acids (calculated as acetic acid).

The primary wine distillate contains 52–86% by volume ethanol and is considered as an intermediate product. It is used as the raw ingredient in the production of adulterated brandy by aging from 6 months to several years in wooden casks. Hard oak wood is used predominantly (barrels are made from "limousin" wood, holding about 300 l). Wild chestnut and other woods are also used. During aging, the wine distillate extracts phenolic compounds and colors of the wood, thus acquiring the typical golden-yellow and, occasionally, greenish-yellow color of brandy. Simultaneously, oxidation and esterification reactions mellow and polish the flavor and aroma. In order to improve quality, it is common to add an essence prepared by extraction of oakwood, plums, green walnuts or deshelled almond with a wine distillate and also sugar, burnt sugar ("couleur") and 1% dessert wine to sweeten the brandy. In addition, treatment of brandy with clarifying agents and filtering agents is also common. The desired alcohol content is obtained by dilution of brandy with water.

20.3.2.3.2 Fruit Liquor (Fruit Brandy)

Fruit liquors are also called cherry or plum waters or bilberry or raspberry spirits. Production of fruit liquor will be illustrated by cherry and plum liquors. Kirschwasser is made mostly in southern Germany (Black Forest's cherry water), France and Switzerland (Chriesiwasser). Whole fruits of the various sweet cherry cultivars are partly crushed together with the seeds and are pounded into a pulp. The fruit is left to ferment for several weeks, using a pure yeast culture. The fermented mash is then distilled in a copper still on an open fire or is heated with steam.

During distillation the first and last fractions are separated. The main distillate contains 60% by volume or more alcohol. It is usually diluted with water to about 40–50% by volume alcohol and is marketed as clear, colorless brandy. The low levels of benzaldehyde and hydrogen cyanide which both contribute to the flavor are derived from the enzymatic cleavage of seed amygdalin. Kirschwasser, as is the case with Marasca from Dalmatia or Italy, is often used as an admixture in liqueur or cordial production (curacao, cherry brandy, maraschino, etc.).

Plum brandy is produced from fully-ripe plums in a similar way to Kirschwasser, though mostly no seed crushing is involved. Besides Germany and Switzerland (Pfluemli water), major producers are the Balkan states, Czech Republic and France. In addition to the common plum, the highly aromatic yellow plum, mirabelle, is also fermented. Mirabelle liquor is a desirable admixture to liqueurs containing fruit extract.

Fruit spirits are obtained from fresh or frozen fruit pulp or juice to which alcohol has been added prior to distillation. Fruits and berries used for this purpose are apricot, peach, bilberry, raspberry, strawberry, red currant, etc. "Williams" is a pear brandy made exclusively from the pear variety "Williams Christ". (E,Z)-2,4-Decadienoic acid ethylester (formation, cf. 5.3.2.2) has been identified as the characteristic aroma substance.

Pome fruit liquor is obtained from freshly fermented apple or other pome fruits, either whole or crushed, or their juices, without prior addition of sugar-containing materials, sucrose or alcohol of some other origin. The alcohol content of liquor from pome fruits is at least 38% by volume. Hydrogen cyanide plays an important role in the chemical composition of fruit liquors of either stone or pome fruit. The cherry liquor sold on the market contains about 0.3–60 mg of hydrogen cyanide per liter of alcohol. In the same range are the concentrations of benzaldehyde (at least 20 mg/l) and the bouquet substances (about 7–15 mg/100 ml). Plum brandy contains less hydrogen cyanide (0.6–21.3 mg/l).

20.3.2.3.3 Gentian Liquor ("*Enzian*")

Gentian brandy is a product obtained by distilling the fermented mash of gentian roots, or in which gentian distillate is used. The raw materials are the roots of many plants of the gentian family which, in the fresh state, contain substantial amounts of sugars (6–13%) in addition to the bitter glycoside-type compounds, such as gentiopicrin, amarogentin and others. The major production regions are the Alps (Tyrol, Bavaria, Switzerland) as well as the French and Swiss Jura mountains.

20.3.2.3.4 Juniper Liquor (*Brandy*) and Gin

Juniper brandy is obtained from pure alcohol and/or grain distillate by the addition of juniper distillate or its harsh, raw brandy. The use of juniper oil is uncommon. Juniper spirit is made exclusively from the distillate of whole juniper berries or from a fermented aqueous extract of juniper. The berries of *Juniper communis* are processed into brandy in Germany, Hungary, Austria, France and Switzerland. Pure juniper brandy is also used as an intermediate product for the production of alcoholic beverages with a juniper flavor as, for example, in Geneva gin. The alcohol of this gin is obtained by distillation of a cereal mash prepared from kiln-dried smoked malt. Juniper brandy also flavors the Bommerlunder from the state of Schleswig-Holstein and the Doornkaat of East Friesland in Germany. Common gin is made from juniper distillates and spices, and contains at least 38% by volume alcohol. Dry gin has an alcohol content of at least 40% by volume.

20.3.2.3.5 Rum

Major rum-producing countries are in the West Indies (Jamaica, Cuba, Barbados, Puerto Rico, Guyana and Martinique) and also Brazil and Mauritius.

Rum production in sugar cane-cultivating regions uses the sugar syrup or the freshly pressed extract, often with the addition of such by-products as foam skimmings, molasses, press-skimmings and their extracts, and distiller's wash ("dunder"), the residue leftover from a previous distillation. The sugar-containing solutions are diluted and allowed to ferment spontaneously at a maximum temperature of 36 °C and then are usually distilled in simple pot stills. Parts of aromatic plants are occasionally added to increase the aroma of the fermenting mash. This results in rum brands with different aromas. The quality of individual products fluctuates greatly. Especially highly regarded is Jamaican rum, which is marketed in various quality grades. A general classification divides them into drinking and blending types. Export rums have an alcohol content of about 76–80% by volume ("original rum"). Rum has the most intense aroma of all the distilled spirits enjoyed as drinks. This is acquired only after long aerobic aging in casks, by absorption of extracted substances from oakwood, and by formation of esters and other aroma constituents during aging. Original rum contains about 80–150 mg acids per 100 ml, calculated as acetic acid. A large part occurs in free form as acetic and formic acids, the rest, along with other low molecular weight fatty acids, is esterified. The ester content and composition are of utmost importance for the assessment of aroma quality.

20.3.2.3.6 Arrack

Arrack is made from rice, sugar cane molasses, or sugar-containing plant juices (primarily from sweet coconut palm extract or its bloom spadix) by fermentation and subsequent distillation. Dates are used for the same purpose in the Middle East.

Countries which produce arrack are Indonesia (Java), Sri Lanka, India (Malabar coast) and Thailand. Well-known brands are Batavia and Goa arracks. In comparison to rum, arrack is not available in very many varieties. It is imported as the "original arrack" with an alcohol content of 56–60% by volume, from which "true arrack" is obtained by dilution with water to 38–50% by volume alcohol. At least a tenth of the alcohol in arrack blends must be from genuine arrack. Arrack is used for hot drink preparations, for Swedish punch, as an admixture for liqueurs, and in baking and as a flavoring ingredient in candy manufacture. Batavia brand arrack, with an alcohol content of about 57% by volume, contains on the average 92 mg acids, 189 mg esters, 21 mg aldehydes and 174 mg higher alcohols per 100 ml of ethanol.

20.3.2.3.7 Liquors from Cereals

Typical products are grain alcohol and whiskey (American and Irish brands are usually spelled with an "e", while Scottish and Canadian brands tend to use "whisky"). Different cereals (rye, wheat, buckwheat, oats, barley, corn, millet) are used. The cereals are first ground, mixed with acidified water, and made into an uniform mash by starch gelatinization. Saccharification is then accomplished by incorporating 15% kiln-dried malt in a premashing vat and stirring constantly at 56 °C. Saccharification proceeds rapidly through the action of malt diastase enzymes. The enzymes are inactivated by heating the mash to 62 °C. This step is followed by rapid cooling of the mash to 19–23 °C. The sweet mash is fermented by a special yeast and is then distilled. Grain liquors are obtained by distilling the mash, while malt liquors commonly are produced by distillation of the wort. Simple stills are used for distillation in small plants, while both distillation and rectification are achieved on highly efficient, continuously run column stills in industrial-scale production. According to the process used, the yield is 30–35 l of alcohol per 100 kg of cereal (e. g., rye), while the quality and character of the spirits vary greatly. Simple stills, with an unsophisticated separation of head and tail fractions, provide characteristic products rich in grain fusel oils. A modern distillery is able to remove the fusel oils to a great extent, yielding a high percentage grain alcohol, from which it is then possible to make a mellow, tasty, pure grain brandy with a subtle aroma. The final flavor of all these products is dependent on well-conducted aging in wooden casks.

Whiskey, depending on the kind, is made by different processes. The raw material for Scotch single malt whiskey is barley malt which has been exposed to peat moss or coal smoke during kiln drying. Such smoked malt is mashed at 60 °C and filtered. The resulting wort is then fermented at 20–32 °C after the addition of yeast (*Saccharomyces cerevisiae*). Irish whiskey is never made from smoked malt. The distillation is conducted in two steps, sometimes in simple pot stills. The harsh, raw liquor is collected in the first distillation step. The undesirable harsh components are removed in the head and tail fractions in the second distillation.

In the production of Scotch grain whiskey the saccharified starch is distilled in continuous column stills. The character of the distillate is neutral, with less aroma than malt whiskey. In both Scotch whiskey processes, the distillates, with about 63% by volume ethanol, have to be stored/aged in order to develop their full aroma. This is best achieved by aging in old sherry casks or in charred casks. At the end of processing, the alcohol content is reduced to a drinkable level, about 43% by volume. Depending on the desired flavor or current preferences, the malt whiskey might be blended with grain whiskey ("blended whiskey"). American whiskey is made from corn, rye or wheat by saccharification with malt enzymes, fermentation of the wort, followed by doubledistillation in column stills and aging, usually in charred oakwood casks. The corn distillate content of bourbon whiskey is at least 51% by volume and that of corn whiskey is at least 80% by

Table 20.28. Odorants of whisky

Aroma substance	Concentration (mg/l)	
	Malt whisky[a]	Bourbon whisky[b]
Ethanol	316,000	316,000
2-Methoxyphenol	0.025	0.056
5-Methyl-2-methoxyphenol	0.0019	0.0011
4-Methyl-2-methoxyphenol	0.01	0.016
4-Ethyl-2-methoxyphenol	0.017	0.059
2-Methylphenol	0.034	0.003
4-Methylphenol	0.017	0.008
3-Methylphenol	0.008	0.004
4-Ethylphenol	0.016	0.166
3-Ethylphenol	0.0033	n.d.
Eugenol	0.027	0.24
3-Methylbutanol	568.1	1062.1
2-Methylbutanol	194.2	423.8
2-Phenylethanol	11.2	13.87
Ethylbutanoate	0.76	0.55
Ethylhexanoate	2.07	1.99
Ethyloctanoate	12.3	8.35
Ethyl-2-methylpropanoate	0.52	0.13
Ethyl-3-methylbutanoate	0.21	0.052
(S)-Ethyl-2-methylbutanoate	0.092	0.030
(S)-Ethyl-2-hydroxy-3-methylbutanoate	0.005	0.003
(2S,3S)-Ethyl-2-hydroxy-3-methylpentanoate	0.004	0.003
3-Methylbutylacetate	4.02	2.59
2-Phenylethylacetate	4.10	1.94
Methylpropanal	1.74	0.23
3-Methylbutanal	0.65	0.34
Vanillin	0.68	2.13
(3S,4S)-cis-Whisky lactone	0.39	2.49
(3S,4R)-trans-Whisky lactone	0.07	0.34
γ-Nonalactone	0.11	0.12
γ-Decalactone	0.010	0.002
2,3-Butandione	0.39	0.033
(E)-β-Damascenone	0.024	0.011
(E)-2-Nonenal	0.024	0.009
(E,E)-2,4-Decadienal	0.006	0.039
1,1-Diethoxyethane	21.86	15.33

[a] Single malt whisky from Scotland, stored for 8 years in an oak cask.
[b] American Kentucky straight bourbon whisky, stored for at least 3 years in a charred oak cask.

volume. Rye whiskey contains at least 51% by volume distillate from rye, while wheat whiskey must contain mostly distillate from wheat.

Table 20.28 presents data on the composition of the aromas of malt whisky (MW) and bourbon whisky (BW). A comparison shows that the same odorants are present in both drinks, but in different amounts. The concentrations of the esters and of 2,3-butanedione are higher in MW and the concentrations of 2- and 3-methylbutanol, eugenol, vanillin and whisky lactone are higher in BW. The extraction yield of the three last mentioned aroma substances clearly increases on storage of BW in charred casks. On longer storage of MW, this effect is also achieved in addition to an increase in the esters, e.g., an 18 year old MW contains (mg/l): eugenol (0.09), vanillin (2.2), cis- and trans-whisky lactone (1.1), ethylhexanoate (3.7) and ethyloctanoate (22.2). In MW (stored for 10 years) made from strongly smoked malt, the phenol fraction (mg/l) is higher than in the MW shown in Table 20.28: 2-methoxyphenol (1.5), 4-methyl-2-methoxyphenol (0.6) and 2-methylphenol (1.3) 4-methylphenol (1.2).

20.3.2.4 Miscellaneous Alcoholic Beverages

Many liquors are made "cold" by simply mixing the purified alcohols of various brands with water and are named according to the place of origin: Klarer, Weisser, East-German, etc. Such mixes often contain flavorings (seasonings, spices), e. g., freshly distilled or aged grain liquor, extracts of caraway, anise, fennel, etc., as well as sugar, essence, essential oils or other flavoring substances. These products are designated as aromatized liquors. Some examples are:

Vodka (in Russian = diminutive of water) is made of alcohol and/or grain distillate by a special process. In all cases the characteristic smoothness and flavor must be achieved. The flavor should be neutral. The extract content is 0.3 g/100 ml and the alcohol content is at least 37.5% by volume.

Aquavit is a liquor flavored primarily with caraway or dill seed. It is made from a distillate of herbs, spices or drugs and contains at least 37.5% by volume alcohol (potato alcohol or grain distillate). It is a favorite type of liquor in the Scandinavian countries.

Bitters are made from alcohol and bitter and aromatic plant or fruit extracts and/or their distillates, fruit saps and natural essential oils, with or without sugar, i. e. starch syrup. This group of products includes Boonekamp, bitter drops, English and Spanish bitters, and Angostura. The so-called "Aufgesetzter" is made of black currants and spirit or grain alcohol.

Absinthe is a liqueur flavored with aromatic constituents of wormwood and other aromatic plants. It becomes turbid after dilution with water.

Other Products. Some special liquors of regional importance should be mentioned: tequila and mescal from Mexico and South America, made from fermented sap of the agave cactus; and liquors from the Middle East, made of sultana raisins, figs or dates.

20.3.3 Liqueurs (Cordials)

Liqueurs are alcoholic beverages with at least 15% (advocaat 14%) by volume alcohol and at least 150 g/l of sugar (expressed as invert sugar) and flavored with fruit, spices, extracts or essences.

20.3.3.1 Fruit Sap Liqueurs

Fruit liqueurs contain the sap of fruits which give the liqueur its name. The lowest concentration of sap is 20 l per 1000 l of end-product (25% by volume alcohol). Cherry brandy, a special type of cherry liqueur, consists of cherry sap, cherry-water, sucrose or starch syrup, wine essence and water.

20.3.3.2 Fruit Aroma Liqueurs

These liqueurs are alcoholic beverages made of natural fruit essences, distillates or fruit extracts.

20.3.3.3 Other Liqueurs

Other liqueurs include:

Crystal liqueur, which contains sugar crystals (e. g., "crystal caraway").

Allasch, a special aromatic alcohol- and sugarrich caraway liqueur with at least 40% by volume alcohol.
Ice liqueur, which is mixed and drunk with ice (e. g., lemon ice liqueur), and has an extract content of at least 30 g/100 ml and a minimum alcohol content of 35% by volume.
Gold water, a spice liqueur containing gold leaf as a characteristic ingredient.
Fragrant vanilla liqueur, the aroma of which is derived exclusively from pod-like vanilla capsules (vanilla beans).
Honey liqueur ("Baerenfang", "Petzfang", the "bear traps") has at least 25 kg of honey in 100 l of end-product.
Swedish punch is made of arrack and spices and has an alcohol content of at least 25%. Cocoa, coffee and tea liqueurs are made from the corresponding extracts of raw materials. Emulsion liqueurs are chocolate, cream and milk liqueurs, mocca with cream liqueur, egg liqueur (the egg cream, "Advokat"), egg wine brandy, and other liqueurs with eggs added. The widespread and common egg liqueur is made from alcohol, sucrose and egg yolk. Herb, spice and bitter liqueurs are made from fruit saps and/or plant parts, natural essential oils or essences, and sugar. Examples are anise, caraway, curacao, peppermint, ginger, quince and many other liqueurs.

20.3.4 Punch Extracts

Punch extracts or punch syrups, known simply as punch, are concentrates which are diluted before they are drunk. Rum or arrack punches contain 5% rum or 10% arrack, calculated relative to the total alcohol content. Aromatization with artificial rum or arrack essences, or with fruit ethers or esters, is not commonly done.

20.3.5 Mixed Drinks

Mixed drinks or cocktails are mixtures of liquors, liqueurs, wines, essences, fruit and plant extracts, etc.
Mixed drinks include alcopops, i. e., sweet drinks made by mixing lemonade with distilled alcohol, beer or alcoholic drinks. The alcohol content is between 2.5 and 7% by volume. This category also includes instant drink powders, which mainly consist of sugar, acidifiers, aromas and coloring substances. The alcohol is adsorbed on a sugar/dextrose matrix. If the powder is dissolved in water as instructed, a drink with an alcohol content of 4.8% by volume is obtained.

20.4 References

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