Chemical Composition of Beverages and Drinks

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Contents

Abstract

Chemical constituents are summarized for a selection of important beverages: fruit juices, carbonated nonalcoholic drinks (including mineral/springwater, soda water, soda pop, cola drinks, root beers, and tonic water), functional beverages (sports, health, energy, and relaxation drinks), and alcoholic beverages (wine, cider, beer, rice wine, spirits, and their flavorings). Major chemical

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constituents reviewed include pigments, colorants, carbohydrates, sweeteners, acids, volatile compounds, phenolic compounds, terpenoids and steroids, nitrogen compounds (especially amines, amino acids, and proteins), minerals, vitamins, ethanol (for alcoholic beverages), carbon dioxide (for carbonated drinks), and preservatives. General relationships between chemical content and methods of processing are emphasized for several key beverages.

Introduction

Knowledge of the chemical composition of a beverage is important for both understanding the organoleptic character of the beverage and for maximizing its commercial value. While it is impossible in a work of this kind to be totally comprehensive, this chapter summarizes the main chemical constituents of common drinks in two parts: fruit juices, nonalcoholic carbonated drinks, and nonalcoholic functional beverages in the first part and alcoholic beverages in the second.

Fruit juices and alcoholic beverages (many of which are derived from fruit juices) are discussed in terms of the common categories of natural chemical constituents that they contain. These include pigments, carbohydrates, acids, volatile compounds, phenolic compounds, amino acids, peptides, proteins, and other organic nitrogen compounds, minerals, vitamins, and bitter/astringent compounds. Additionally, ethanol and carbon dioxide contents are discussed for relevant beverages. Also considered are legal additives, such as colorants, flavorants, sweeteners, and preservatives, as well as potentially toxic substances that are formed naturally during processing (e.g., ethyl carbamate in wines and distilled spirits). The major processing methods for several kinds of beverages are described, tabulated, or illustrated in outline, as these are a major influence on the chemical composition of the final products and hence on their organoleptic character.

Nonalcoholic carbonated beverages and functional drinks (apart from unflavored mineral or springwater) are treated from the point of view of purified water to which has been added a selection of chemical ingredients. These include carbon dioxide, salts, sugars and/or low-calorie sweeteners, colorants, flavorants, vitamins, amino acids, and special active ingredients, such as central nervous system (CNS) or smooth muscle stimulants (e.g., caffeine, creatine) or relaxants (e.g., melatonin, L-theanine), either as pure substances or as part of plant extracts (e.g., guarana, ginseng, green tea). In contrast to other sections, most of the data in the Nonalcoholic Functional Drinks section comes from product labels or company Web sites and hence are anonymous, in order to avoid advertising.

In some cases, component concentration data may be only approximate values, being results, for example, of semiquantitative chromatographic (e.g., GC/MS) determinations that use just one internal standard. Nevertheless, such data can still give a broad understanding of chemical composition.

Agricultural, industrial, and microbiological contaminants originating from raw materials are not generally included, except in a few important cases.

Chemical Composition of Nonalcoholic Beverages and Functional Drinks

Fruit Juices

Several methods are available for the commercial production of fruit juices. The simplest of these is pressing, which gives a cloudy product with a shelf life of only a few days, even at chill temperature storage. The shelf life can be extended somewhat by the use of a light pasteurization step. Freshly pressed juice (such as apple, lime, or orange) is considered by many to have the best flavor. However, most commercial fruit juices are the results of more elaborate processes that involve filtration and/or concentration steps (evaporation, usually at reduced pressure), followed by restoration (i.e., adding back flavor compounds, pulp) or reconstitution (i.e., diluting with water) toward the end of the process. Fruit juices that have been processed without evaporation and reconstitution steps are called NFC (not from concentrate) juices. Restoration or reconstitution is performed in such a way as to give a product that is the same as the original pressed juice so that the essential composition and quality factors of the juice are maintained (Heredia et al. 2013 and references therein). These juices are generally pasteurized and aseptically packaged, giving them much longer shelf lives at ambient storage (Ashurst 2012 and references therein). Apart from the above, fruit juices, usually in the form of concentrates or sometimes in decolorized or deionized forms, are important ingredients of soft drinks, some carbonated varieties of which are discussed in Nonalcoholic Carbonated Beverages. Additionally, many fruit juices are obtained expressly for winemaking. Some of their chemical components survive into the wine, but many are lost or changed.

This section deals solely with the chemical composition of pure fruit juices, obtained by any of the above processes and without the inclusion of additives, such as sugar or preservatives, which is forbidden in many countries. The focus is on more common juices made from fruit grown in temperate climates, but depending on available data, certain aspects of the chemical composition of some less common juices are included, particularly those that are frequently converted to wine or are ingredients of soft drinks.

Pigments

The major pigments of red-purple fruit juices, such as those of black currant, blueberry, red/black cherry, black grape, blood orange, or strawberry, are anthocyanins, mostly anthocyanidin 3-*O*-glycosides, but there are many variations. Figure 1 displays the six fundamental anthocyanidins (the aglycone part of anthocyanins), along with examples of glycosides and acylated glycosides that constitute anthocyanin fruit juice pigments. Table 1 displays the major anthocyanins found in selected juices, along with total anthocyanin content (TAC), either as a typical value or as a range. TAC is often quoted as mg cyanidin or cyanidin 3-*O*-glucoside equivalents per L or per 100 g fresh weight.

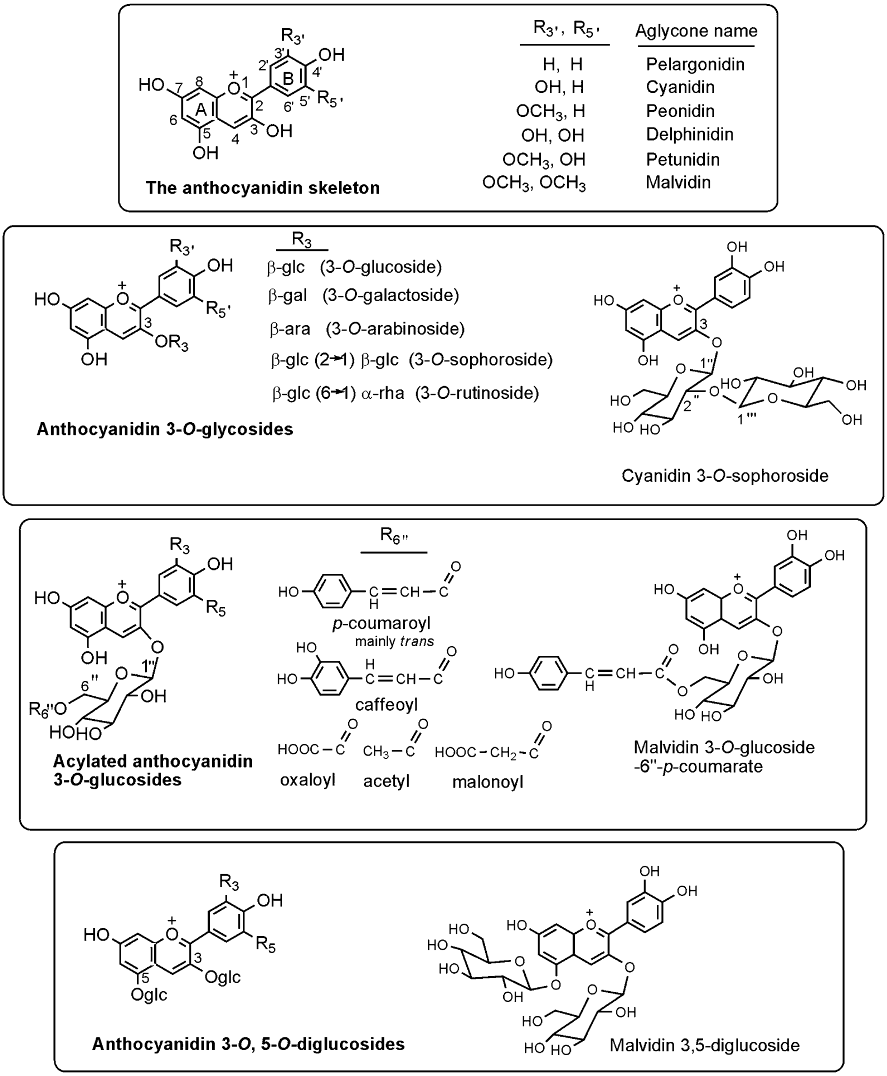


Fig. 1 Structures of some fruit juice anthocyanins

The most common anthocyanins are cyanidin glycosides, except for black grape juice where the bulk of the anthocyanins (50–90 %) are malvidin derivatives. Strength of color and TAC depend on several factors, including the variety and condition of the fruit and the juicing process, especially with regard to skin contact and heat, enzyme, or other treatments.

Additional to monomeric anthocyanins, lower concentrations of anthocyanin oligomers may be present in grape juice, depending on the extent of extraction from

Table 1 Major anthocyanin pigments in red-purple fruit juices[a]

Juice	Major anthocyanins	Typical total anthocyanin content[b]
Bilberry/blueberry *V. myrtillus*/ *Vaccinium corymbosum*	Malvidin 3-*O*-galactoside, delphinidin 3-*O*-glucoside, cyanidin 3-*O*-glucoside, delphinidin 3-*O*-arabinoside, petunidin 3-*O*-glucoside, malvidin 3-*O*-glucoside	3,800
Blackberry *Rubus* spp.	Cyanidin 3-*O*-arabinoside, cyanidin 3-*O*-dioxaloylglucoside, cyanidin 3-*O*-malonylglucoside, peonidin 3-*O*-glucoside	1,256–1,978
Black currant *Ribes nigrum* L.	Cyanidin 3-*O*-rutinoside, delphinidin 3-*O*-rutinoside, delphinidin 3-*O*-glucoside, Cyanidin 3-*O*-glucoside, petunidin 3-*O*-glucoside, peonidin 3-*O*-rutinoside	2,620
Blood orange *Citrus sinensis* (L.) Osbeck	Cyanidin 3-*O*-glucoside, cyanidin 3-*O*-6″-malonylglucoside, delphinidin 3-*O*-glucoside	*43–291*
Cherry (red/black) *Prunus cerasus L.* (sour) *Prunus avium L.* (sweet)	Cyanidin 3-*O*-glucosylrutinoside[c] cyanidin 3-*O*-rutinoside, cyanidin 3-*O*-sophoroside[d], pelargonidin 3-*O*-rutinoside, cyanidin 3-*O*-glucoside, peonidin 3-*O*-rutinoside	*350–634*
Grape (black) *Vitis Vinifera*, *V. labrusca*, *V. riparia*, etc.	Malvidin 3-*O*-glucoside, malvidin 3-*O*-galactoside-6″-acetate, malvidin 3*O*-, 5*O*-diglucoside[e], delphinidin 3-*O*-glucoside, malvidin 3-*O*-galactoside-6″-*p*-coumarate, petunidin 3-*O*-glucoside, peonidin 3-*O*-glucoside	*800–1,600*
Raspberry (red) *Rubus idaeus* L.	Cyanidin 3-*O*-sophoroside, cyanidin 3-*O*-glucoside, pelargonidin 3-*O*-glucoside	351–491
Strawberry (red) *Fragaria x ananassa* Duch	Pelargonidin 3-*O*-glucoside, cyanidin 3-*O*-glucoside pelargonidin 3-*O*-rutinoside	39.4–136.1 *442*

[a]Data from McKay et al. (2011, pp. 419–435) and references therein, unless specified otherwise
[b]TAC (mg cyanidin 3-*O*-glucoside equivalents/kg fruit mass *or mg/L juice*)
[c,d]Data from Damar and Ekşi (2012); [c]main anthocyanin in sour cherry juice (140–321 mg/L); [d](2.6-21.5 mg/L) in sour cherry juice
[e]Found at high levels in the juice of *V. riparia* and *V. rupestris* grapes and hybrids of these with *V. vinifera*. It is absent or very minor in juice from *V. vinifera* varieties

the skins during the juicing process. These are flavan–flavylium dimers and trimers with C(4)-C(8) links (type A) or C(2)-O-C(7) and C(4)-C(8) links (type B) (Buglass and Caven-Quantrill 2013 and references therein). Also, low levels of vitisins (pyranoanthocyanins formed by reaction of anthocyanins with carbonyl compounds, such as acetaldehyde and pyruvic acid) have been found in blood orange juice (Hillebrand et al. 2004). Vitisins are generally much more evident in young red wines (see Fig. 10).

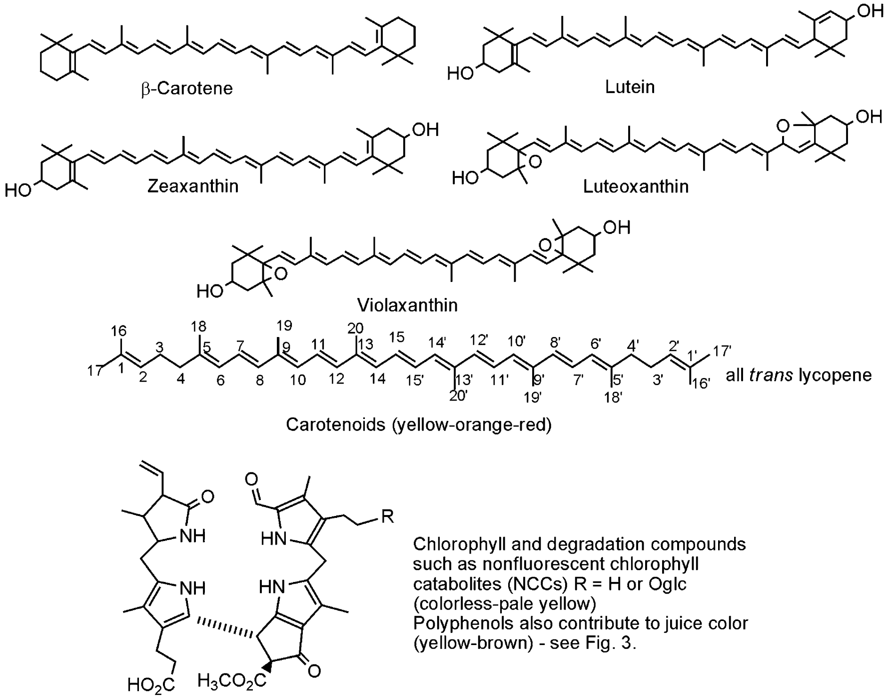


Fig. 2 Structures of some non-purple fruit juice pigments

Polyphenols (flavan-3-ols and their condensation oligomers, flavanones, flavones, and flavonols) (see Fig. 2 and Table 2 for examples), carotenoids (Fig. 2), and possibly chlorophyll and chlorophyll degradation products, are the major pigments of pale fruit juices. The latter have been found in apple, pear, and white grape juice, whereas certain carotenoids are also evident in red grape juice and wine, as minor pigments (McKay et al. 2011, pp. 419–435 and references therein).

Flavanone 7-*O*-glycosides are the most abundant flavonoids in all citrus juices (Tripoli et al. 2007 and references therein). Neohesperidoside flavanones (naringin, neohesperidin, and neoeriocitrin) are mainly present in bergamot, grapefruit, and bitter orange juices, whereas flavanone rutinosides (hesperidin, narirutin, and didymin) are present in bergamot, orange, mandarin, and lemon juices. See "Phenolic Compounds" for further discussion.

The major pigment of tomato juice and red grapefruit juice is the carotenoid all-*trans*-lycopene (Fig. 2): it comprises 80–90 % of the carotenoid content of freshly pressed tomato juice, but its concentration gradually diminishes with storage time, via conversion to a number of geometric isomers. Heat treatment during tomato juice processing leads to lesser formation of lycopene geometric isomers (5-*cis*-, 9-*cis*, and 15-*cis*-lycopene) over a 56-day storage time (Vallverdú-Queralt et al. 2013). The main pigments of cherry tomatoes are all-*trans*-lycopene (80–90 %), β-carotene (4.3–12.2 %), and α-carotene, phytoene, and phytofluene (together, ~6.8 %) (Lenucci et al. 2006).

Table 2 Major pigments of non-purple fruit juices[a]

Category	Examples	Comments
Carotenoids	α-Carotene, β-carotene (all-*trans*), (13-*cis*)-carotene	Carotenoids are present in many fruit juices, such as those of white grapes, apricot/peach, and citrus fruits, especially oranges. Some are very minor pigments of black grape juice. Lycopenes are prominent in tomato juice. Isomerizations can occur on heat treatment processes
	Oxygenated carotenoids: 2′, 3′-anhydrolutein, α-cryptoxanthin, β-cryptoxanthin, lutein, (13-*cis*)-lutein, (13′-*cis*)-lutein, zeaxanthin	
	Epoxy and furanoyl carotenes: antheraxanthins, auroxanthins, luteoxanthins, mutatoxanthins, and violaxanthins	
	Lycopenes (mainly *all-trans* lycopene)	
Phenolic compounds[b]:		In many juices, including apple and pear juice
Chalcones	Butein, chalconaringenin	Apple and pear juice
Dihydrochalcones	Phloretin, phloridzin	In many fruit juices
Flavan-3-ols	(+)-Catechin, (−)-epicatechin	Especially citrus fruit juices
Flavones (and *iso*flavones) and flavonols	Apigenin, tangeretin (usually as glycosides)	In many fruit juices
	Kaempferol, quercetin (and glycosides)	
Flavanones and flavanonols	Hesperitin, naringenin (usually as glycosides), Dihydroquercetin	Especially citrus fruit juices
Flavan-3,4-diols	Cyanidol	Especially pear juice
Procyanidin oligomers	Dimers, trimers, and upwards, of (+)-catechin, (−)-epicatechin	Especially in cider apple and perry pear juice
Chlorophyll and degradation products	Nonfluorescent chlorophyll catabolites (NCCs) and other chlorophyll breakdown products	In many pale juices, including apple, white grape, and pear juice

[a]Some of these (e.g., some carotenoids and flavonoid phenols) are also present in purple juices (e.g., black grape juice), where provision of color is dominated by anthocyanins
[b]Simple phenols and phenolic compounds of the hydroxybenzoic acid and hydroxycinnamic acid type (including quinic acid derivatives) contribute more to taste but may provide color indirectly via nonenzymic browning reactions

Carotenoids are also major pigments in orange juice, 5–23 mg/L being typical total carotenoid concentrations (Meléndez-Martínez et al. 2009). The main carotenoids of orange juice appear to be (9-*cis*)-violaxanthin, (all-*trans*)-violaxanthin (+*cis*-isomers), (9-*cis*)- or (9-*trans*)-antheraxanthin, zeaxanthin, mutatoxanthin epimers, and β-cryptoxanthin (others being <1 mg/L concentration) (Meléndez-Martínez et al. 2009).

Volatile Components

Hundreds of volatile compounds have been detected in fruit juices. Many of these (e.g., alcohols, carbonyl compounds, carboxylic acids, lactones, norisoprenoids) are secondary metabolites of biochemical pathways involving amino acids, carotenoids, or fatty acids. Others (e.g., esters, ethers, and terpenoids) occur during ripening of fruit (Heredia et al. 2013). Some abundant or important volatile compounds (key odorants) of selected juices are given in Table 3. The odor threshold value (OTV) (or perception threshold) of a volatile is defined as the minimum concentration (often in water) at which the volatile can be detected organoleptically. OTVs of some key volatiles are given in Table 3. Odor activity value (OAV) (=concentration/OTV) was designed to indicate the extent of contribution of a compound to the global aroma: OAV $>$ 1 has been suggested as a necessary condition for probable significant contribution.

Usually only a fraction of the many volatile compounds in a particular juice are odor active (i.e., with OAV $>$ 1) at the concentration levels found in that juice. Aroma reconstitution methods can suggest the number and levels of odor-active compounds needed to reproduce the juice aroma. However, these results may not be universally accepted, for a number of reasons, including aroma perception subjectivity and omission of key (usually minor) compounds. Nonvolatile components (e.g., polyphenols), as well as scarce volatiles, can influence the perception of more abundant volatile compounds. Also, biological factors (e.g., genetics, agricultural practices, climate) and technological factors (e.g., method of juice preparation, storage) can influence global juice aroma.

In some cases, one or two volatile compounds can be highly suggestive of the whole juice aroma. Examples include 4-hydroxy-3,5-dimethyl-3(2*H*)-furanone (strawberry), *p*-1-menthene-8-thiol (grapefruit), methyl anthranilate (grape, *Vitis labrusca*, etc.), aromatic alcohols and carbonyls (juice of stone fruit, such as apricot, cherry, and peach), 4-mercapto-4-methyl-2-pentanone (grape, *V. vinifera* var. Sauvignon blanc), 1-(*p*-hydroxyphenyl)-3-butanone (raspberry), allyl carboxylates (pineapple), and 4-methoxy-2-methyl-2-butanone (black currant).

In general, however, many other compounds (often at low levels), as well as key odorants, contribute to global juice aroma/flavor and should be included, as far as possible, in aroma reconstitution experiments.

Many fruit juice volatile compounds (especially alcohols and including terpenols) exist partially or entirely as glycosides, which are odorless until they are hydrolyzed to release the odorant aglycone. This can occur during fermentative conversion of juice to wine or by the addition of β-glucosidase or pectinase enzymes during juice preparation (see Fig. 13) (Buglass and Caven-Quantrill 2013).

Phenolic Compounds

This subsection focuses on non-anthocyanin, nonvolatile phenolic compounds, many of which contribute to color and/or are important contributors of bitter and/or astringent sensations in the taste and mouthfeel of fruit juices. Important classes of phenolic compounds, with examples, can be found in Table 4, while selected structures are displayed in Fig. 3. In general, juices from fruit that are specifically grown to produce cider, perry (pear cider), or wine have the highest total phenolic content (TPC), which is measured in gallic acid equivalents (GAE) and is usually quoted in mg GAE/L or mg GAE/100 g FW (fresh weight). See Table 5.

Table 3 Principal aroma/flavor compounds of fruit juices[a]

Fruit juice	Characteristic aroma compounds
Apple (*Malus domestica* Bartch. or *M. sylvestris*)	**Alcohols**: 1-butanol, 1-hexanol, 2-methyl-1-butanol; **carbonyls**: *cis*-2-hexenal; **esters**: butyl hexanoate, ethyl butanoate, ethyl 2-methylbutanoate, hexyl acetate, hexyl butanoate, hexyl hexanoate, 2-methylbutyl acetate; **norisoprenoids**: β-damascenone
Apricot (*Prunus armeniaca* L.)	**Alcohols**: 2-phenylethanol; **carbonyls**: benzaldehyde; **terpenoids**: linalool, α-terpineol, 4-terpineol
Blackcurrant (*Ribes nigrum* L.)	**Carbonyls**: 1-octen-3-one; **esters**: ethyl butanoate, ethyl hexanoate, methyl butanoate; **norisoprenoids**: α-damascenone; **pyrazines**: 2-methoxy-3-isopropylpyrazine; **terpenoids**: cineole, linalool, 4-terpineol; **sulfur compounds**: 4-methoxy-2-methyl-2-butanethiol
Citrus juices:	**Carbonyls**: 4,5-epoxy-*trans*-2-decenal, 1-hepten-3-one, *cis*-3-hexenal; **esters and lactones**: ethyl butanoate, wine lactone; **sulfur compounds**: *p*-1-menthene-8-thiol, 4-mercapto-4-methyl-2-one
Grapefruit (*Citrus* x *paradisa* Macfad.), lemon (*Citrus limon* (L.) Burm. f.), Orange (*Citrus sinensis* (L.) Osbeck)	**Alcohols**: ethanol, methanol; **carbonyls**: 2-methyl-3-buten-2-ol; 4-methyl-2-pentanone, perillaldehyde; **esters**: ethyl acetate **terpenoid**s: carvone, geranial, limonene, linalool, neral, γ-terpinene, α-terpineol, terpinen-4-ol
	Carbonyls: acetaldehyde, octanal; **esters**: ethyl butanoate; **terpenoids**: citral, limonene, linalool, α-pinene
Grape (*Vitis vinifera* L., *V. labrusca*, *V. riparia*, *V. rupestris*, etc.	**Alcohols**: hexan-1-ol, 2-phenylethanol; **carbonyls**: 2,3-butanedione, decanal, 2-*cis*-6-*trans*-nonadial; **esters**: ethyl butanoate, ethyl 2-methylbutanoate, methyl anthranilate[b]; **furans**: 4-hydroxy-2,5-dimethyl-3(2H)-furanone; **pyrazines**: 3-isobutyl-2-methoxypyrazine, 3-isopropyl-2-methoxypyrazine; **terpenoids and norisoprenoids**: β-damascenone, geraniol[c], linalool[c] **sulfur compounds**: 3-(methylsulfanyl)propanal
Peach (*Prunus persica* (L.) Bartch var. persica	**Carbonyls**: benzaldehyde; **esters and lactones**: γ-decalactone, ethyl acetate, hexalactone, methyl acetate; **norisoprenoids**: β-damascenone
Pear (*Pyrus communis* L.)	**Esters**: ethyl 2,4-decadienoate; **terpenoids**: *trans*, *trans*-α-farnesene
Pineapple (*Ananas comosus* (L.) Merr.	**Esters and lactones**: allyl hexanoate, ethyl and methyl 2-hydroxybutanoate, ethyl and methyl 2-hydroxyhexanoate, ethyl and methyl 2-methylbutanoate, methyl 2-methylpropanoate, γ−nonalactone, δ-octalactone, γ-octalactone; **furans**: 4-hydroxy-2,5-dimethyl-3(2H)-furanone; **terpenoids and isoprenoids**: *trans*-β-damascenone
Strawberry (*Fragaria x ananassa* Duch.)	**Carbonyls**: 2,3-butanedione, *cis*-3-hexenal, **esters**: ethyl and methyl butanoate, methyl 2-methylpropanoate; **furans**: 4-hydroxy-2,5-dimethyl-3(2H)-furanone
Tomato (*Lycopersicon esculentum* Mill.)	**Alcohols**: *cis*-3-hexenol 3-methylbutanol; **carbonyls**: hexanal, *cis*-3-hexenal, *trans*-2-hexenal, 6-methyl-5-hepten-2one; **norisoprenoids**: α-ionone; **thiazoles**: 2-isobutylthiazole

[a]Data from McKay et al. (2011), Heredia et al. (2013) and references therein
[b]Important in *V. labrusca, riperia* and other American species (and some hybrids)
[c]Prevalent in muscat and/or traminer varieties of *V. vinifera*

Table 4 Important non-anthocyanin phenolic compounds in fruit juices

Class	Examples	Comments
Hydroxybenzoic acid type	*p*-Hydroxybenzoic acid, gallic acid, gentisic acid	Usually present as glycosides in apple, grape and pear juice
Hydroxycinnamic acid derivatives	Caffeic acid, *p*-coumaric acid, ferulic acid, sinapic acid	In many fruit juices, including black and white grape juice
		Caffeic and *p*-coumaric acids are often present as quinic acid derivatives (e.g., chlorogenic acid ≡ caffeoylquinic acid) – these are constituents of apple and pear juice
		Glucosides and tartrate esters (e.g., caftaric acid) are found in grape juice
Chalcones; dihydrochalcones	Butein, chalconaringenin, licochalcone, okanin; phloretin	Phloridzin (phloretin 2′-glucoside) is a component of apple and pear juices
Flavan-3-ols	(+)-Catechin and (−)-epicatechin	Present as aglycones in many fruit juices, such as apple, citrus, grape, and pear juices
Flavones	Apigenin, diosmetin, luteolin, nobiletin, sinensetin, tangeretin	Both types are mostly present as glycosides. Flavones are common in citrus fruit juices. Also polymethoxy derivatives are found in orange juice. Flavonol glycosides (e.g., quercetin-3-*O*-rutinoside or rutin) are components of most fruit juices
Flavonols	Isorhamnetin, kaempferol, myricetin, quercetin, rhamnetin	
Flavanones; Flavanonols	Didymin, heridictyol, hesperitin, isosakuranetin, narigenin; Dihydroquercetin	Flavanones are important components of citrus juices, usually as neohesperidosides (7-*O*-β-glc-(2–1)-α-rha) or rutinosides (7-*O*-β-glc-(6–1)-α-rha)
Flavan-3,4-diols	Cyanidinol	Especially prevalent in perry pear juice
Condensed tannins: procyanidins and condensed proanthocyanidins (>10 flavan monomer units)	Dimers, trimers, and upwards of (+)-catechin and (−)-epicatechin, with 4–8 (sometimes 4–6) links or with a 4–8 and a 2–7 ether link	In apple, pear, and grape juices in particular, especially in black grape juice and cider apple and perry pear juices after some skin contact
Stilbenes	Piceatannol, resveratrol	In juice of blueberry and related fruits (e.g., huckleberry). Also in black grape juice
Hydrolyzable tannins (glucosidic esters of gallic acid, ellagic acid, and other phenolic acids)	Castalin, castalagin, ellagitannin, vescalin, vescalagin	Ellagitannin is found at low concentrations in some fruit juices (especially blackberry, raspberry, and strawberry); higher levels if seeds are ruptured during juicing

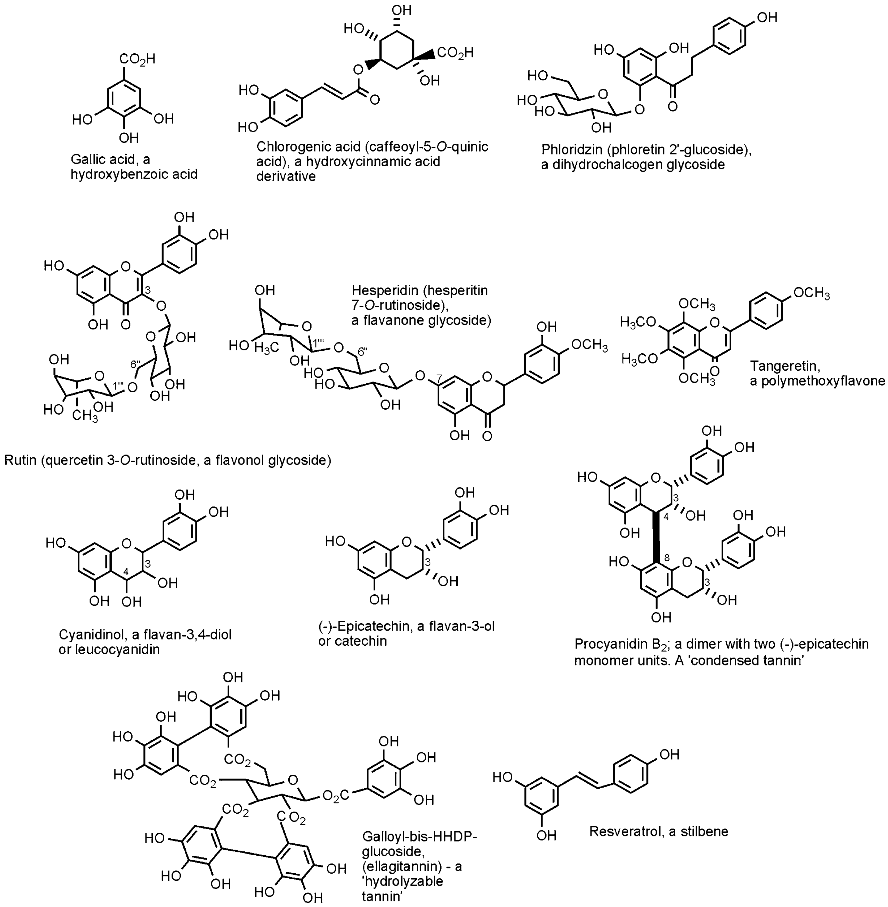


Fig. 3 Structures of some fruit juice phenolic compounds

The simplest phenols, hydroxybenzoic acids, are usually present as glycosides (mostly glucosides) in fruit juices: free forms are more prevalent in wine, especially red wine. Hydroxycinnamic acids are present as glucosides and also as esters of tartaric acid (e.g., *p*-coumaryl tartaric acid or coutaric acid and cafeyl tartaric acid or caftaric acid) or quinic acid (e.g., coumaroylquinic acid; Fig. 3). Many hydroxycinnamic acids, in their various forms, are significant components of apple, grape, pear, and other fruit juices, where some are involved in "browning" (see Fig. 11). Also, caffeic and *p*-coumaric acids can combine with anthocyanidin 3-*O*-glucosides to form small quantities of acylated anthocyanins in black grape and other purple fruit juices (Fig. 1).

Chalcones and dihydrochalcones are comparatively rare, but phloretin and phloridzin in particular are important phenolic constituents of apple and pear juices. Monomeric flavonoid phenols are generally widespread throughout fruit juices, the

Table 5 Total phenolic content (TPC) and phenolic composition of selected fruit juices

Juice	TPC (mg GAE/L)	Major phenolic components (mg/L)
Apple[a] (from specific eating apples)	154.4–178.0	Hydroxycinnamic acids (56.8–67.7), dihydrochalcones (9.8–35.2), flavan-3-ols (7.6–54.6), procyanidins (32.3–46.8), flavonols (1.6–3.6)
Apple[b] (from German cider apples)	261.2–970.0	Hydroxycinnamic acids (138.5–592.6), dihydrochalcones (33.5–171.0), flavan-3-ols (32.8–249.1), procyanidins (32.0–143.4), flavonols (4.9–26.7)
Apple[c] (commercial juices)	109.9–495.0	Hydroxycinnamic acids (68.6–259.0), dihydrochalcones (9.4–75.8), flavan-3-ols (14.0–102.1), procyanidins (tr.–60.9), flavonols (tr.–13.5)
Cherry (sweet)[d,e]	44.3–87.9	Chlorogenic acid (0.60–2.61), *p*-coumaric acid (0.77–7.20), epicatechin (0.43–3.70), neochlorogenic acid (4.74–11.9), rutin (2.06–5.78)
Grape[f]	~300 (white) ~2,000 (black)	Hydroxybenzoic and hydroxycinnamic acids as glycosides (100–200 in black grape juice) (10–20 in white grape juice), flavonols as glycosides (~100 in black grape juice) (1–3 in white grape juice), flavan-3-ols (~1,000 in black grape juice) (100–200 in white grape juice), procyanidins (~1,000 in black grape juice) (100–300 in white grape juice), flavanonols as glycosides (2.3–116), flavan-3,4-diols (2.3–116 in white grape juice), flavones (3–93 in white grape juice only)
Grapefruit[g]	–	Flavanones: narirutin 4′-glucoside(9–15), naringin 4′-glucoside (16–21), rhoifolin 4′-glucoside (0–16), neoeriocitrin (0–4), narirutin (136–163), naringin (420–480), neohesperidin (6), rhoifolin (0–23), naringin-6′-malonate (24–33), poncerin (8–10)
Grapefruit[h]	441.09–725.71	Hydroxybenzoic acids: gallic acid (3.18–4.53), *p*-hydroxybenzoic acid (0.87–2.45), protocatechuic acid (1.87–3.70), vanillic acid (0.58–5.30)
		Hydroxycinnamic acids: caffeic acid (4.15–6.90), chlorogenic acid (3.12–5.17), *p*-coumaric acid (13.70–16.30), ferulic acid (14.09–26.46), sinapic acid (9.21–13.44)
		Flavanones: didymin (4.30–12.48), hesperidin (8.47–10.25), naringin (270.21–464.13), narirutin (63.80–120.06), neohesperidin (14.72–24.24), poncirin (16.98–26.02)
Orange[i]		Flavanones: naringenin 7-rutinoside-4′-glucoside (3.1), hesperetin 7-rutinoside-3′-glucoside (5.1), naringenin 4′-methyl-7-rutinoside (9.2), naringenin 7-rutinoside (33.2), hesperetin 7-rutinoside (86.3)

(*continued*)

Table 5 (continued)

Juice	TPC (mg GAE/L)	Major phenolic components (mg/L)
Tomato[j]	92.8–128.9	Hydroxycinnamic acids: caffeic acid (0.15–0.47), caffeic acid glycoside (0.22–0.68), chlorogenic acid (0.84–1.56), cryptochlorogenic acid (0.47–0.95), dicaffeoylquinic acid (0.15–0.27), ferulic acid glycoside (1.92–4.52)
		Flavanones: naringenin (3.60–7.04), naringenin 7-*O*-glucoside (0.13–0.58)
		Flavonols: kaempferol 3-*O*-glucoside (0.57–1.17), kaempferol 3-*O*-rutinoside (1.59–3.57), Quercetin (0.13–0.55), rutin (5.03–8.91)

[a]Kahle et al. (2005); *Malus domestica*: Fuji, Golden Delicious, Granny Smith, Red Delicious
[b]Kahle et al. (2005); *Malus sylvestris*: Bittenfelder, Bohnapfel, Boskoop, Brettacher, Kaiser Alexander, Kaiser Wilhelm, Winterrambur
[c]Kahle et al. (2005); probably mostly *M. domestica* blends
[d]Usenik et al. (2008); *Prunus avium* L.
[e]TPC in mg GAE/100 g FW; composition in mg/100 g FW
[f]Ribereau-Gayon et al. (2000, pp. 129–186); Amerine and Ough (1980, pp. 175–199); *V. vinifera*
[g]Hsu et al. (1998); Actually juice of two common *Citrus grandis* Osbeck x *Citrus x paradisi Macfad. crosses: Melogold and Oroblanco*
[h]Kelebek (2010); (*Citrus x paradisi Macfad.*) *Handerson*, *Rio red*, *Ruby red*, *Star ruby*
[i]Tomás-Navarro et al. (2014); actually juice of Citrus hybrid between mandarin and sweet orange (*Citrus sinensis* L. var. "Ortanique")
[j]Vallverdú-Queralt et al. (2013)

major flavonoid classes being flavones, isoflavones, flavonols, flavanones, flavanonols, flavan-3-ols (catechins), and flavan-3,4-diols (leucoanthocyanins or anthocyanogens). Of these, flavan-3-ols and flavonols are almost ubiquitous in fruit juices, probably partly because they are located in both the pulp (or pericarp) and skins of fruit, whereas others, such as flavones, are concentrated in skins or peel. Flavanones are usually the most abundant flavonoids of citrus juices, while flavones, located mostly in the peel, are usually present only at low or trace levels (or are undetectable), although polymethoxylated flavones exist in tangerine and some other citrus juices. Flavanonols (e.g., dihydroquercetin or taxifolin) are found in grape juice, and flavan-3,4-diols are significant constituents of pear juice. The majority of flavonoid phenols exist mainly as *O*-glycosides in fruit juices: exceptions include flavan-3-ols, which are always present as aglycones, and a few flavones in citrus peel that exist as *C*-glycosides.

Oligomeric and polymeric flavonoid phenols (condensed tannins) are also important in many juices, including apple, bilberry/blueberry, cherry, grape, and pear juices. They are generally known as procyanidins and mostly consist of (+)-catechin and/or (−)-epicatechin monomer units. Type B (the most common) has C(4)-C(8) or C(4)-C(6) interflavan bonds, whereas type A has an addition ether bond between C(5) or C(7) on the lower flavonoid unit and C(2) on the upper unit. Procyanidins exist largely as aglycones, with dimers and trimers being most common, but polymers of up to 17 units exist in cider apple juice.

Flavan-3-ols, procyanidins, and other polyphenols are also capable of forming oligomers with anthocyanins or their derivatives, but these are more important in wine (Fig. 10). Hydrolyzable tannins such as ellagitannins (Fig. 3) are rare in juices (e.g., cherry, raspberry, and strawberry juices) but are more common in oak-aged wine.

Carbohydrates

Free sugars are crucial to the palatability of fruit juices, but carbohydrates in general, including their derivatives (such as sugar acids and reduced monosaccharides or polyols), are present in juices in many different guises, as outlined in Table 6. Total free sugars are often estimated from measurement of total soluble solids, using either a hydrometer or refractometer.

Table 7 lists typical values for common fruit juices, using the °Brix (Balling or Plato) scale, which is probably the most widely used scale for this purpose. It is an approximate measure of mass of sugar (in g) per 100 g juice – % sugar (w:w).

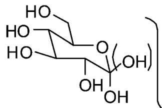
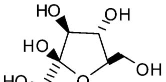
It can be seen from Table 8 that the most abundant fruit juice free sugars are the disaccharide sucrose (saccharose), along with the monosaccharides D-fructose and D-glucose, the first two being especially prevalent. Other free sugars exist in fruit juices but usually at low to very low levels: these include the monosaccharides L-arabinose, D-galactose, L-rhamnose, D-ribose, and D-xylose; the disaccharides lactose, maltose, melibiose, and trehalose; and the trisaccharide raffinose. Juice of *V. vinifera* grapes contain only minute amounts of sucrose and no trehalose, whereas most other fruit juices (including those of other *Vitis* species, such as *V. labrusca*) contain considerable, even dominant, amounts of sucrose.

With respect to relative sweetness, if sucrose has a rating of 1, fructose rates 1.73, glucose rates 0.74, and the pentoses (L-arabinose, etc.) rate about 0.4 so that, if the total sugar content of two juices is the same, the juice with the higher fructose–sucrose–glucose ratio will be sweeter.

Depending on the processing methods, varying amounts of pectic substances, oligomers and polymers of β-D-glucose, and oligomers and polymers of L-arabinose and D-xylose are present (Table 6). All of these are "fibrous" and are "soluble" or "insoluble" according to the extent of polymerization and branching, the insoluble materials forming part of the cloud. They arise from the breakdown of pectic and cellulosic structural materials of the fruit. If β-glucanase and xylanase enzymes (for cellulose/arabinoxylan degradation) and pectinase (pectolase) enzymes (for pectin degradation) have been used in the juicing process and if the juice has been filtered, then it will contain only relatively small amounts of soluble oligomers and monomers (including low-trace levels of rare sugars and derivatives – see Table 6). Freshly pressed juice, however, will contain a significant amount of fibrous material (dietary fiber) – see Table 10.

Polyols (sugar alcohols), such as sorbitol, are present in apple, cherry, and pear juices in particular but not in grape juice that has been prepared from healthy fruit. However, grapes that have been infected by the fungus *Botrytis cinerea* will give juice that contains low levels of glycerol, mesoinositol, and sorbitol. Under the right conditions, this is favorable for the production of certain types of wine, but table grapes grown to produce juice for drinking should always be healthy.

Table 6 Carbohydrates in fruit juices

Carbohydrate context	Comments
Free sugars	
α(β)-D-Glucopyranose   β-D-Fructofuranose Sucrose: α–D-glcp-(1-2)-β-D-fruf	These are the major free sugars of fruit juices. Fructose is probably the most important overall. Glucose and fructose are by far the main free sugars of grape juice, but sucrose is abundant in many fruit juices, such as apple, citrus, peach, pear and strawberry juices. β-D-galactose is found at low levels in some juices (e.g. grape juice, ~0.1 mg/L). Other disaccharides; lactose, maltose, melibiose, and raffinose are present at very low levels in many juices.
Gluconic acid, *meso*-inositol, mannitol and sorbitol (sugar alcohols)	Gluconic acid is the major sugar acid of fruit juices. Apple and pear juices are relatively rich in sorbitol. *meso*-Inositol is found in grape juice.
Glycosidic units	
β-L-Arabinose, β-D-glucopyranose, β–D-galactose α-L-rhamnose, β-D-xylose (monosaccharides) Rutinose (β–D-glc-(6-1)-α-L-rha), neohesperidose, (β–D-glc-(1-1)-α-L-rha), sophorose, (β–D-glc-(2-1)-β-D-glc), sambubiose (β–D-glc-(2-1)-β-D-xyl) (disaccharides)	These are the main monosaccharide sugars of the wide range of glycosides of odorous alcohols (including terpenols) and phenols (including simple phenols and flavonoid phenols) found in all fruit juices. The sugar units are usually linked to the aglycone by ether (C-O-C) bonds, but sometimes by C-C bonds.
Sugar components of pectic substances	
α-D-Galacturonic acid and methyl galacturonate β-L-Rhamnose, α-L-arabinose	These units form the backbone of fruit pectic substances. L-rhamnose forms part of the rhamno-glacturonan regions of pectic substances; L-arabinose occurs in side chains and in regions of the main chain.
β-D-Apiose, α-L-fucose, 2-*O*-methyl-α-L-fucose, β-D-glucuronic acid, β–deoxy-D-lyxo-heptulosaric acid, 2-keto-3-deoxy-D-manno-2-octulosic acid, β-3-*C*-carboxy-5-deoxy-L-xylose and 2-*O*-methyl-α-D-xylose	These rare sugars are found in rhamnogalact-uronan II regions of pectic substances. These regions are resistant to pectinase action and may be the only pectic substances found in fruit juices made using total liquefaction by pectinase enzymes.
Sugar components of cell wall polysaccharides	
β-D-glucopyranose, β-D-xylose, α-L-arabinose	These are the monomers of cellulose, which together with pectic substances and lignins forms the cell walls of fruit. Glucose polymers are called β-glucans and xylose polymers are known as β-xylans. Polymers of β-D-xylose and α-L-arabinose are sometimes known as pentosans.

Uronic acids (sugar acids), principally galacturonic acid, are found in many fruit juices, including grape juice, where total uronic acid concentration is generally 100–300 mg/L.

Acids

Like sugars, acids are also crucial to the palatability of fruit juices – without them they would taste flat and sugary, many would have different colors, and they would all be highly prone to microbiological spoilage. Table 7 displays the total acidity of

Table 7 Total soluble solids and total acid content of selected fruit juices[a]

Fruit	Apple[b]	Apricot	Bilberry	Blueberry	Blackberry	Black currant
Total soluble solids (°Brix)[c]	11–17	13–14	8–12	11–13	8	10
Total acidity (g/L)	2–10	6–15	8	3	12	30
Fruit	Cherry	Grape (table)	Grape (wine)	Grapefruit	Guava	Mango
Total soluble solids (°Brix)	13–18	14–20	18–32	8–11	8–10	11–15
Total acidity (g/L)	10–26	3–6	6–9	12–14	5	11–14
Fruit	Orange	Peach	Pear[b]	Pineapple	Strawberry	Tomato
Total soluble solids (°Brix)	11–13	11–15	13–17	12–18	8	5–7
Total acidity (g/L)	10–13	4–9	3–10	9–12	12	3–5

[a]Typical values or ranges. Data from Amerine and Ough (1980, pp. 45–73), Chinnici et al. (2005), Shamsudin et al. (2005), Cheng et al. (2007), McKay et al. (2011, pp. 419–435), Li et al. (2012)
[b]Lower °Brix values and lower total acidities tend to be associated with cider apples and perry pears
[c]Total soluble solids (an approximate measure of sugar content) ~g sugar/100 g juice

selected juices, where it can be seen that there is a wide acidity range, from mildly acidic apple or grape juices to highly acidic black currant juice.

Table 8 shows that the most common and most abundant fruit juice acids are citric and malic acids, but in general juice organic acids are mostly low-molecular-weight mono-, di-, and tricarboxylic acids with pK_a values in the range 3.01–5.74. They all exist largely as free (molecular or undissociated) acids, but those with lowest pK_a(1) values, especially L-(+)-tartaric acid (3.01), citric acid (3.09), and L-(−)-malic acid (3.46), will be present in partial salt form (see "Salts" subsection). To these we can add the inorganic acids phosphoric and sulfuric acids, which will be present mainly as dissociated salts, ascorbic acid (see "Vitamins" subsection), the sugar acids, and the very weakly acidic phenolic acids mentioned in previous subsections.

Other carboxylic acids found in juices include tartaric acid (especially important in grape and pomegranate juice), acetic, isocitric, pyruvic, quinic, succinic, and some other acids of the citric acid cycle/glycolysis pathway.

Amino Acids, Peptides, and Proteins

Of the total nitrogen content of ripe fruit juices, as determined by the Kjeldahl or Dumas methods, normally less than 10 % is present as inorganic nitrogen (mainly NH_4^+); amino acids and peptides make up about 30–40 % each and the rest is made up of mainly proteins, along with small amounts of amines, amino sugars, *N*-heterocycles, and *N*-containing vitamins.

Amino acids include the "magic twenty" protein components, plus citrulline, hydroxyproline, norvaline, and ornithine (all L-α-amino acids), as well as β-alanine and γ-aminobutanoic acid (GABA). Table 9 displays the total amino acid content

Table 8 Major acids and free sugars of selected fruit juices

Juice	Apple	Apricot	Grape	Grapefruit	Mandarin	Mango
Acids (g/L)	M (1.4–5.6)[a]	M (2.3–5.1)[a]	T (4.0–8.0)[b]	C (19–24)[c]	C (12–17)[d]	M (6.9–10)[e]
	C (tr.–1.1)	C (2.1–3.2)	M (2.0–5.0)	M (1.8–3.0)	M (3.8–8.0)	C (1.6–2.6)
	S (0.2–0.8)	S (0.1–0.8)	S (0.5–1.0)	S (0.2–0.6)	S (0.8–3.7)	S (0.9–1.6)
		Q (tr.–0.4)	U (0.1–0.3)			T (0.1–0.9)
						A (0.16)
Sugars (g/L)	Fr (60)[g]	Su (35–69)[a]	Fr (80–130)[b]	Su (29–35)[c]	Su (28–68)[d]	Fr (50–53)[e]
	Gl (17)	Gl (45–63)	Gl (70–120)	Fr (22–27)	Fr (9.2–22)	Su (33–80)
	Su (25)	Fr (33–44)		Gl (22–25)	Gl (6.9–20)	Gl (20–28)
	So (5)					

Juice	Peach	Pear	Pomegranate	Strawberry
Acids (g/L)	M (1.5–5.6)[a]	C (1.5–2.0)[a]	C(2.0–10.0)[f]	C (0.5–1.0)[g]
	C (1.0–1.9)	M (0.5–1.2)	M (3.0–3.5)	M (0.1–0.2)
	S (0.1–1.5)	S (0.4–1.0)	T (0.2–0.6)	Q (t-0.2)
		Q (t-0.07)		S (0.02)
Sugars (g/L)	Fr (22–75)[a]	Fr (48–68)[a]	Fr (40–50)[f]	Gl (2.9–6.4)[g]
	Su (20–77)	So (15–28)	Gl (40–50)	Fr (1.8–3.5)
	Gl (37–43)	Gl (17–20)		Su (0.9)
		Su (1.7–15)		

Key: *A* Acetic, *C* Citric, *Q* Quinic, *S* Succinic, *T* Tartaric, *U* Uronic (sugar acids). Sugars: *Fr* Fructose, *Gl* Glucose, *Su* Sucrose, *So* Sorbitol, *tr.* trace

[a]Chinicci et al. (2005)

[b]Ribéreau-Gayon et al. (2000, pp. 3–40; 55–80)

[c]Kelebek (2010)

[d]Sdiri et al. (2012)

[e]Li et al. (2012)

[f]Mena et al. (2012)

[g]Gündüz and Özdemir (2014)

and the most abundant amino acids in selected fruit juices. They are predominantly L-isomers, but it is evident that the levels of individual amino acids in juice depend on processing methods. Generally lower levels have been found in pomegranate, strawberry, and tomato juices prepared from concentrates or by using some kind of heat treatment than in freshly squeezed juices (Vallverdú-Queralt et al. 2013). Likewise, concentrations of D-isomers (e.g., D-PRO) are higher in heat-processed juices (Tezcan et al. 2013).

Oligopeptides (up to tetrapeptides), such as glutathione, and polypeptides (<10,000 Da molecular weight) constitute a considerable part (~30–40 %) of the organic nitrogen content of juices but have not been extensively studied. Proteins are present in juices in concentration up to ~300 mg/L. Grape juice has several of molecular weight 10,000–100,000 Da but with the majority being in the 20,000–50,000 Da range. Many of the proteins are typical of fruit proteins and include chitinases, lipid transfer proteins, pathogen-related proteins, ripening-

Table 9 Total amino acid content and major α-amino acids of selected fruit juices

Juice	Total amino acid content (mg/L)	Major amino acids (most abundant on left). All L isomers, except where specified otherwise
Apple[a]	~800	ASN, ASP, NVAL, SER, GLU, ALA, PRO, ILEU, THR ~ VAL, LEU ~ PHE
Grape[b]	1,500–4,000	PRO, ARG, GLU, SER, ALA, α-ABA, THR, ASP
Pear[c]	~2,700	ASP, GLU, LEU, LYS ~ SER ~ VAL, ALA, GLY ~ ILEU ~ PRO, PHE, ARG, CYS ~ HIS, MET, TYR
Pomegranate[d]	733–3,374	SER, L-PRO, ALA, D-PRO, GLU, TRP, ARG, ASP, ASN, LEU
Strawberry[e]	418.7–464.5	ALA, SER, ASP, GLU, THR, VAL, GLY ~ ILEU, TYR, LUE ~ PHE, LYS
Tomato[e]	445.0–768.8	GLU, PHE, SER, HIS, ASP, LYS, ILEU, ARG, VAL, ALA, MET, GLY

[a]Phenomenex Inc. (2014) Application data (*NVAL* Norvaline)
[b]Buglass and Caven-Quantrill (2013) and references therein; α-ABA, α-aminobutanoic acid
[c]USDA National Nutrient Database for Standard Reference Release
[d]Tezcan et al. (2013); one juice also contained D-LEU
[e]Vallverdú-Queralt et al. (2013)

related proteins, thaumatin-like proteins, and vacuolar invertase 1, G1N1. Similar proteins are found in wine (see Table 13; Wigand et al. 2009).

Inorganic Cations and Anions (Electrolytes)

Fruit juices can be significant sources of mineral nutrients, which are present as salts of various inorganic and organic acids (Table 10). The macronutrients are Ca, K, Mg, N, Na, and P, the metals existing as their cations, N as NH_4^+ (ammonium), and P as phosphate anions. Micronutrients, often called trace elements, include B, Cu, Fe, Mn, Se, Si, and Zn.

If juice is evaporated to dryness, the dry extract (usually ~15–30 g/L juice) contains all the nonvolatile organic matter, plus inorganic compounds. When the dry extract is combusted at 525 °C, in a stream of air, all organic salts (acetates, tartrates, etc.), except ammonium salts, are converted to inorganic salts, mostly carbonates, the resulting ash usually being ~1.5–3.0 g/L juice. The total inorganic salt content can be estimated by titration.

Potassium is the most abundant ion, followed by calcium and phosphate, then N (as NH_4^+), and magnesium. Sodium is normally found at lower levels in juice (1–4 mg/100 g juice), an exception being pomegranate juice, which has ~9 mg/100 g juice (Table 10). The most abundant inorganic anions (after phosphates) are chloride and sulfate. Of the micronutrients, Fe is usually found at higher levels than Zn, although some juices, such as pomegranate juice, are good sources of dietary B and Mn.

Many minerals may persist into alcoholic beverages during fermentation and other processes, although some, like Ca and P, may be partially removed by precipitation, while others, such as Ca, NH_4^+, SO_4^{2-}, Na, Cu, Fe, and others, may accumulate (deliberately or by accident) at certain stages of the process.

Table 10 Total mineral, vitamin, and dietary fiber content of selected fruit juices[a]

Juice	Mineral content (mg/100 g juice)	Vitamin content (/100 g juice)	Total dietary fiber (g/100 g juice)[b]
Apple	K = 101, Ca = 8, P = 7, Mg = 5, Na = 4; Fe = 0.12, Zn = 0.02	Vit. C = 0.9 mg, niacin = 0.073 mg, vit. B_6 = 0.018 mg, riboflavin = 0.017 mg, vit. E = 0.01 mg	0.5
Blood[c] orange	K = 171.2, P = 8.8, Mg = 6.7, Ca = 5.9, Na = 1.3; Fe = 0.25, Zn = 0.12, Cu = 0.113, Mn = 0.076, Se = 0.001	–	–
Clementine	K = 177, Ca = 30, P = 21, Mg = 10, Na = 1; Fe = 0.14, Zn = 0.06	Vit. C = 48.8 mg, niacin = 0.636 mg, thiamin = 0.086 mg, vit. B_6 = 0.075 mg, riboflavin = 0.030 mg, vit. E = 0.20 mg, folate = 0.024 mg,	0.3
Grape	K = 104, P = 14, Ca = 11, Mg = 10, Na = 5; Fe = 0.23, Zn = 0.08	Vit. C = 0.12 mg, niacin = 0.12 mg, vit. B_6 = 0.04 mg, pantothenic acid = 0.04 mg,	–
		Vit. A = 0.4 μg (8 I.U.), vit. K = 0.4 μg	
Grapefruit	K = 143, Ca = 12, P = 12, Mg = 9; Fe = 0.08, Zn = 0.07	Vit. C = 33 mg, niacin = 0.269 mg, vit. B_6 = 0.043 mg, thiamin = 0.037 mg, riboflavin = 0.020 mg, folate = 0.012 mg, vit. A = 0.005 mg (101 I.U.)	–
Lemon	K = 103, P = 8, Ca = 6, Mg = 6, Na = 1; Fe = 0.08, Zn = 0.05	Vit. C = 38.7 mg, niacin = 0.091 mg, vit. B_6 = 0.046 mg, thiamin = 0.037 mg, folate = 0.020 mg, riboflavin = 0.015 g, vit. E = 0.15 mg, vit. A = 0.005 mg (101 I.U.)	0.3
Orange	K = 200, P = 17, Ca = 11, Mg = 11, Na = 1; Fe = 0.20, Zn = 0.05	Vit. C = 50.0 mg, niacin = 0.400 mg, thiamin = 0.090 mg, vit. B_6 = 0.040 mg, riboflavin = 0.030 mg, folate = 0.030 mg, vit. A = 0.010 mg (200 I.U.), vit. E = 0.04 mg, vit. K = 0.1 μg	0.2
Pear	K = 130, Ca = 12, P = 12, Mg = 8, Na = 8, Zn = 0.08	Vit. C = 34 mg, niacin = 0.300 mg, riboflavin = 0.030 mg, thiamin = 0.010, vit. B_6 = 0.010 mg, folate = 0.004 mg, vit. E = 0.09 mg, vit. K = 0.003 mg	0.4

(*continued*)

Table 10 (continued)

Juice	Mineral content (mg/100 g juice)	Vitamin content (/100 g juice)	Total dietary fiber (g/100 g juice)[b]
Pineapple	K = 130, Ca = 13, Mg = 12, P = 8, Na = 2; Fe = 0.31, Zn = 0.11	Vit. C = 43.8 mg, Niacin = 0.636 mg, vit. B_6 = 0.100 mg, thiamin = 0.058 mg, riboflavin = 0.021 mg, vit. E = 0.02 mg, folate = 0.018 mg, vit. A = 2.5 μg (51 I.U.)	0.2
Pomegranate	K = 214 Ca = 11.0, P = 11.0, Na = 9.0; Mg = 7.0, Fe = 0.080, Zn = 0.080, Mn = 0.080	Vit. E = 0.36 mg, pantothenic acid = 0.28 mg, niacin = 0.24 mg, vit. C = 0.080 mg, vit. B_6 = 0.040 mg, folate = 0.024 mg, vit. K = 0.010 mg	–

[a]Data from USDA (2014) National Nutrient Database for Standard Reference Release, unless stated otherwise. Metals as cations, P as phosphate
[b]Fresh whole fruit generally possess higher levels of fiber, followed by freshly pressed juice (e.g., 1.5–2.4 g/L for citrus fruits)
[c]Cautela et al. (2009)

Vitamins

Like the parent fruits, juices are good sources of a wide range of vitamins. Table 10 displays the main vitamin content of selected juices, where it can be seen that vitamin C (ascorbic acid) is the most abundant and most widespread vitamin, having high levels in citrus juices (typically ~50 mg/100 g juice). High levels are found in black currant and guava juices too (181 and 110 mg/100 g juice, respectively). Niacin is usually the next most abundant vitamin (~0.2–0.4 mg/100 g juice), followed by vitamin B_6 (pyridoxine), thiamine (B_1), riboflavin (B_2), vitamin E, pantothenic acid, folate, and vitamin K. An exception is pomegranate juice, which has pantothenic acid as the main vitamin, and it has relatively high levels of folate and (particularly) vitamin K (e.g., ~0.010 mg/100 g juice – about 25 times the concentration in grape juice).

Vitamin levels are generally higher in freshly pressed juices – processing steps, such as pasteurization and evaporation, are known to deplete the juice vitamin content somewhat. Likewise, vitamin levels tend to be lower in alcoholic beverages made from fruit juices, although some, especially B vitamins and vitamin C, can be added legally at certain production stages.

Other Components

Nonvolatile triterpenoids, such as limonin, nomilin, nomilinic acid, obacunone glucosides, and aglycones, are found in citrus juices. During fruit maturation, total glucoside concentration rises, while total aglycone level drops, often to below taste perception levels (~6 mg/L juice): glucosides are tasteless, but aglycones are bitter and can be a cause of consumer rejection. Total limonoid glucoside levels vary between about 60 mg/L for some grapefruit hybrid juices, through ~190 mg/L for grapefruit juices, and ~320 mg/L juice for some sweet orange juices (Hsu et al. 1998). Some grapefruit cultivar and hybrid citrus juices have total aglycone levels above the taste threshold.

Pentacyclic triterpenoids (again nonvolatile), such as maslinic acid, oleanolic acid, ursolic acid, and derivatives, are found in the waxy skins of many fruits, including apples and pears. See Fig. 25. They are potent in vitro anticancer agents. Ursolic acid is present at levels up to 1.6 g/kg fruit in apples, and cloudy juices contain low levels of these compounds, depending on the processing (Fuller et al. 2011, pp. 1093–1110 and references therein).

Nonalcoholic Carbonated Beverages

Carbonated drinks form an important part of the soft drinks industry. They can be divided into the following major categories:

- Mineral water and soda water
- Fruit drinks
- Cola- and root beer-type drinks
- Tonic water

Apart from (unflavored) mineral water and most soda water, all categories have added compounded flavor mixtures, sugar, or low-calorie sweeteners, and some have added colorants. The carbonation level of most drinks is around 3 vols CO_2 per vol liquid, which gives internal pressures of ~2 atm at 4 °C and ~2.5–3 atm at 21 °C.

Carbonated Mineral Water and Soda Water

Carbonated mineral water is sourced from natural springs or from deep subterranean aquifers, where it is carbonated by natural CO_2 at above atmospheric pressure. Nowadays, the CO_2 is usually removed at source and then added back when the water is bottled, typically at 4 °C and under CO_2 pressure of 1.2 atm. During its long contact with rock, the water acquires many mineral ions, its mineral profile depending largely on local geology (Table 11). Bottled mineral water must conform to national standards of purity and must be consistent with regard to pH and mineral content. It is permissible to remove undesirable constituents, such as volatile sulfur compounds (e.g., in hot volcanic springwater), Fe^{2+}/Fe^{3+},or Mn^{3+}, prior to treatment with ozone and/or UV light (to kill microorganisms) before bottling.

Water that flows through limestone or chalk tends to be alkaline, with high HCO_3^-, Ca^{2+}, and Mg^{2+} content – and sometimes with high sulfate and Na^+ content too – whereas water flowing through basalt or other volcanic rock tends on the acidic side, with lower total dissolved solids (TDS) (Table 11).

Table 11 Major mineral content (mg/L) of some bottled carbonated mineral waters[a]

Dolomite (Italy) (limestone)	Vergèz Languedoc (France) (limestone)	Eiffel (Germany) (dolomite limestone)	Fiji (volcanic)	Cachet Spring (French Alps) (granite)
pH = 7.8	pH = 5.46	pH = 6.0	pH = 7.7	pH = 7.2
Ca^{2+} = 180	Ca^{2+} = 155	Ca^{2+} = 348	Ca^{2+} = 17	Ca^{2+} = 80
Cl^- = 180	Cl^- = 25	Cl^- = 40	Cl^- = 5	Cl^- = 6
HCO_3^- = 238	HCO_3^- = 445	HCO_3^- = 1,816	HCO_3^- = 140	HCO_3^- = 360
Mg^{2+} = 52.3	Mg^{2+} = 6	K^+ = 11	K^+ = 0	K^+ = 1
Na^+ = 57	Na^+ = 11	Mg^{2+} = 108	Mg^{2+} = 13	Mg^{2+} = 26
Sulfates = 459	Sulfates = 38	Na^+ = 118	Na^+ = 18	Na^+ = 6
NO_3^- = 2.2	NO_3^- = 18	NO_3^- = 18	Sulfates = 0	Sulfates = 12
Si (silicate) = 7.5		Sulfates = 38	Si (silicate) = 94	
TDS[b] = 960	TDS = 688	TDS = 2,479	TDS = 220	TDS = 330
Tŷ Nant (Wales) (granite, sedimentary)	Clairvic spring, (Auvergne, France) (volcanic)	Napa Valley (US) (hot spring)	Vichy (Allier, France) (volcanic)	Catalàn (Girona) (Spain) (volcanic)
pH = 6.8	pH = 7.0			pH = 6.82
Ca^{2+} = 22.0	Ca^{2+} = 11.5	Ca^{2+} = 2	Ca^{2+} = 103	Ca^{2+} = 54.1
Cl^- = 14.0	Cl^- = 13.5	Cl^- = 200	Cl^- = 235	Cl^- = 601.5
HCO_3^- = ?	HCO_3^- = 71	HCO_3^- = 25	HCO_3^- = 2,989	HCO_3^- = 2,135
Mg^{2+} = 11.5	K^+ = 6.2	K^+ = 14	K^+ = 66	K^+ = 48
Na^+ = 22.0	Mg^{2+} = 8	Mg^{2+} = 0	Mg^{2+} = 10	Mg^{2+} = 9.2
Sulfates = 4.0	Na^+ = 11.6	Na^+ = 170	Na^+ = 1,172	Na^+ = 1,110
NO_3^- < 0.1	Sulfates = 8	Sulfates = 110	Sulfates = 138	Sulfates = 138
Dry residue = 165 (at 180 °C)	Si (silicate) = 31.7			(Si) silicate = 76.8
	TDS = 131	TDS = 521	TDS = 4,713	TDS = 3,052

Sulfates = SO_4^{2-} and HSO_4^-
[a]The identity of each mineral water is given by the location of the source, not by brand name
[b]Total dissolved solids

Flavored carbonated mineral water has enough added fruit essences (e.g., lemon, lime, or apple) to give just a light flavor, which means that the flavor and bittering component content will be low.

Nonalcoholic "spritzers" are more substantially flavored sparkling water. They lie between flavored mineral water and fruit drinks, having typical carbohydrate content, protein content, and fiber content of 60–70 g/L, ~1 g/L, and ~1 g/L, respectively.

Soda water (sparkling water or seltzer water) refers to any water (even domestic tap water) that is artificially carbonated, often at CO_2 pressures as high as ~8 atm, at 8 °C. Commercial examples are usually filtered or purified water (which must conform to national purity standards) that contains low levels of added salts (e.g., sodium or potassium bicarbonate or citrate, potassium sulfate, or disodium phosphate). This is the kind of soda water that is used in "mixers," say with whisky. Additionally, some manufacturers add sucrose syrup and vanilla essence and/or other extract (such as quillaja) to make a sparkling drink sometimes known as "cream soda".

Fruit Drinks

Carbonated fruit drinks ("pop," "lemonade," "soda pop") constitute a major part of the soft drinks industry. They are made with purified water (or even springwater or natural mineral water in some cases), fruit juice (typically 2–10 % v:v), possibly compounded flavors containing fruit extracts or essential oils, sugar syrup and/or low-calorie sweetener, and possibly coloring. The fruit juice is used in concentrated form (~6× original strength), obtained by heat evaporation, membrane concentration, or cryoconcentration (Ashurst 2012 and references therein). Essences, essential oils, and extracts are used as ingredients in compounded flavor formulations and, as such, are individually likely to constitute no more than ~0.1 % (w:v) of the fruit drink. Compounded flavor mixes are especially important in the manufacture of cola- and root beer-type drinks. The range of volatile flavor compounds and bitter compounds for a particular fruit drink is similar to that in the pure fruit juice or alcoholic beverage containing that fruit (Table 3 and Fig. 25), but citrus drinks have lower levels of terpene hydrocarbons, as most of these are removed from the essential oil before compounding (Ashurst 2012).

Nowadays, high-fructose corn syrup and sucrose syrup are the main sugar source, sometimes in combination with a very small quantity of low-calorie sweetener or intense sweetener. In diet (low-calorie) versions of soft drinks, a combination of low-calorie sweeteners (e.g., saccharin and aspartame), always at very low concentration, is often used. See Fig. 4 for examples of low-calorie sweeteners and intense sweeteners.

Beverage colorants, deemed "natural" in most countries, are extracts or concentrates of fruit or vegetable and include annatto, beet juice, grape skin extract, β-carotenes, paprika, and saffron. Also included is cochineal, of animal origin. Synthetic colorants include Brilliant Blue (FD&C 1, E135), Indigotine (FD&C 2, E132), Erythrosine (FD&C 3, E127), Allura Red (FD&C 40, E129), Tartrazine (FD&C 5, E102), and Sunset Yellow (FD&C 6, E110). Caramel, in its various forms (E150a-d) is the most widely used beverage colorant (Buglass and Caven-Quantrill 2012), especially regarding cola and similar drinks. Plain caramel (E150a), made from sugar and acid (or alkali or salts) (but with no ammonia or sulfite), will supply low levels of monomeric and polymeric *O*-heterocycles (furans and pyrans), whereas ammonia caramels (E150c, d) supply additional low levels of monomeric and polymeric *N*-heterocycles (imidazoles and pyrazines).

Preservatives used in soft drinks include benzoates, dimethyl dicarbonate (DMDC), sorbates, and sulfites, depending on national regulations, and with maximum levels generally around 200 mg/L.

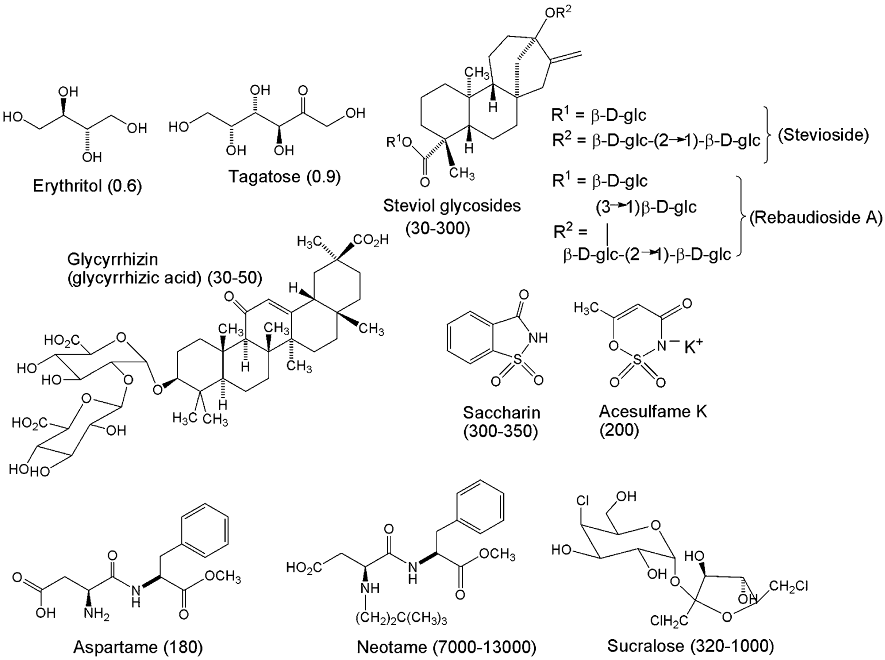


Fig. 4 Natural and synthetic low-calorie sweeteners used in soft drinks (approximate sweetness relative to sucrose = 1)

Cola- and Root Beer-Type Drinks

Modern cola drinks are made of sweetened, acidified, colored carbonated purified water, with a compounded flavor mix consisting of a source of caffeine, essential oils of citrus, cinnamon, and vanilla, along with gum arabic as an emulsion stabilizer. Sometimes other essential oils, such as nutmeg, are included. Caffeine content is usually 100–200 mg/L. The acidulant is phosphoric acid and/or citric acid, the sweetener is either sucrose syrup or high-fructose corn syrup (HFCS), and the colorant is caramel. Diet versions use low-calorie sweeteners (Fig. 4), and clear cola drinks (without caramel) are also available.

Cocaine, one of the original bitter agents, has not been used in cola drinks for many decades, because of its addictive nature. Some cola manufacturers use catuaba bark (*Trichilia catigua*) extract, which gives bitter but nonaddictive tropane alkaloids, catuabines A–D.

The compounded flavor mix for root beers is more complex than that for cola drinks (Table 12), but like cola, the combination of essential oils, extracts, and other ingredients differs between manufacturers and are trade secrets. Root beers usually possess a more spicy and bitter character than cola drinks.

Historically, the major flavor component was extract of *Sassafras albidum* root, but safrole, this oil's major component, has been shown to be carcinogenic

Table 12 Ingredients and selected organoleptic components of root beers[a]

Ingredient (part of plant used)	Botanical name	Major organoleptic components
Sassafras (root)	*Sassafras albidum*	Safrole, terpenoids, saponins
Sarsaparilla (root)	*Smilax regelii*, *S. glyciphylla*	Terpenoids, polyphenols, saponins
Wintergreen (leaf, berry)	*Gaultheria procumbens*	Methyl salicylate
Licorice (root)	*Glycyrrhiza glabra*	Anethole, glycyrrhizin
Birch sap	*Betula lenta*, *B. nigra*	Sugars
Black cherry (bark)	*Prunus serotina*	Lignins, saponins
Spruce (sap, needle)	*Picea rubens*, *P. mariana*, *P. sitchensis*	Bornyl acetate, camphene, δ-3-carene
Burdock (root)	*Arctium lappa*	Acids, polyphenols, polyacetylenes, inulin and other fibrous carbohydrates, arctigenin, arctiin
Dandelion (root)	*Taraxacum officinale*	*o*- and *m*-xylene, 2-ethyl-1-methylbenzene, heneicosane, tricosane, taraxacin
Root beer plant (root)	*Piper auritum*	Safrole, terpenoids, polyphenols
Cinnamon (bark)	*Cinnamomum verum*	Estragole, ethyl cinnamate
Nutmeg (fruit)	*Myristica fragrans*	Eugenol, elemicin, myristicin
Aniseed (fruit)	*Pimpinella anisum*	Anethole, ethyl cinnamate
Star anise (fruit)	*Illicium verum*	Anethole
Ginger (root)	*Zingiber officinale*	ar-Curcumene, zingiberene, zingiberol, gingerol
Clove (fruit)	*Syzygium aromaticum*	Acetyleugenol, eugenol, eugenin
Mint (leaf)	*Mentha* spp.	(−)-carvone, menthol, menthone
Fennel (seed)	*Foeniculum vulgare*	Anethole, anisaldehyde, apiole, dillapiole, limonene, (+)-carvone
Fenugreek	*Trigonella foenum-graecum*	Saponins, fibrous carbohydrates
Cassia (bark)	*Cinnamomum aromatica*	Benzaldehyde, chavicol, cinnamaldehyde
Soapbark	*Quillaja saponaria*	Polyphenols, saponins
Allspice (corn or seed)	*Pimenta dioica*	Eugenol, caryophyllene
Balsam	*Abies balsamea*	Benzyl benzoate, benzyl cinnamate, cinnamic acid
Hop (flower)	*Myroxylon balsamum*	Humulene, myrcene
	Humulus lupulus	

[a]Only a certain combination of these will be used by a particular manufacturer, usually as extracts or essential oils. This is not an exhaustive list. See also Table 19

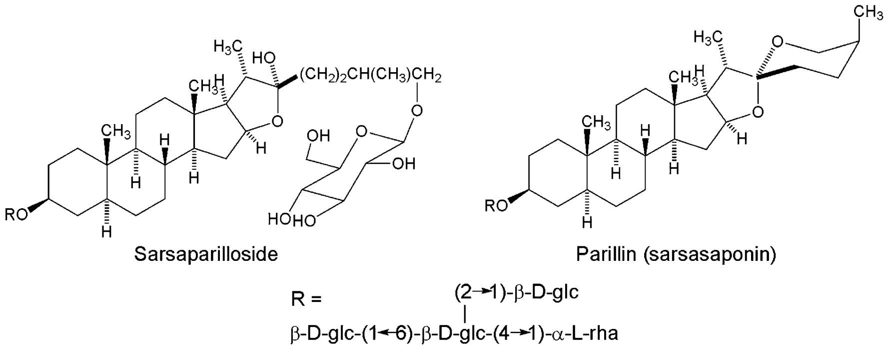


Fig. 5 Bitter saponins (triterpenoids) in sarsaparilla (*Smilax regelii*), a flavoring ingredient of root beers. These and other saponins aid foaming

in mice (there is no evidence for carcinogenicity in man). Nowadays, either "safrole-free" sassafras root extract or some substitute is used in commercial examples. Sweeteners are as for other soft drinks, but molasses or honey is sometimes used. "Sarsaparilla" and "dandelion and burdock" are carbonated soft drinks, like root beers, but are made with much more limited flavor mixes, as implied by their names. Table 12 lists a few compounds of organoleptic importance in the essential oils or extracts used in these two drinks, and Fig. 5 gives the structures of two of many bitter saponins (triterpenoid or steroidal glycosides) found in sarsaparilla root extract; these compounds also aid the foaming properties of such drinks. Root beers and related drinks are usually colored with caramel. Ginger beer (or ale) is a carbonated drink flavored with ginger essence or powder (and sometimes other essences), sucrose of HFCS, or low-calorie sweeteners; they are not usually colored. See Table 12 for major chemical components of ginger.

Note that root beers and ginger beer can be made as alcoholic versions (the originals were probably alcoholic), using a yeast culture and added citric acid for balance. Filtration after mixing thoroughly with yeast, fermenting for a short time at ~20 °C, then cooling to ~4 °C, and stoppering give an effervescent, mildly alcoholic drink (0.5–2 % ABV, depending on fermentation time). Whether these drinks are classified as soft or alcoholic depends on national regulations.

Tonic Water

Tonic water or Indian tonic water is a sweetened carbonated drink flavored with cinchona bark extract or quinine. Nowadays, the quinine content is low (the United States Food and Drug Administration – USFDA – specifies a maximum level of 83 mg/L), so the drink is ineffective as a prophylactic against malaria (requiring ~2,000 mg per day for adults), which was its original purpose. It is widely used in cocktails or mixers (e.g., with citrus juices or gin).

Table 13 Carbohydrate, mineral, and protein/amino acid content of sports drinks[a]

Component	Concentration range (mg/L)	Usual level or range (mg/L) in drinks that contain them
Sugars	0–76 (g/L)	~60 (g/L)
Na^+	170–3,750	420–845
K^+	0–450	84–250
Mg^{2+}	0–420	–
Ca^{2+}	0–340	25–125
Cl^-	0–1,270	340–380
Protein	0–85	~33
Amino acids	0–15 (g/L)	–

[a]Data from labels of selected drinks

Functional Nonalcoholic Beverages

Functional drinks are those that claim to provide some sort of specific physiological function, along with health benefits. Only ready-to-drink products (a large and growing market) are discussed in detail here. They can be subdivided into the following general categories (with a certain amount of overlap):

- Sports, performance, and recovery drinks
- Health beverages
- Energy and rejuvenation beverages
- Relaxation drinks

Fermented functional drinks, such as kefirs, soy beverages, fermented whey, kombucha (fermented tea), and fruit vinegars (made from fruit wines), although some of the most nutritious of such beverages, are not dealt with here.

Sports, Performance, and Recovery Drinks

These generally still (non-carbonated) drinks are designed to promote rehydration and to be a source of fuel for rapid metabolic conversions that are required during vigorous exercise. They claim to prevent dehydration and to increase athletic performance. The first generation of such drinks were purified water that contained electrolytes and/or carbohydrates and sometimes fruit flavorants and colorants, but modern versions can contain, besides these, a combination of amino acids, proteins, vitamins, lecithin, L-carnitine, chromium picolinate (a regulator of carbohydrate metabolism), and herb extracts. Sports drinks can be classified as hypotonic, isotonic, or hypertonic, depending on concentrations of minerals (lower, similar, and higher levels, respectively, of minerals in comparison with the human body). Caffeine is not a component of sports drinks but is a major component in most energy beverages. Table 13 summarizes the sugar, mineral (electrolyte), and protein content of sports drinks, where it can be seen that Na^+ is the major electrolyte (~460–930 mg/L), being needed to replenish the sodium lost in sweat.

Electrolyte-only sports drinks are sometimes called rehydration drinks – their function is to replenish lost moisture and minerals. Most sports drinks contain sugars, often a mixture of fructose, glucose, and sucrose, for optimum metabolism during strenuous exercise (Reents 2007). Many modern sports drinks contain amino acids or protein (Table 13), in response to observations that their presence aids athletic performance. Also present in some sports drinks are additional ingredients listed above – it is here that there is some overlap with health beverages.

Health Beverages

Many drinks are called "healthy," but this subsection considers only ready-to-drink products that are marketed specifically as "health drinks" for normal individuals and are not necessarily associated with sporting activities. Some companies provide concentrates for mixing with water to make a "health drink." Some of these can be highly complex mixtures of powders of seaweed, cereals, fruit, vegetables, herbs, or mushrooms. These will supply a wide range of phytochemicals (carbohydrates, fats, amino acids, proteins (including enzymes), terpenoids, phenolic compounds, minerals, vitamins, and others) associated with particular components, along with dietary fiber.

Typical ready-to-drink health beverages consist of purified water, with added minerals (but not Na^+) and vitamins: they are generally devoid of carbohydrates, fats, amino acids, and proteins. They contain flavorings (e.g., natural flavorings or those from fruit/vegetable concentrates), citric acid (acidulant), calcium lactate (electrolyte), possibly caramel or other colorant, and low-calorie sweeteners, such as a sucralose/acesulfame-K combination (Fig. 4). The vitamin content (typically A, B complex, C, D, and E) per bottle (usually 237 mL) often supplies ~15–70 % of the daily requirement.

Some health drinks ("calorie-burning drinks") focus on people who seek to lose weight. These drinks frequently contain relatively high levels of the polyphenol epigallocatechin gallate (EPCG) or tea extract (EPCG is a component of tea) or chlorogenic acid (a coffee component). The polyphenols reduce the effectiveness of carbohydrates and other sources of calorific nutrition, and additionally, they are themselves effective antioxidants and may enhance beneficial gut flora activity.

Energy/Rejuvenation Beverages

This category of functional (often carbonated) drinks is quite separate from sports drinks. Energy drinks provide a wide range of central nervous system (CNS) and/or muscle stimulants, the most common of which is caffeine (a methylxanthine), often (at least in part) derived from natural extracts, such as guarana or yerba mate extract. These extracts are a source of many other phytochemicals, including other methylxanthines that can have quite different physiological functions to caffeine (Fig. 6).

The caffeine content of energy drinks ranges from about 150 mg/L to over 3,500 mg/L, with typical values of 200–400 mg/L, whereas cola and related drinks typically have 100–150 mg/L caffeine content. Although the caffeine and other non-calorific stimulants in energy drinks create a feeling of alertness and confidence, these substances are not a source of metabolic energy like carbohydrates, for example.

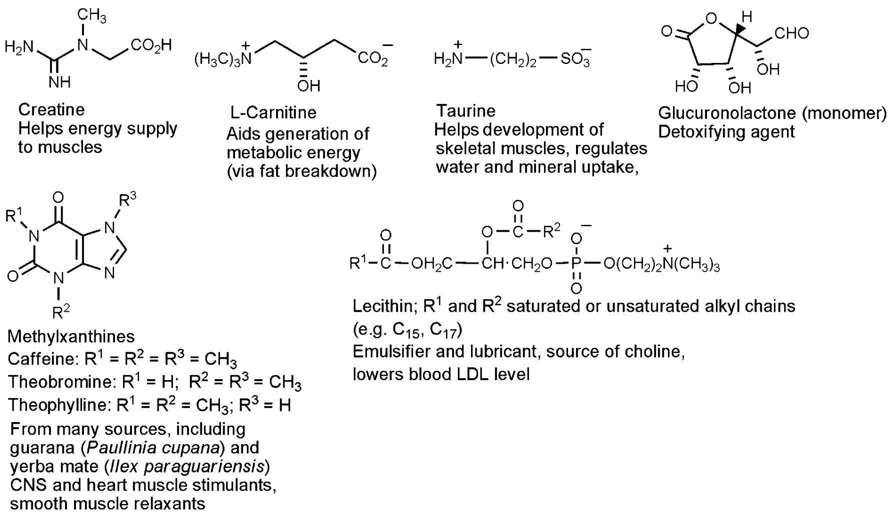


Fig. 6 Active chemical constituents frequently used in energy beverages

Apart from caffeine, common ingredients of energy drinks include high-fructose corn syrup or sucrose syrup, carnitine, creatine, glucuronolactone, inositol, maltodextrose, and/or taurine, as well as extracts of açaí berry (*Euterpe oleracea*), catuaba bark (*Trichilia catigua*), *Epimedium* spp., ginkgo (*Ginkgo biloba*), ginseng (*Panax* spp. mainly), guarana (*Paullinia cupana*), *Gymnema sylvestre*, *Polygonum cuspidatum*, white thistle (*Silybum marianum*), and/or yerba mate (*Ilex paraguariensis*). The extracts can supply a wide range of natural chemicals, including alkaloids, amino acids, carbohydrates (including dietary fiber) terpenoids, steroids, flavonoid and other polyphenolic compounds, and vitamins, many of which are antioxidants; selected examples can be found in Fig. 7, where it can be seen that terpenoids, steroids, and polyphenolic compounds are usually found as glycosides.

These extracts, or in some cases individual components, have been found to have physiological activity; for example, ginkgolides aid mental concentration, ginsenosides can be either CNS stimulants or relaxants (Qi et al. 2011), catuabines (from *Trichilia catigua*) are CNS stimulants, and icariin (from *Epimedium* spp.) is a smooth muscle relaxant. The concentrations of individual plant extract-derived physiologically active components in functional beverages will be in general very low, so with normal usage, an "overdose" situation will not occur. Nevertheless, energy drink labels carry warnings of the type: "Consumption of more than two cans in a day may be harmful to your health. Not to be used for pregnant women, breast feeders, children under the age of 16, people with heart disease, high blood pressure, diabetes, allergy to caffeine, and athletes during exercise."

Also, drinkers of functional beverages should assess the likelihood of antagonism between beverage active ingredients and current medication or other aspects of diet, such as ethanol intake. "Diet" versions contain low-calorie sweeteners, such as sucralose and/or acesulfame-K.

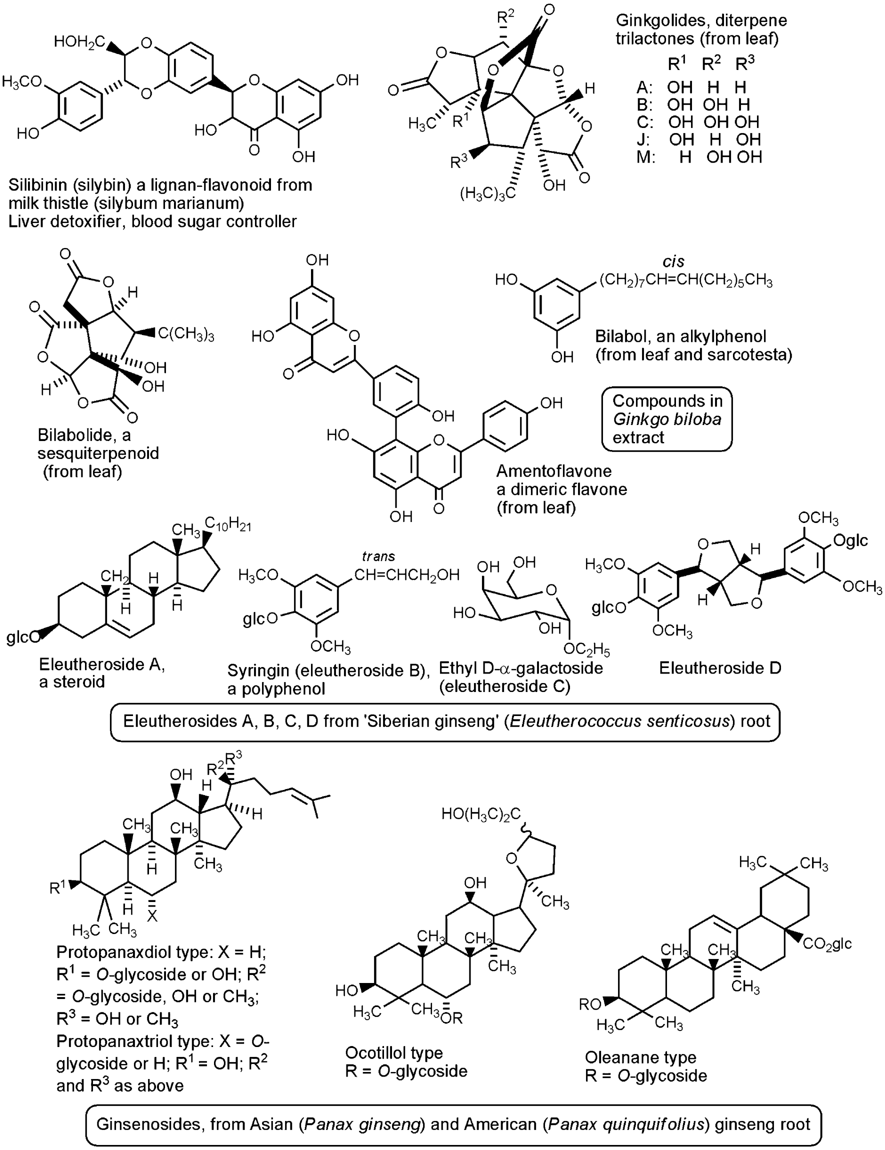


Fig. 7 Characteristic chemical components of some plant extracts used in energy beverages

Relaxation Drinks

Currently (2014) having a relatively modest share of the functional beverage industry, relaxation drinks are designed to provide the consumer with a feeling of relaxation that accompanies loss of anxiety. This is achieved mostly by including in the drink components that interact with inhibitory neurotransmitter receptors, such

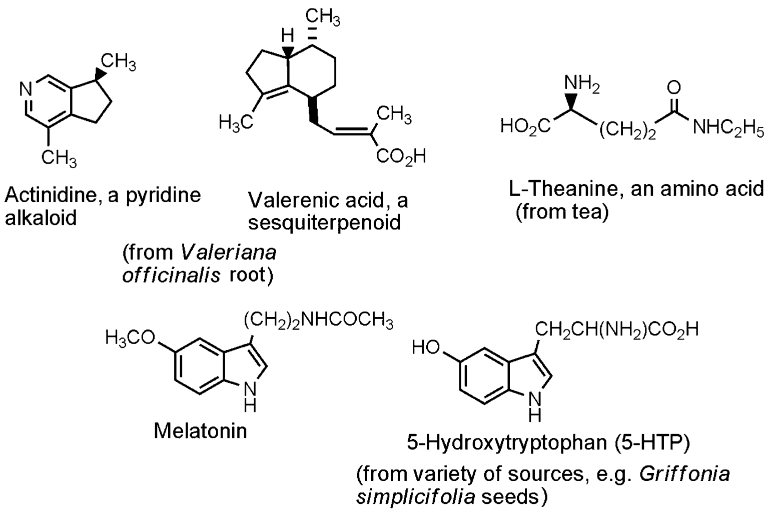


Fig. 8 Structures of some active components of relaxation drinks

as GABA and serotonin receptors, or those that block excitatory neurotransmitter receptors, especially glutamate receptors.

Typical relaxation drinks consist of a purified water base with flavorant, sweetener, and possibly colorant, along with one or more active ingredients, which include L-theanine (from tea), valerian (*Valeriana officinalis*) root extract (which contains alkaloids like actinidine, sesquiterpenoids like valerenic acid, γ-aminobutyric acid (GABA) and many other compounds), 5-hydroxytryptophan (5-HTP) (precursor of serotonin), and melatonin (Fig. 8).

Chemical Composition of Alcoholic Beverages

This section deals with compositions of major fermented alcoholic drinks – wine, cider, beer, and related cereal-based beverages – as well as distilled products: brandy, fruit spirits, whisk(e)y and related spirits, flavored spirits (such as gin and arak), and liqueurs.

Many changes of composition occur when drinks such as wine, cider, beer, and rice wine are produced from their respective raw materials or precursors – grape or fruit juice, apple juice, hopped or flavored wort, or rice porridge. Some of the original components disappear completely, but some survive through to the final product. Totally new components appear as a result of alcoholic, malolactic, and other fermentations and also because of various other production practices. The most notable new component is, of course, ethanol, followed in many beverages by glycerol. Typical ethanol concentrations of major alcoholic beverages are shown in Table 14, and these are further discussed in the relevant subsections. When fermented drinks are distilled to produce spirits, most nonvolatile components are

Table 14 Ethanol, water, and nonvolatile component composition of alcoholic beverages[a]

	Beverage				
Component	Wine	Beer	Cider	Rice wine	Spirit
Water (g/L)	810–910[c]	920–950	900–960	950–960	340–680
Ethanol (g/L)[b]	80–110[c]	30–50	20–75	50–144	280–560[f]
Carbohydrate (total) (g/L)	1.0–.100	15–37[d]	0.14–25	–	Trace[g]
Free sugars (g/L)	1.0- > 100	Trace-30	Trace-20	17.92–27.48[e]	Trace[g]
Fiber (g/L)	Trace	Trace-10	Trace-3.0	–	Trace
Amino acids, peptides, and proteins (g/L)	0.2–3.0	2.0–6.0	0.2–0.5	0.60–1.05[e] 76.33–102.93[h]	Trace–3.0
Calorific value (Cal/L)	640–1,000	280–450	300–400	–	2,240

[a]Typical values or ranges. Data from Fuller et al. (2011, pp. 961–992) and references therein, unless specified otherwise
[b]These figures multiplied by 0.125 will give the % alcohol by volume (%ABV)
[c]Not including fortified wines and vins de liqueur: these would have ~128–176 g/L ethanol
[d]Includes α-glucans (dextrins), many of which are non-fermentable
[e]Data from Shen et al. (2012) and references therein, for clear rice ("yellow") wine
[f]The most common ethanol content is 320 g/L (=40 % ABV). Some liqueurs and other spirit-based drinks have 128–240 g/L
[g]Cask-aged spirits may contain wood-derived carbohydrates
[h]Data in g/kg from Kang et al. (2014) for cloudy makkoli

lost (Table 14) and many aroma compounds become more concentrated in the highly ethanolic product. The organoleptic impact can be enhanced or altered by various production processes, such as cask aging and inclusion of flavorings.

Wine

Wine is strictly the fermented juice of freshly crushed and pressed grapes: it is this beverage that is the main topic of this subsection. However, wine made from other fruits ("fruit wine" or "country wine," often via rather different processes) is important in some areas and hence is given some consideration later. A summary of the basic (grape) winemaking processes is given in Fig. 9. For a particular wine, its chemical composition is derived from the exact details of its processing, as well as from the genetic identity of its grapes and the agricultural and climatological background to the their cultivation. Likewise, deviations from the basic schemes of Fig. 9 (such as fortification with spirit, drying of grapes, biological aging, oxidative aging, and heat treatments) can make significant differences to the composition. The following paragraphs include outlines of how these factors can influence wine composition.

Wine Color

The anthocyanin and related pigments of black grape must (Fig. 1, Table 1) are also present at high levels in new red wine (total anthocyanin content: 100–1,500 mg/L,

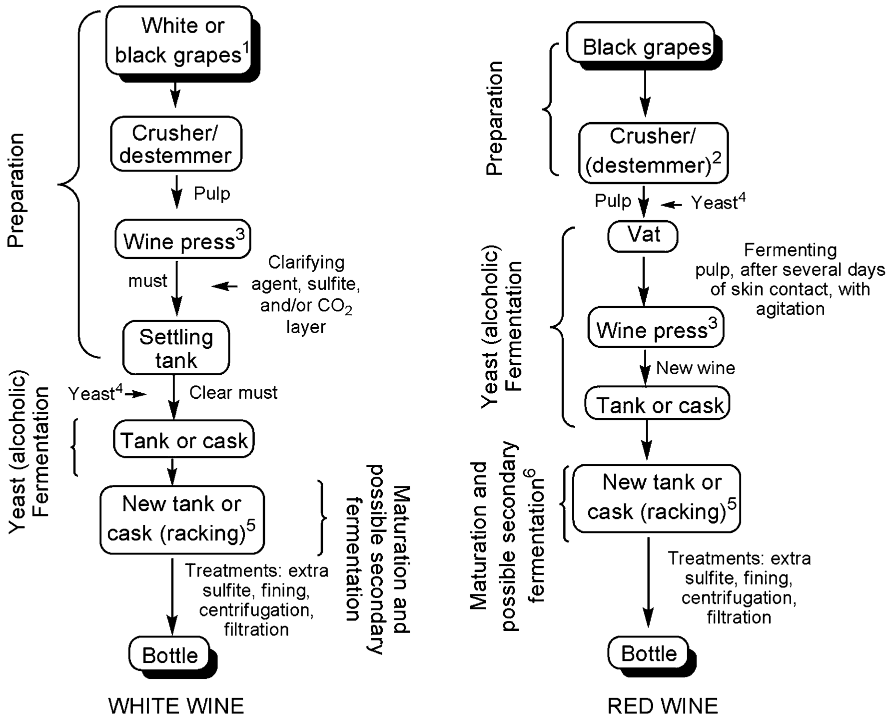
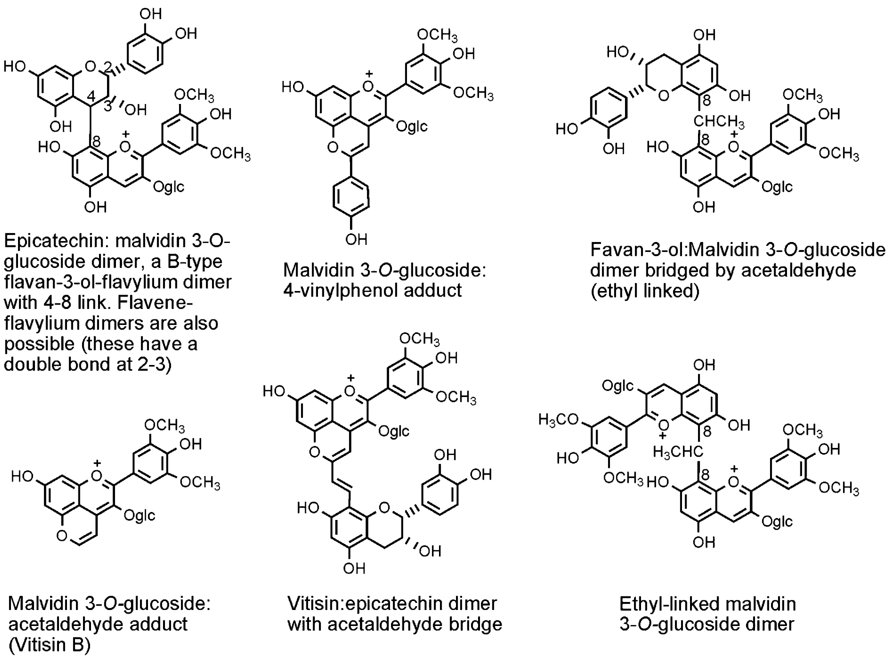


Fig. 9 The basic production processes for white and red wine. *1* If black grapes used, pressing the crushed grapes in immediate. *2* Some red wines are made without removing the stems. *3* Free fun juice/wine is sometimes fermented separately from press juice/wine. *4* Pure yeast cultures tend to be added to white grape must made in cool climates, otherwise the natural yeasts from the skins are often allowed to ferment the must, especially that from warmer climate black grapes. *5* The number of rackings are according to tradition or the will of the winemaker, as is the duration of maturation. Sulfite levels are checked at each racking. *6* Nearly all red wines and some white wines undergo secondary (malolactic) fermentation

total phenol content: 0.5–4 g/L). However, during maturation these rather reactive pigments are progressively converted to a large number of more stable pigments, through a variety of reactions that can involve small molecules like acetaldehyde, as well as other monomeric or oligomeric polyphenols. These reactions include the formation of:

- Castavinols via the addition of 1,2-diketones (like diacetyl) across the 2 and 4 pyrylium ring positions
- Pyranoanthocyanins (vitisins) by addition of carbonyl compounds such acetaldehyde and pyruvic acid across the 5-OH position of ring A and the pyrylium ring 4 position
- Adducts with 4-vinylphenol, again involving the 5-OH position of ring A and the pyrylium ring 4 position



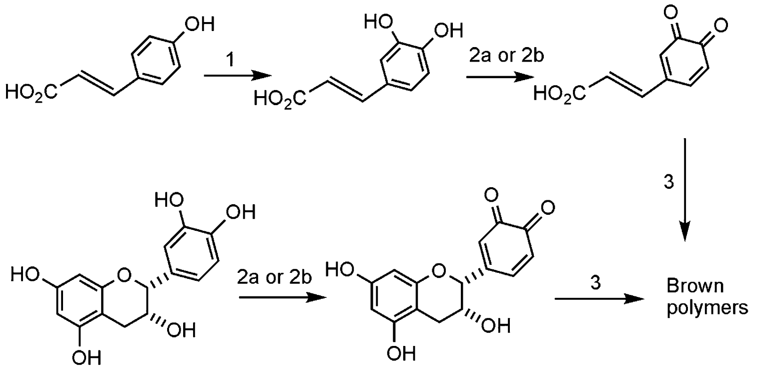
See Figs. 1 and 3 for examples of other pigment and nonpigment polyphenols in fruit juice. Some of these, such as anthocyanin glycosides, procyanidins, other oligomers/polymers, and hydrolyzable tannins are also present in red wine

Fig. 10 Some pigment polyphenols in red wine (Buglass and Caven-Quantrill 2013 and references therein)

- Dimers with an ethyl link (acetaldehyde bridge) by reaction between two anthocyanin monomers (at ring A 8 position) and acetaldehyde
- Oligomers by reaction between an anthocyanin (or vitisin) and a flavan-3-ol or procyanidin oligomer, with or without ethyl or acetaldehyde bridges

Some of these products are illustrated in Fig. 10. Many of these new pigments absorb light of ca. 520 nm and hence are purple-red, explaining why red wines remain red after 2 years maturation in bulk before bottling, despite almost complete disappearance of the original anthocyanins during this time. However, due to the larger oligomers and the procyanidins formed concurrently by condensation of flavan-3-ols (Figs. 1 and 11), they tend to be orange-yellow, and so red wines gradually turn through brick red to brown as they age further. Additionally, the bigger polymers precipitate (possibly as polyphenol–protein complexes) after long maturation times, eventually leaving a phenol-depleted, paler, browner wine.

Like white grape juice, the main contributors to white wine color appear to be certain polyphenols (up to 300 mg/L), carotenoids (up to 750 µg/L), and possibly chlorophyll and degradation products (a few ng/L). White wines, like many pale juices, can undergo enzymic or nonenzymic browning, especially at low sulfite



Key: 1 polyphenoloxidase (PPO) 2a PPO 2b O_2, Cu^{2+} and/or Fe^{3+} 3 polyphenol

Fig. 11 White wine enzymic and nonenzymic browning mechanism outline (illustrated for (−)-epicatechin and *p*-coumaric acid)

levels. This is caused by the oxidation of catechol or galloyl units of polyphenols to *o*-quinones, which then form brown polymers by reacting with other polyphenols (Fig. 11).

Ethanol, Carbohydrate, and Carbohydrate Derivative Content

Summaries of ethanol and carbohydrate content of wines are given in Table 14. Wine ethanol content varies from around 6 % ABV (6 % v:v) for some semi-sparkling sweet wines (e.g., Lambrusco and Moscato), through 8–12 % for wines from cooler climates, to 13–16 % for those of warmer climates and special wines made from dried grapes (e.g., Amarone della Valpolicella and Vin Santo), finally up to ca. 22 % for some fortified wines. For dry or semidry wines (<10 g/L residual sugars), the %ABV is directly related to ripeness (sugar content) of the grapes, but sweet wines (30- > 100 g/L residual sugars) can have low (~8 % for Trockenbeer-enauslesen or ~2 % for Tokaji Aszú Essencia) or high (13.5–15.5 % for Sauternes) ethanol levels.

Like grapes, the most abundant residual wine sugars are fructose and glucose, and since glucose is more easily fermented by yeast, fructose is the dominant sugar of sweet wines. Sucrose is present only at trace levels, if at all. Law generally forbids the addition of raw sugar (e.g., sucrose) to wine, but concentrated sterile grape juice (süssreserve) can be used as a sweetener of certain wine categories (e.g., Qualitätswein bestimmte Anbaugebiete – QbA wines of Germany).

Small quantities (0– ~130 mg/L) of other monosaccharides, notably arabinose, galactose, rhamnose, ribose, and xylose are present in wine: some of these are the result of the degradation of grape pectic substances during fermentation, especially if exogenous pectinases have been used. Trehalose is the dominant disaccharide of wine (trace levels to ~600 mg/L), particularly in wines made from grapes infected by *Botrytis cinerea* ("botrytised" or "nobly rotted" grapes), such as Sauternes and Quarts de Chaume. Other disaccharides are normally found at lower than the 5 mg/L level.

Wine polysaccharides (up to ~750 mg/L) exist as neutral pectic substances, yeast mannoproteins, and protein conjugates, the most abundant being arabinogalactan proteins (~300 mg/L). Other pectic substances of grape juice are hydrolyzed during fermentation to monosaccharides and galacturonic and glucuronic acids, at levels of 200–1,400 mg/L, although concentrations up to 7,500 mg/L have been recorded for botrytised wines (Amerine and Ough 1980, pp. 45–73 and references therein). Gluconic acid is usually found in wine at concentrations less than 500 mg/L but up to ~6,000 mg/L in wine from botrytised grapes.

Chemically, polyhydric alcohols, glycerol, butanediols, mannitol, mesoinositol, and sorbitol are reduced sugars: the first named is normally the most abundant organic compound (1–20 g/L) in wine, after ethanol. Its presence improves the appearance and mouthfeel of wine due to increased viscosity. It is produced mainly by yeast metabolic processes, but again it is more abundant in botrytised wine, whose grape juice may already have up to 5 g/L before fermentation. Average levels of mannitol and sorbitol in wine are ~100 mg/L and ~300 mg/L respectively, but once again these are higher in wine from botrytised grapes.

Volatile Compounds

Wine odor and flavor are of utmost importance. Volatile compounds that give rise to wine aroma and bouquet, together with various tastants (acids, sugars, salts, phenolic compounds, and others) contribute much to flavor, often simply described as “taste.” Human perception of odor is complex and is not considered here, so odor descriptors of volatile wine substances (Table 15) refer to basic perception at levels found in wine. This is because descriptors vary enormously with concentration and also according to the presence or absence of co-components, both volatile and nonvolatile.

Wine volatiles have basically three origins, as outlined in Fig. 12: grape must (“varietal aroma”), fermentation (yeast and possibly bacterial metabolic products) and chemical reactions, and wood contact (mainly oak) during maturation (“oak aroma”). Particular volatile components can have more than one origin – for example, certain volatile phenols like *p*-ethylphenol and *p*-vinylphenol can come from MLF (via the shikimate pathway) or from contact with toasted oak. Note that many wines have no oak contact – they are fermented and matured in stainless steel or other non-wooden vessels.

During fermentation of grape must, the levels of many volatiles, like certain alcohols, carbonyl compounds, and terpenoids, decrease and are augmented with or replaced by high levels of acetate and ethyl carboxylate esters (especially C_6, C_8, C_{10}), some terpenoids, and certain norisoprenoids (derived from juice carotenes).

Many volatiles exist in grape juice as odorless glycosides or L-cysteine conjugates (Fig. 13). Alcoholic fermentation may release some odorous aglycones due to the action of yeast *O*-glycoside hydrolases, but this can be enhanced legally by the addition of pectolytic enzymes during fermentation. Additionally, odorous sulfur compounds (Fig. 13) are released from their cysteine conjugates seconds after swallowing due to the action of saliva lyases.

Although a single volatile compound may influence aromas of particular wines (see Table 15 for many examples) to a recognizable degree, in reality, this

Table 15 Summary of volatile components of wine and examples of some key odorants[a]

Chemical class	Examples with typical concentrations or ranges (μg/L, unless otherwise stated)	Examples of key odorant (OTV in ng/L) [aroma descriptors]	Typical example of wine source
Acetals	Acetal (1,1-diethoxymethane) ($4.5–6.4 \times 10^4$)	Acetal (4,000–42,000) [fruity]	Sherry, vin jaune
Alcohols	Ethanol (6–16 % ABV), 2-methyl-1-propanol (10^5), 3-methyl-1-butanol (isoamyl alcohol) (2×10^5), 2-phenylethanol (5×10^4)	2-Phenylethanol (2.0×10^6) [Rose]	Muscat
Carbonyls	Acetaldehyde[b] (up to 2.8×10^5), diacetyl (20–5,400)	Diacetyl (6,500–15,000)	Chardonnay
		Phenylacetaldehyde [floral, honey]	Pedro Ximénez, Sauternes
Carboxylic acids	Acetic acid (5×10^5), formic acid (5×10^4)		
Carboxylate esters	Ethyl acetate (up to 5×10^5), ethyl hexanoate (600–1,800), ethyl octanoate (1,100–1,700), diethyl succinate (100–1,400), isoamyl acetate (40–6,100), 2-phenylethyl acetate (200–5,100)	Isoamyl acetate ($2.5 \times 10^5–4.1 \times 10^6$) [banana, fruity]	Tempranillo
Lactones	γ-Butyrolactone (10^3), dodeceno-γ-lactone (140–270), *cis*, *trans*-oak (whisky) lactones, wine lactone (100)	*trans*-Oak lactone (490,000) [coconut, toasted oak]	Oak-aged wines
Norisoprenoids (C_{13})	*trans*-β-Damascenone (0.005–6.5), β-ionone (up to 2.5)	*trans*-β-Damascenone (40–60) [sweet, floral]	Pedro Ximénez, Muscat
Organosulfur compounds[c]	3-Mercaptohexanol (0.15–3.5), 3-mercaptohexyl acetate (up to 0.5), 3-mercapto-3-methylbutanol (0.02–0.15), 4-mercapto-4-methyl-2-pentanol (0.015–0.15), 4-mercapto-4-methyl-2-pentanone (up to 0.15), phenylmethanethiol (0.005–0.02)	3-Mercaptohexanol (60) [fruity, sulfury]	Sauvignon Blanc, Cabernet Sauvignon
		3-Mercaptohexyl acetate (4) [tropical fruit]	Verdejo
		4-Mercapto-4-methyl-2-pentanone (0.6) [sulfury, black currant]	Gewürztraminer, Sauvignon blanc, Scheurebe
Phenols	2-Methoxyphenol (3,600), 2-methoxy-4-vinylphenol ($4,500–2.5 \times 10^4$), vanillin (4.5×10^4)	Vanillin (2×10^5) [vanilla]	Oak-aged wines

(*continued*)

Table 15 (continued)

Chemical class	Examples with typical concentrations or ranges (μg/L, unless otherwise stated)	Examples of key odorant (OTV in ng/L) [aroma descriptors]	Typical example of wine source
Pyrazines	2-Methoxy-3-ethylpyrazine, 2-methoxy-3-isobutylpyrazine (up to 0.05), 2-methoxy-3-*sec*-butylpyrazine, 2-methoxy-3-isopropylpyrazine	2-Methoxy-3-isobutylpyrazine (15) [herbaceous, green pepper]	Cabernet Sauvignon
Terpenoids	Citronellol (2–12), geraniol (5–506), hotrienol (25–127), linalool (6–473), rotundone, α-terpineol (3–87)	*cis*-Rose oxide (200) [rose, spicy]	Gewürztraminer
		Rotundone (6) [green pepper]	Shiraz (Syrah)

[a]Data from Buglass and Caven-Quantrill (2013), Ribéreau-Gayon et al. (2000, pp. 129–186) and references therein
[b]In most wines, much of the acetaldehyde is bound to SO_2, as the bisulfite addition compound
[c]Present in grape must and wine mainly as L-cysteine conjugates

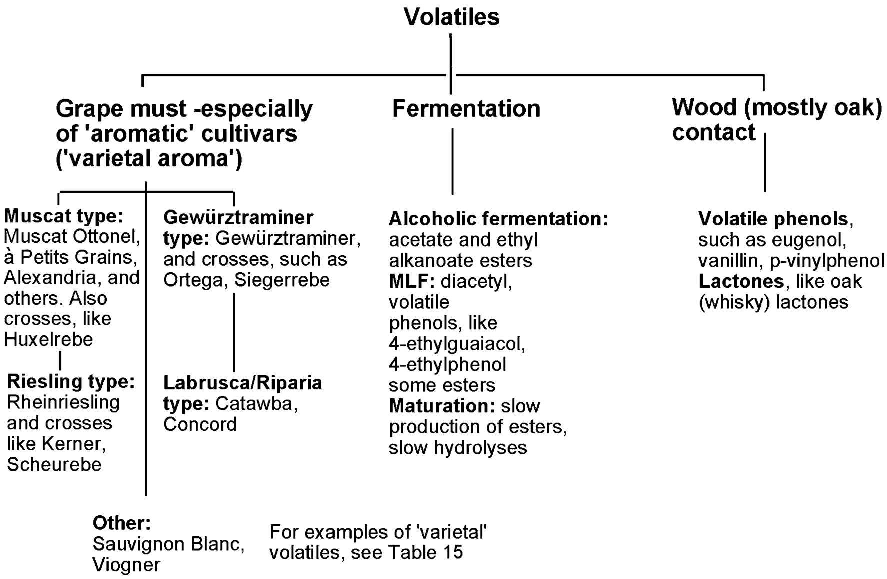


Fig. 12 Origins of wine volatile compounds

compound usually exists in many wines, so that it is the overall volatile component profile that ultimately defines the full aroma of each wine.

Acids

Acids are essential to wine quality: they provide the wine with a sourness that balances fruity, sweet, salty, and bitter/astringent organoleptic sensations.

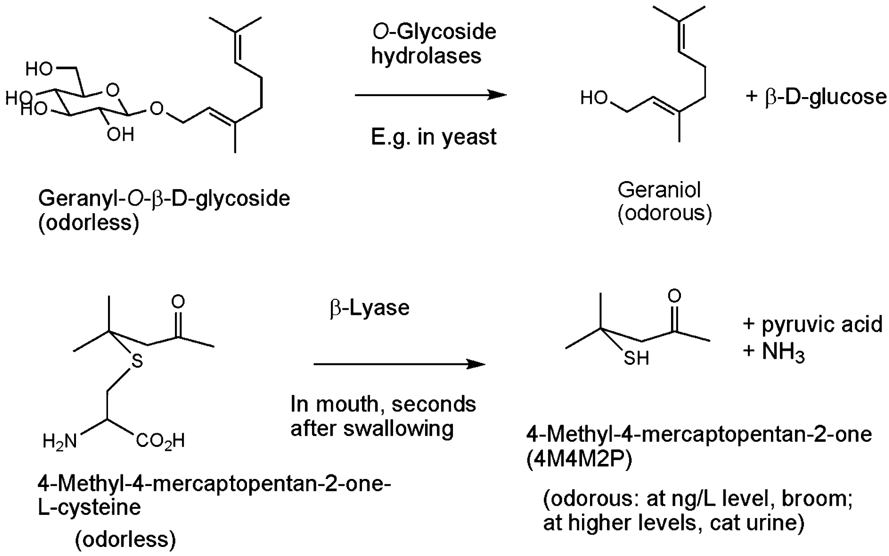


Fig. 13 Release of odorous compounds by enzyme action

Moreover, they endow the wine with longevity and contribute to wine color and, in time, to wine flavor. Of course, too much or too little acidity can be unpleasant and will give a wine with unbalanced "taste." Wine acids are derived from grape juice and/or yeast metabolic pathways that operate during fermentation, although low levels of phenolic acids are wholly or partially derived from oak contact. The levels of the major original grape acids are generally lowered somewhat during alcoholic fermentation, either as a result of yeast activity (L-malic acid, ~5–20 %) or because of precipitation of salts (L-tartaric acid, ~10 %).

The major wine acid is L-(+)-tartaric acid, usually found in concentrations of 2–4 g/L. Wine that has not undergone malolactic fermentation (MLF) – most white wine and some red wine – also has significant levels of L-(−)-malic acid (2–4 g/L). Succinic acid is also a significant wine acid (~1 g/L), as is D-lactic acid, at lower levels (usually $<$ 500 mg/L) and, also at low levels, acids from various yeast metabolic pathways (e.g., citric, fumaric, pyruvic, and shikimic acids). L-Lactic acid is abundant (1–4 g/L) only in wines that have experienced MLF, in which case the malic acid levels of such wines will be very low (often a few hundred mg/L or less). Sugar acids are discussed in the previous paragraphs.

Acetic acid is the main volatile acid of wine: low levels (well below 1 g/L) are beneficial to wine flavor, but higher levels are suggestive of spoilage, mostly by *Acetobacter* microorganisms.

Amino Acids, Peptides, and Proteins

The total amino acid and ammonium (NH_4^+) content of wine ($<$1.5 g/L up to 50 mg/L, respectively) is generally lower than that of the original grape juice (1.5–4 g/L up to

Table 16 Summary of identified proteins in Portugieser red wine (From Wigand et al. 2009)[a]

Band (experimental molecular weight/kDa)	Theoretical molecular weight/kDa	Identification	Origin
1 (9)	11.7, 11.8	Lipid transfer proteins (LTPs)[b]	Grape
2 (12)	11.7, 11.8	LTP isoform 4 + LTP	Grape
3 (25)	24.0–27.2	Three thaumatin-like proteins (TLPs)[c] + endochitinase[d] class IV	Grape
4 (37)	71.5	Hydrolyzed vacuolar invertase 1 GIN 1[e]	Grape
	48.0	Protein TOS1 precursor	Yeast
5 (47)	71.5	Hydrolyzed vacuolar invertase 1 GIN 1	Grape
	23.2–48	Three cell wall and matrix precursor proteins	Yeast
6 (61)	23.2–53.0	Four fungal protein precursors	Yeast
	71.5	Hydrolyzed vacuolar invertase 1 GIN 1	Grape
7 (77)	71.5	Vacuolar invertase 1 GIN 1	Grape
	23.2	Cell wall protein precursor	Yeast[f]
8 (150)	53.0	Glycosidase precursor	Yeast[f]
	53.0	Endochitinase precursor	Yeast[f]

[a]Determined using SDS-PAGE electrophoresis and LC-MS
[b]LTPs are defense proteins located in grape skins and hence will be absent or at lower levels in rose or white wines. They are possible allergens
[c]TLPs are implicated in haze formation; they are possible allergens
[d]Endochitinases are grape antifungal defense proteins and possible allergens
[e]Vacuolar invertases are found in grape pulp and are responsible for hexose accumulation during ripening
[f]All the higher-molecular-weight yeast proteins are likely to be glycoproteins

300 mg/L, respectively), because of net utilization of these substances by yeast during alcoholic fermentation and (where appropriate) by bacteria during malolactic fermentation. MLF is known to deplete the wine of arginine, glutamic acid, histidine, and tyrosine; moreover if *Pediococcus cerevisiae* is the MLF agent, histidine is decarboxylated to the biogenic amine histamine (see "Other Components").

Protein content of wine varies from a few mg/L to over 400 mg/L. Most proteins are in the molecular weight range 12–65 kDa and are mostly grape-derived, possible allergenic, defense proteins. Higher-molecular-weight proteins, probably extensively glycosylated (e.g., mannoproteins), are generally of yeast origin, and sometimes fining proteins (e.g., egg albumen) can be found in wine. Heating (see "Fortified Wines") and fining with bentonite reduces protein content. Table 16 lists the proteins found in a red wine, along with brief descriptions of their origins and characteristics.

Minerals and Vitamins

Cations and anions in wine help to maintain its acid–base buffer capacity and some, like K^+, Mg^{2+}, Ca^{2+}, and Na^+, endow a certain saltiness of taste, which is more

Table 17 Mineral and vitamin content of alcoholic beverages[a]

Beverage	Wine (mean value)	Beer	Cider	Rice wine[b]
Minerals[c]				
K (mg)	90–1,840 (880)	300–500	727	549–713
P (mg)	10–820 (291)	110–200	80	–
Ca (mg)	6–208 (88.9)	4–140	70	108–166
Mg (mg)	21–173 (96.9)	50–100	50	183–224
Na (mg)	6–309 (37.5)	50–100	50	28–61
Cl (mg)	5–596 (72.2)	120–350	–	–
S (mg)	70–4,390 (823)	107–400	–	–
B (mg)	2–112 (20)	–	–	–
Fe (mg)	Trace–90 (7.9)	Trace–0.6	2.1	0.18–2.2
Zn (mg)	Trace–8.8 (1.6)	Trace–3.0	0.5	3.5–5.1
Mn (mg)	0.14–17.4 (2.0)	Trace–0.3	2.5	5.2–6.4
Cu (mg)	Trace–3.7 (0.52)	Trace–0.7	–	0.59–0.70
Se (μg)	Trace–3.0	Trace–3.4	0.8	–
Vitamins				
B_1 (thiamine) (mg)	2–58 (8.7)	0.03–0.09	–	–
B_2 (riboflavin) (mg)	0.08–0.25 (0.16)	Trace–0.4	0.03–0.5[d]	–
B_3 (niacin) (mg)	0.8–2.1	2.0–8.0	0.1–1.0[d]	–
B_5 (pantothenate) (mg)	0.47–1.87 (0.89)	0.3–1.0	–	–
B_6 (pyridoxine) (mg)	0.22–0.82 (0.46)	0.1–0.9	–	–
B_{12} (cyanocobalamin) (μg)	Trace–1.6×10^{-4}	Trace–0.8	–	–
Vitamin C	Trace	Trace	–	–
Folate (μg)	Trace–12	6.2–68.2[e]	–	–
Biotin (μg)	Trace–4.6 (2.1)	Trace–10	–	–
Choline (mg)	48–64	77–123	–	–
Betaine (mg)	2.4–3.2	60–88	0.3–1.1	–
Nicotinic acid (mg)	0.99–2.19 (1.73)	–		–

[a]Typical values or ranges for non-distilled drinks in mg/L or μg/L. Data from Fuller et al. (2011, pp. 961–992) or Amerine and Ough (1980, pp. 153–174) or Hough et al. (1982, pp. 776–838) and references therein, unless specified otherwise. Minerals and vitamins are effectively lost on distillation, so spirits are not included in the table. Spirit-based drinks, such as some alcopops, cocktails, and fruit liqueurs, may have some minerals and vitamins returned
[b]Data from Shen et al. (2012): Chinese "yellow wine," values rounded down to 2 or 3 significant figures
[c]Metals as cations, P as phosphates, S as sulfates, B as borates
[d]Data from Goverd and Carr (1974)
[e]Data from Owens et al. (2007)

obvious in dry white wines. Typical mineral content of wines are displayed in Table 17. Certain grape juice electrolytes (e.g., calcium, sulfate, and phosphates) are depleted during processing by precipitation, but at the same time, levels of others may increase: Na^+ from sodium metabisulfite (preservative), ion exchangers, and concrete vats; calcium sulfate from use of gypsum in sherry making; and diammonium phosphate from added yeast nutrient. Also, grapes treated with Cu, Mn, and Zn fungicides (Bordeaux mixture, mancozeb, and zineb, respectively) may give wine with higher concentrations of these ions. Additionally, sodium chloride levels may be higher in wines originating from coastal vineyards, and iron and copper ions can be picked up by contact with these metals during processing, but this is uncommon these days. Very low levels of contaminant toxic metal cations (e.g., Cd, Cr, Hg, Ni, Pb, Sn) might be present, but concentrations of all minerals will be well below their toxicity levels, as required by law.

Wine is not well endowed with vitamin content, although vitamin B_1 is present at higher levels than grape juice, due to yeast autolysis or possibly because it has been added (along with diammonium phosphate) as a yeast nutrient before fermentation. Table 17 summarizes the vitamin content of wine.

Other Components

Biogenic amines, principally histamine and tyramine, are formed in wine as a result of decarboxylation of α-amino acids during alcoholic and malolactic fermentation. Figure 14 gives an outline of this, with examples and other information. These amines are of interest because of their potentially allergenic character toward some predisposed individuals (Önal 2007).

Ethyl carbamate (urethane), a mild carcinogen, is found in wine at levels 0–24 μg/L, although higher concentrations are found in fortified, heat-treated wines, Asian rice wines, and especially spirits. It is formed by reaction of urea (a fermentation byproduct) with ethanol (Fuller et al. 2011, pp. 1093–1110).

Sulfite exists in wine naturally, but because it is very widely used as a preservative in the wine industry, it is generally present in wine at concentrations of ~100- ~ 400 mg/L. The most active form is molecular SO_2, but much of this is bound to carbonyl compounds and phenols in wine. Like amines, sulfite is potentially allergenic. Legal total sulfite levels depend on national regulations but generally should not exceed ~260 mg/L for dry wines and ~400 mg/L for sweet wines.

Carbon dioxide, a major fermentation product, is essential in the production of sparkling and semi-sparkling wines – in lesser amounts it can add an attractive mouthfeel to young wines ("pétillant" or "spritzig" wines). Full sparkling wines (vins mousseux) such as cava and champagne contain 11–12 g CO_2/L wine or ~6 L CO_2/L wine, which is equivalent to a 750 mL bottle internal pressure of ~6 atm at ~10 °C. Semi-sparkling wines (crémant, perlé, spumante) have bottle CO_2 pressures of 2 atm or less, while for pétillant or spritzig wines, this will be just over 1 atm.

Fortified Wines

These are wines with added grape spirit. They range from fino and manzanilla sherry; sercial and verdelho madeira, where small quantities of spirit are added late in the process, through port; bual and malmsey madeira; vins doux naturels (VDN); Australian liqueur muscats, where larger amounts of spirit are added early to stop fermentation, to vins de liqueur, where spirit is added to the grape must (no fermentation). Ethanol content (%ABV) of fortified wines is from ~16

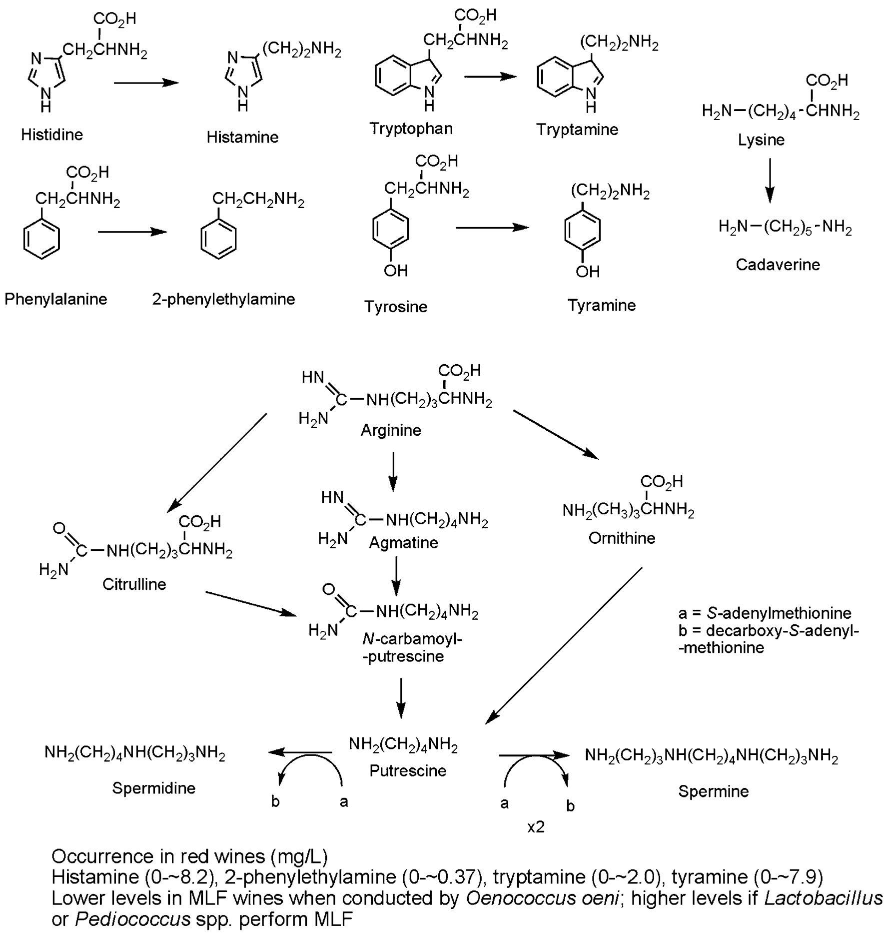


Fig. 14 Formation and distribution of biogenic amines in wine (Önal 2007 and references therein)

(fino and manzanilla sherry) – through ~17.5 (vins de liqueur) and 18–20 (most port, oloroso sherry, madeira, and VDN) – to 22+ (aged tawny port).

Several specific features essential in the manufacture of the best-known fortified wines have direct impact on the chemical composition of such wines, as summarized in Table 18.

Aromatized Wines

Aromatized wines are those flavored by the inclusion of aromatic substances of plant origin. They are also generally fortified with grape spirit or mistelle (a mixture of grape must and grape spirit). The best known is vermouth (16–18 % ABV), originating in northern Italy but now made in many countries. The flavorings, added

Table 18 Summary of influence on composition of special features in the production of some fortified wines[a]

Fortified wine type	Special features of production	Influence on wine composition (typical concentrations in mg/L)
Fino and manzanilla sherry	1. Grapes dusted with gypsum ("yeso") to aid formation of flor	1. Increased acidity
	2. "Biological aging" in part-filled cask: flor velum forms on surface, depletes O_2, prevents some oxidations, and utilizes amino acids	2. Pale color and higher levels of acetaldehyde, other carbonyls, acetal, 2,3-butanedione (acetoin), lower alcohols (e.g., isoamyl alcohol), lower fatty acids, and some lactones
Oloroso sherry	1. As above	1. As above
	2. Oxidative aging for long periods in cask: wines undergo enzymic and nonenzymic browning	2. Deeper color due to more flavonoid polymers. Low levels of acetaldehyde and higher levels of acetate and ethyl alkanoate esters, as well as some furans, methional, and sotolon[b]
Madeira	Estufagem: wines undergo heat treatment. Best wines kept in casks in south facing loft for 2 years or more. Undergo Maillard and related reactions, like Strecker degradation	Deeper color due to more flavonoid polymers. Some Maillard and Strecker products at high levels – HMF[c] (~361), methional, phenylacetaldehyde, γ-(methylthio)butanoic acid (~5.7), 2-phenylpyruvic acid (~9.6). Also 1,3-dioxolanes formed from acetaldehyde and glycerol
Ruby port	1. Short fermentation on pulp (with continual agitation), stopped by mixing with grape spirit; one with high aldehyde content preferred	1. Persistent deep red color due to formation of more stable vitisins, aldehyde-bridged oligomers, and others (Fig. 10). Survival of β-carotenoids, sulfur compounds, and other fermentation-sensitive compounds in young wine
	2. Standard (oxidative) cask aging for ~2 years	2. Slow development in bottle (e.g., slow conversion of β-carotenoids to odorous norisoprenoids)
Tawny port	1. As above	1. As above
	2. Much longer highly oxidative cask aging, with frequent forced racking (high exposure to O_2)	2. Brown coloration and faster conversion of β-carotenoids to odorous norisoprenoids, faster depletion of sulfur compounds, formation of 5-HMF[c] and sotolon[b] (~1)

[a]From McKay et al. (2011, pp. 383–418) and references therein
[b]Sotolon = 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone
[c]5-HMF = 5-hydroxymethyl-2-furaldehyde

to a white wine base, are extracts or essential oils of herbs, bitter roots, and bark (collectively known as "botanicals"). Red vermouth contains caramel, and mistelle is used to sweeten and fortify sweet vermouth. The chemical composition of vermouth is similar to the white wine base but with a large number of extra components (mostly at the μg/L or ng/L levels) derived from the botanicals and (for red vermouth) caramel. Examples of notable botanical components and their plant origins are given Table 19, but note that a particular compound may be present in several botanicals and may even be present in the base wine.

Resinated wines are white (and occasionally rosé) wines flavored with pine resin: retsina (of European Union (EU) designated origin Greece and Cyprus; 12.0–12.5 % ABV), fermented with pieces of Aleppo pine (*Pinus halepensis* Miller) resin, is the most famous example. Typically, retsina has significantly higher levels of terpenoids (pinenes, caryophyllene, cembrene, limonene, myrcene, terpinolene, and many others), as well as polyphenols (flavan-3-ols, *p*-coumaric acid, gallic acid, tyrosol, and others) that are mainly derived from the resin.

Fruit Wines

In a few cases, fruit wines can be made like grape wines: by crushing and pressing the fruit (with or without fermentation on the pulp), after minor adjustments of acidity and sweetness. However, in most cases, the fruit pulp is too low in sugar and too high in acid (see Table 7) and hence has to be considerably diluted with water and then brought up to balance with added sugar, acids, and (most likely) grape tannins, prior to fermentation. Concentrated grape juice might also be used to make these wines, and therefore much of their chemical composition originates from adjuncts (e.g., malvidin pigments from black grape juice, grape tannins, and citric acid and/or tartaric acid). Pectinase enzymes are very likely to have been used in the processing, thus releasing some less common sugars, uronic acids, and a little methanol. Table 20 lists some phenolic compounds and volatile compounds of selected fruit wines.

Cider

“Cider” is defined here as fermented apple juice (USA: hard (apple) cider), a drink that is popular in many European countries and is becoming well known worldwide. It can be produced from cider apples (*Malus sylvestris*) or dessert/culinary apples (*Malus domestica*), in which case the more strongly alcoholic versions are sometimes called apple wine. Cider from cider apples is usually notably higher in polyphenolic content, giving it more body (tannic taste and mouthfeel) than other cider.

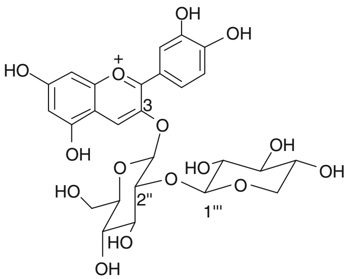
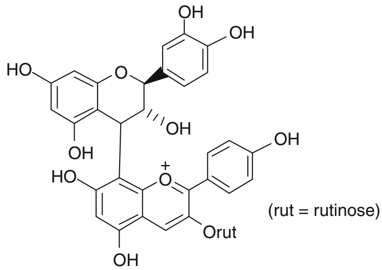
Different methods of production have a direct bearing on the chemical content of cider, and so will be outlined here. The two extreme production methods are the traditional and factory or industrial processes (Fig. 15), although in practice, many small producers may use some intermediate process. Traditional cider is made from the juice of freshly crushed and pressed apples, often using “spontaneous” fermentation, a minimum of added sulfite, often involving malolactic fermentation (MLF), and generally without filtration or pasteurization but often including some kind of

Table 19 Some flavor and bitter components of vermouth

Flavor components: monoterpenoid hydrocarbons							
Camphene	*p*-Cymene	Limonene	Myrcene	α-,β-Pinene	Sabinene	α-Terpinene	γ-Terpinene
(coriander, juniper)	(oregano)	(citrus)	(hop)	(citrus, juniper)	(coriander, juniper)	(hyssop, juniper)	(oregano)
Oxygenated monoterpenoids							
Camphor	1,8-Cineol	Citronellol	Linalool	Pinocamphone	α-Terpineol	4-Terpineol	α-, β-Thujone
(coriander sage)	(hyssop, mugwort)	(citrus, rose)	(coriander, hop, hyssop)	(hyssop)	(hyssop, juniper)	(juniper)	(mugwort, wormwood)
Aromatic monoterpenoids				**Sesquiterpenoids**			
Anethole	Estragole	Eugenol	*p*-Thymol	α-Bisabolol	β-Caryophyllene	Chamazulen	
(aniseed, star anise)	(basil, cinnamon)	(basil, cloves, cinnamon)	(oregano, thyme)	(chamomile)	(chamomile)	(chamomile)	
Bitter components							
Crategolic acid (cloves), oleanolic acid (cloves), ursolic acid (basil, oregano, thyme) – all pentacyclic triterpenoids							
Amarogentin (gentian), eugenetin, eugenin (cloves), gentiopicroside (gentian), deoxypodophyllotoxin (juniper), quinine (*Cinchona* spp.), santonin (wormwood), sweroside (gentian)							

Botanical names: aniseed (*Pimpinella anisum*), basil (*Ocimum basilicum*), chamomile (*Chamomilla recutita*), cinnamon (*Cinnamomum verum*), clove (*Syzygium aromaticum*), coriander (*Coriandrum sativum*), gentian (*Gentiana* spp.), hop (*Humulus lupulus*), juniper (*Juniperus communis*), hyssop (*Hyssopus officinalis*), mugwort (*Artemisia vulgaris*), oregano (*Origanum vulgare*), rose (*Rosa* spp.), sage (*Salvia officinalis*), star anise (*Illicium verum*), thyme (*Thymus* spp.), wormwood (*Artemisia pontica*)

Table 20 Some polyphenols and volatile compounds of selected fruit wines[a]

Polyphenols (wine where found)
Cyanidin 3-*O*-sophoroside (Fig. 1) (raspberry), cyanidin 3-*O*-sambubioside (elderberry), 5-carboxypyranocyanidin (strawberry), 5-methylpyranocyanidin (black currant), flavan-3-ol/pelargonidin type B dimer (strawberry), ellagitannins (strawberry), piceatannol (a stilbene) (blueberry)
 Cyanidin 3-*O*-sambubioside  Flavan-3-ol/pelargonidin type B dimer
Volatile compounds
Orange wine[b]
Ethyl butanoate (307), 3-methylpentanol (166), linalool (1,640), g-butyrolactone (491), 3-(methylthio)-propanol (166), geraniol (22.5), 2-phenylethanol (27,261)
Clementine/mandarin (*Citrus reticulata* Blanco) wine
Ethyl octanoate, ethyl decanoate, ethyl hexanoate, isoamyl acetate, 2-phenylethanol, ethyl acetate, limonene, ethyl succinate, ethyl dodecanoate, 5-hydroxymethylfurfural, furfural, 5-methylfurfural, 2-methyl-1-propanol, 4,5-dimethylfurfural, furfuryl alcohol
Strawberry wine[c]
Ethyl octanoate, ethyl decanoate, ethyl hexanoate, amyl acetate, isoamyl alcohol, ethyl dodecanoate, ethyl 9-decenoate, *trans*-nerolidol, ethyl cinnamate, octyl acetate, methyl decanoate, decanoic acid, octanoic acid
Black raspberry wine[d]
Isoamyl alcohol (657–1,158), isobutanol (270–464), methanol (266–302), ethyl acetate (87.1–278), 1-propanol (75.2–145), acetaldehyde (24.8–43.2), isoamyl acetate (9.64–46.24), methyl acetate (9.11–15.8), 1-butanol (0–3.61), benzaldehyde (0–3.47), furfural (1.34–2.21), ethyl hexanoate (1.32–1.84), *trans*-β-damascenone (1.25–1.47), 2-phenylethyl acetate (0.89–1.24), acetone (0–1.21), ethyl furoate (0.01–0.23)

[a]From McKay et al. (2011, pp. 419–435) and references therein, unless specified otherwise
[b]From Selli et al. (2008). Most potent odorants out of 35 listed in mg/L
[c]From Kafkas et al. (2006)
[d]From Lim et al. (2012). In mg/L rounded to 3 or 4 significant figures. Range for wines made from juice or juice-pulp or juice-pulp seeds

fining. Hence the product can be hazy (like west of England "scrumpy" and French "cidre fermier") or near bright to bright (like some English cask cider, French "cidre bouché," and cider from northern Spain).

Factory cider is generally made with much greater control and refinements, and in many cases, diluted apple juice concentrate (AJC), obtained locally or bought on the world market, forms part of the must. MLF is often actively discouraged. The product is usually bright, with less pronounced aromas and flavors.

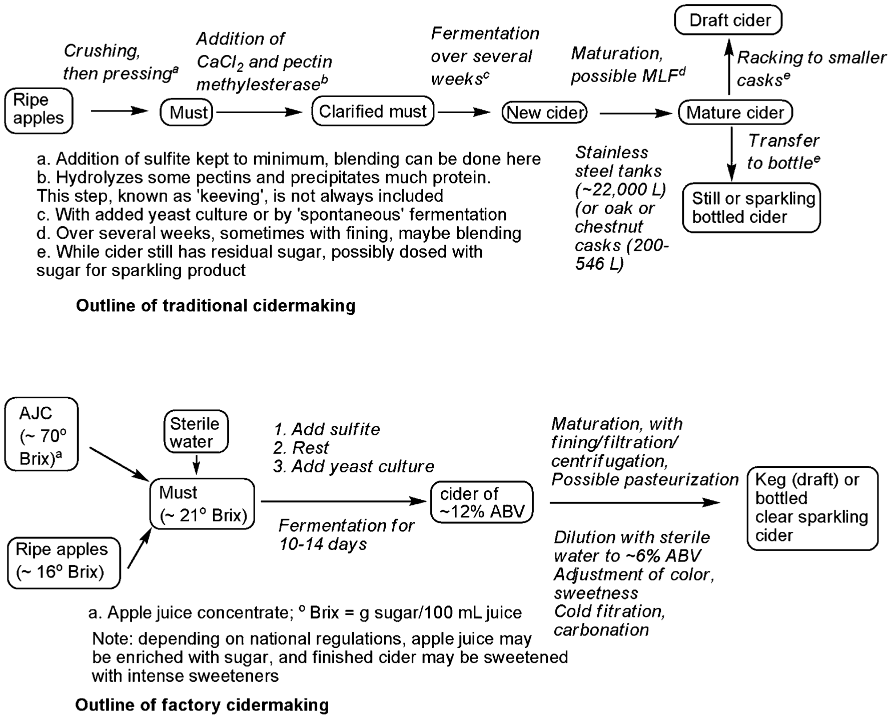


Fig. 15 Outline schemes for traditional and factory cider production (Based on McKay et al. 2011, pp. 231–265)

Ethanol Content

The usual range of ethanol content of cider (Table 17) is from ~2–2.5 % ABV (for sweet cider of Brittany and Normandy) to 5–9 % for most dry European cider. Added sugar (according to national regulations) can raise the % ABV to 12 or more (e.g., for apple wine).

Polyphenol and Acid Content

An outline polyphenol content of English cider is given in Table 21, where probably the lower ends of the ranges correspond to cider produced from non-cider apples, which usually have much lower phenolic content.

The most notable polyphenols are caffeoylquinic acid and *p*-coumaroylquinic acid (hydroxycinnamic acids), phloridzin (phloretin 3-*O*-glucoside) and phloretin 2′-*O*-(2″-xylosylglucoside) (dihydrochalcones), flavan-3-ols, procyanidins (from dimers up to ~60-mers), and flavonols (Fig. 16). Anthocyanins present in the skins of some cider apples are usually present only at very low levels.

The major acids of cider produced without MLF are L-malic, citric and succinic acids, whereas in MLF cider, malic acid is almost depleted and high levels (up to 5 g/L) of L-lactic acid may be observed. Other acids include D-lactic acid, sugar acids, fumaric acid, shikimic acid, and volatile acids (see later).

Table 21 Phenolic components of English cider[a]

Total hydroxycinnamates	Total dihydrochalcones	Total flavonols	Total flavan-3-ols	Total procyanidins	Total phenolic content
10–584[b]	4–93[c]	2–26[d]	7–224[e]	8–722[f]	44–1,559

[a]Data (for 23 ciders of wide range of styles), in mg/L, from Marks et al. (2007). Lower values are associated mainly with ciders produced from either apple juice concentrate or dessert apples
[b]Most abundant hydroxycinnamate: 5-*O*-caffeoylquinic acid (12–437 mg/L)
[c]Most abundant dihydrochalcone: phloridzin (2–71 mg/L)
[d]Most abundant flavonol: quercetin 3-*O*-galactoside (1.1–12.5 mg/L)
[e]Including procyanidin B_2. Most abundant flavan-3-ol: (−)-epicatechin (1–106 mg/L)
[f]Mostly dimers and trimers

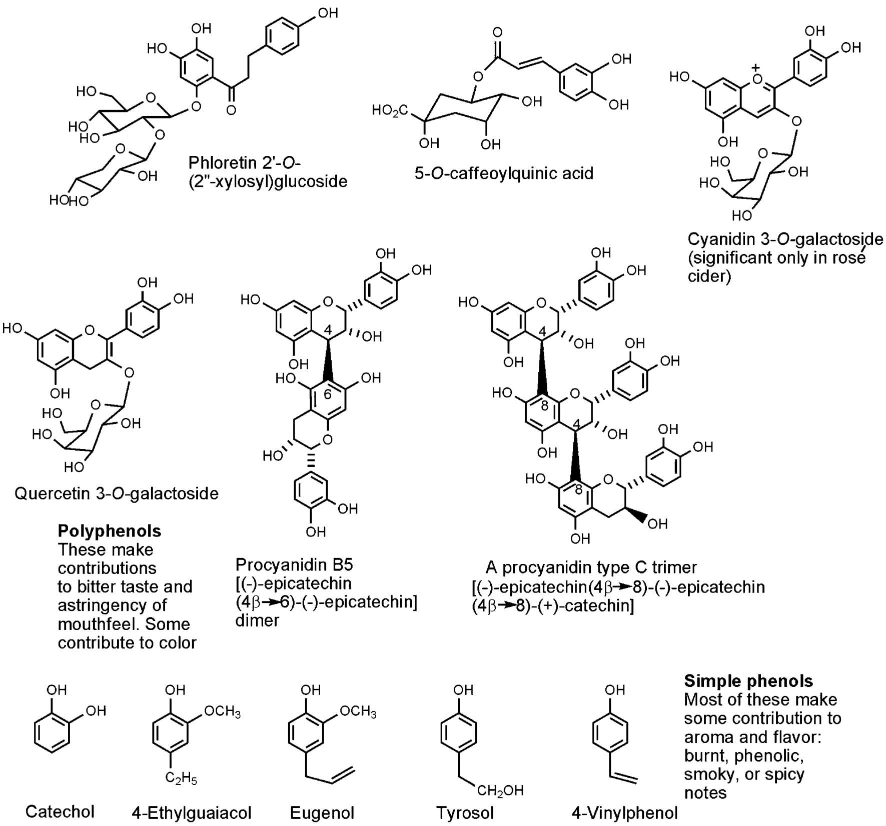


Fig. 16 Some notable phenolic substances in cider

Carbohydrates

Much cider is dry, so residual sugar levels are often low, composed mainly of fructose, sorbitol, and sugars derived from pectin degradation. Acid pectic substances, in particular, are usually highly degraded, especially if keeving has been

Table 22 Volatile compounds of Fuji apple wine[a]

Compound	Concentration (mg/L)	Flavor descriptor	Compound	Concentration (mg/L)	Flavor descriptor
Alcohols (not including ethanol)			**Esters**		
2-Butanol	184.85	Fusel oil	Ethyl acetate	54.8	Fruity
Isoamyl alcohol	232.00	Fusel oil	Ethyl butanoate	2.19	Pineapple
1-Hexanol	2.18	Grassy	Ethyl decanoate	1.50	Fruity
2-Phenylethanol	43.50	Rose	Ethyl hexanoate	0.72	Floral
Acids			Ethyl lactate	4.63	Winey
Acetic	282.93	Vinegar	Ethyl octanoate	1.09	Fruity
Hexanoic	4.75	Sweaty	Diethyl succinate	0.24	Winey
Octanoic	6.11	Sweaty	Isoamyl acetate	16.66	Fruity

[a]Data from Wang et al. (2004). Apple wine (12.0 % ABV) was prepared from Fuji dessert apples, with added sugar, cultured yeast, and pectin methylesterase. Note that no other lower carboxylic acids were found, and phenols were present only at trace levels

used in the manufacturing process (Fig. 15). Typically, they are present up to ~44 mg/L, while neutral pectins and polysaccharides are usually at higher levels (up to ~244 mg/L) (Mangas et al. 1999).

Volatile Compounds

As with wine, many volatile compounds of cider are derived from alcoholic (and possibly malolactic) fermentation, and others originate from the fruit. The most flavor active compounds in cider are given in Tables 22 and 23, the former relating to apple wine type (~12 % ABV) from a dessert apple variety, the latter to traditional cider produced from French cider apples.

It can be seen that the traditional cider is richer in volatile phenols (phenolic, spicy notes), probably derived from MLF, and lower carboxylic acids (cheese notes). Additional to the compounds listed in Tables 22 and 23 is an acetal (green cider notes) formed by reaction between octane-1,3-diol (released from its glucosides during fermentation) and acetaldehyde, a fermentation byproduct (McKay et al. 2011, pp. 231–265 and references therein; Fig. 17).

Organic Nitrogenous Compounds, Minerals, and Vitamins

Thanks to the cidermaking process (especially keeving and fermentation), cider is low in amino acids, peptides, and proteins (Table 17). Proteins, possibly mostly

Table 23 Volatile compounds in French cider (cidre), with aroma descriptors[a]

Alcohols	Carboxylic acids	Esters		Miscellaneous
		Acetates	Ethyl Alkanoates	
3-Methyl-1-butanol (fusel oil)	Butanoic acid (rancid)	Butyl (pineapple)	Butanoate (pineapple)	γ-Butyrolactone (butter)
2-Phenylethanol (rose)	2-Methylbutanoic acid (blue cheese)	Heptyl	Dodecanoate (floral)	α-Farnesene (citrus, herb)
		Hexyl (apple)	Heptanoate (fruit, wine)	2,6-Dimethoxyphenol (medicinal)
		2-Methylpropyl (green apple)	Hexanoate (banana)	2-Methylnaphthalene (camphor)
		3-Methylpropyl (apple)	2-Methylbutanoate (green apple)	Oct-1-en-3-one (mushroom)
		2-Phenylethyl (rose, honey)	3-Methylbutanoate (green apple)	Phenol (phenolic)
			2-Methylpropanoate (fruit)	2-Phenylacetaldehyde (pungent, floral)
			Pentanoate (apple),	1,2,4,5-Tetramethylbenzene (rancid)
			Propanoate (pineapple)	4-Vinyl-2-methoxyphenol (spicy, phenolic)
			Tetradecanoate (sweet, wax)	
			Other alkanoates:	
			3-Methylbutyl octanoate	
			2-Methylbutyl 2-methylbutanoate (berry fruit)	

[a]Other than ethanol. Data from Villière et al. (2012). Most of these compounds have been detected in cider from many other countries, made from many apple cultivars

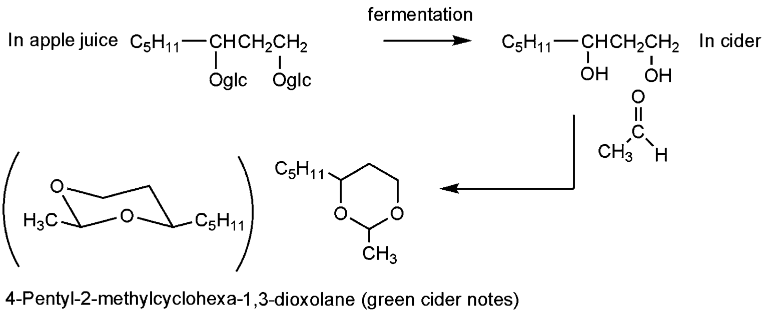


Fig. 17 Formation of odorous acetal in cider (Based on McKay et al. 2011, pp. 231–265)

glycoproteins, of molecular weights 16,000–110,000 Da, exist in cider, with the most abundant one (an apple protein involved in haze formation) having a molecular weight of 36,400 Da. Likewise cider is not rich in minerals and vitamins compared with wine (Table 20).

Perry

Perry (USA: hard pear cider) or pear wine is the fermented juice of pears (perry pears or dessert pears) and is a similar drink to cider. Flavan-1,4-diols (anthocyanogens) (Fig. 3) have a significant presence in perry, unlike cider. Likewise higher sorbitol content of pear juice gives a high final specific gravity to (1.005–1.010) perry compared with cider of the same alcoholic strength.

Beer

Although there are many methods used to produce modern beer, the features common to nearly all of them are:

- Conversion of the starches of malted cereals (principally barley), in a mash of crushed grains and hot water (liquor), to soluble sugars
- Boiling the mash filtrate (wort) with hops (and/or other flavorings)
- Fermentation of the cooled, filtered hopped wort by (usually added) yeast
- Conditioning and processing the beer before releasing it for sale

Unmalted cooked cereal grains, such as rice or maize, as well as other adjuncts, like brewing flours and sugar syrups, can be used as well, according to law or established good brewing practices. An outline of beer production stages is given in Table 24, along with indications of how variations can influence the chemical composition of the finished beer.

Table 24 Important stages in the brewing of beer[a]

Stage	Purpose	Comments
1 (a) Malting	(a) To stimulate production of hydrolytic, redox, and acid regulatory enzymes and to promote a limited degradation of cereal starch, protein, and cellulose. Known as modification	(a) Warm, moist conditions cause germination of the barley grains, which is then stopped by drying
(b) Drying	(b) To stop germination/modification	(b) With hot air. Gives pale malts with malty, biscuity flavors. High degree of enzyme activity
(c) Kilning (roasting)	(c) To produce colored malts, depending on temperature, duration of heating, and initial moisture content of malt	(c) In slotted, rotating drums. Special flavors (e.g., chocolate, coffee) result from caramelization and Maillard reactions. Low or zero enzyme activity
2. Mashing of crushed malted cereal grains	To convert starch to soluble sugars, proteins to smaller peptides and amino acids, and cellulosic polymers to smaller polymers and oligomers: β-glucans and arabinoxylans (pentosans)	Temperature of ~65 °C gives ~80 % fermentable sugars. The partially or non-fermentable sugars are called α-glucans or dextrins. When the cereal/water porridge is filtered, it is called wort
3. Boiling the wort with hops or hop products	To give biochemical and microbiological stability, haze stabilization (by precipitating protein–polyphenol complexes), and to change the flavor profile (by inclusion of hops, promoting thermal reactions, and loss of unwanted compounds, like DMS[b])	Hops are the traditional flavoring. Boiling is needed to convert α-acids to bitter *iso* acids. Many other volatile and nonvolatile compounds are extracted from hops
4. Cooling the hopped wort	To precipitate and remove insoluble material and to prepare for fermentation	Insoluble material is called trub. It is mainly proteins, lipids, and polyphenols
5. Fermentation of the hopped wort	To cause biochemical changes that produce beer	Most beers are fermented with added yeasts (*Saccharomyces cerevisiae* for top fermentation at ~17 °C or *S. uvarum* at ~9 °C or lower for bottom fermentation)[c]
5. Conditioning the new beer	To mature the beer to give a better-flavored product (including removal of unwanted compounds, such as diacetyl)[d] and to maximize solubilization of CO_2	Traditional lager is matured at ~5 °C for many weeks. Ale can be matured at this temperature, but in cask, usually at ~15 °C for 2–3 weeks. Many modern lagers are conditioned at ~ −2 °C for a few days. For most beers, fining, filtration, pasteurization, artificial carbonation or priming, and other steps are included before release for sale

[a]Assuming basic cereal origin is barley, as for most beers
[b]Dimethyl sulfide
[c]Many modern lagers are fermented close to ale temperatures for a few days and then matured at very low temperatures, to speed up turnover
[d]Diacetyl is a strongly odorous fermentation byproduct – it is reabsorbed by yeast and reduced to a flavorless product

Ethanol, Water, and Carbohydrates

Typical ethanol, water, and carbohydrate contents of beer are given in Table 17. Ethanol content of most beers is in the range 3.5–6.5 % ABV, but some strong ales and lagers have up to 12 % ABV: higher values than this indicate that the beer has been freeze-distilled. Much water ("liquor") is used for brewing: it must conform to national purity and safety standards (low heavy metal, nitrate, organic compound content, high clarity, acceptable pH, no pathogenic bacteria, etc. – see Fuller et al. 2011, pp. 1076–1092 and references therein), whether it comes from a private well or some public source. Depending on the desired style of beer, the liquor is often adjusted for acidity and mineral content prior to mashing. For example, permanently hard water (with high $CaSO_4$ and $MgSO_4$ content) is needed for pale ale, very soft water is best for Pilsner, and temporarily hard water (rich in $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$) suits dark beers, like Münchener, porter, and stout. The mineral contents of these beers differ accordingly.

During mashing at ~65 °C, linear amylose starch and branched amylopectin starch are hydrolyzed by α- and β-amylases and limit dextrinase mainly to oligomers (α-glucans or dextrins ~20 %), maltose, and glucose (Fig. 18; Table 25). The latter two are fully fermentable by brewer's yeast, but many oligomers are either only slowly fermentable or (those with α-glc(1–6)α-glc links) non-fermentable and so remain in the finished beer, giving it "body" and a little sweetness. Lower mash temperatures produce more complete hydrolysis, which ultimately results in a strong, drier, "low-carb" or "diet" beer. Higher mash temperatures give less degradation, which produces a weak, sweet "high-carb" beer, like Malzbier, if partially fermented at a very low temperature.

Also during mashing, cereal cell walls are enzymatically degraded to polymeric (insoluble) and, especially, oligomeric (soluble) β-glucans and arabinoxylans (pentosans) (Fig. 18), many of which are linked to polyphenols like ferulic acid. High levels of these compounds in unfinished beer can lead to filtration problems prior to packaging, so many brewers add exogenous pullulanase or pectolase enzymes to effect maximum degradation. However, these soluble fibrous compounds have health benefits (McKay et al. 2011, pp. 132–210 and references therein) – see Table 28 for fibrous carbohydrate contents of beers.

Carbon Dioxide

Carbon dioxide is a major fermentation byproduct and as such is used to provide the "sparkle" and foam ("head") of many beers, such as bottle- and cask-conditioned beers (mostly ales). However, most beers have at least some exogenous CO_2 added up to the time of packaging, and it is these beers – brewery conditioned canister (keg), bottled, and canned beers – that have the highest CO_2 content. Cask-conditioned beers contain <1.0–1.5 L CO_2/L beer; draft keg beers have 2.2–2.8 L CO_2/L beer, and bottled or canned beers contain 2.4–3.0 L CO_2/L beer (McKay et al. 2011, pp. 132–210), corresponding to internal pressures of ~1 atm to ~3 atm at ~10 °C.

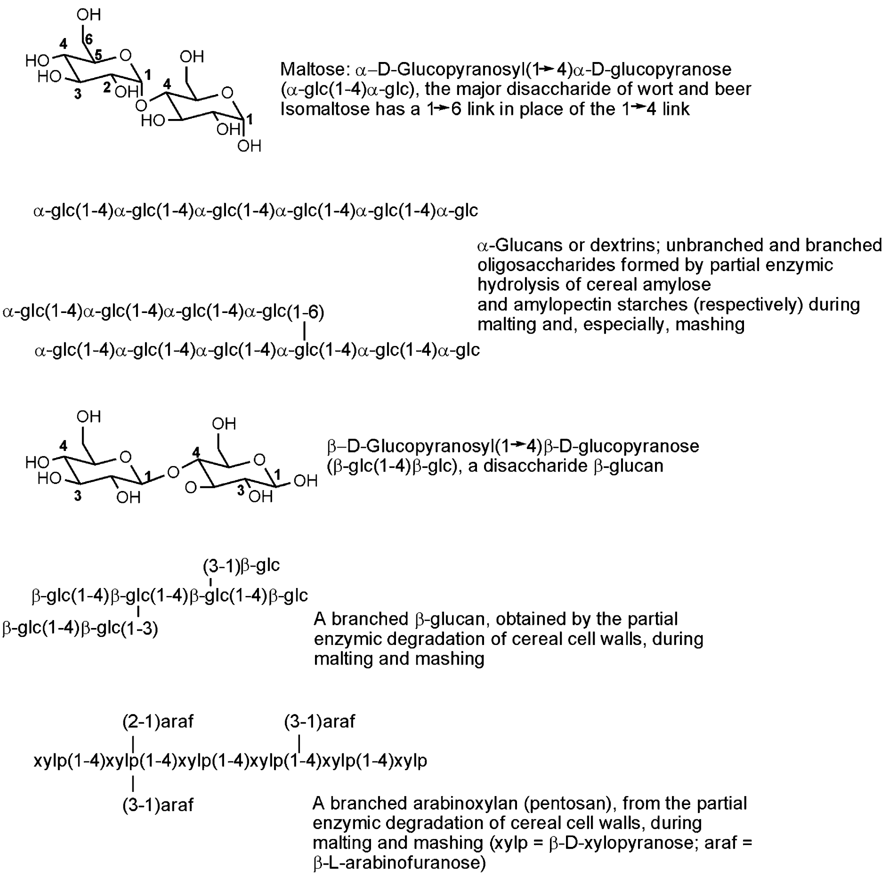


Fig. 18 Carbohydrates of wort and beer

Bitter Compounds

The flower (cone) of the female hop plant (*Humulus lupulus*) is easily the most widely used beer flavorant/preservative, being first documented in brewing in the eighth century AD. Hop cones when boiled with wort release phenolic norisoprenoid α- and β-acids (along with many other substances, including the prenylated dihydrochalcone xanthohumol) into the wort, where isomerization of α-acids to iso-α-acids, oxidation of β-acids, and many other reactions occur (Fig. 19), although isomerization of α-acids is only about 30 % complete in 1 h.

Many of these compounds contribute to the familiar bitter taste of beer, but it is the iso-α-acid stereoisomers that are considered to be the most important. Total iso-α-acid content of beer normally ranges between ~15 mg/L and ~60 mg/L and of particular styles as follows: brown ale (15–30 mg/L), pale ale (20–55 mg/L), Pilsner (20–40 mg/L), stout (~30 mg/L), extra stout, and strong beers (up to 60 mg/L). Generally the most abundant iso-α-acids are the *cis*-isomers,

Table 25 Carbohydrates in beer[a]

Monosaccharides, disaccharides, and α-glucans (dextrins)								
Carbohydrate	Glucose[b]	Fructose	Maltose[c]	Isomaltose	Trehalose	Maltotriose	Maltotetraose	Oligomers
Degree of polymerization	1	1	2	2	2	3	4	5–9
Molecular weight (D)	180.2	180.2	342.3	342.3	342.3	504.5	666.6	828.8–1477.4
Mean no. branches/molecule	–	–	–	–	–	–	0	1–2
β-Glucan and arabinoxylan content[d]								
Beer type	Standard filtered beer			Bottle- or cask-conditioned beer		Strong ale or wheat beer		
Content (g/L)	0.5–3.0			Up to 10.0		Up to 6.0		

[a]Derived from cereal. Data from Duarte et al. (2003) or McKay et al. (2011, pp. 132–210) and references therein
[b]The major monosaccharide
[c]The major disaccharide
[d]Dietary fiber

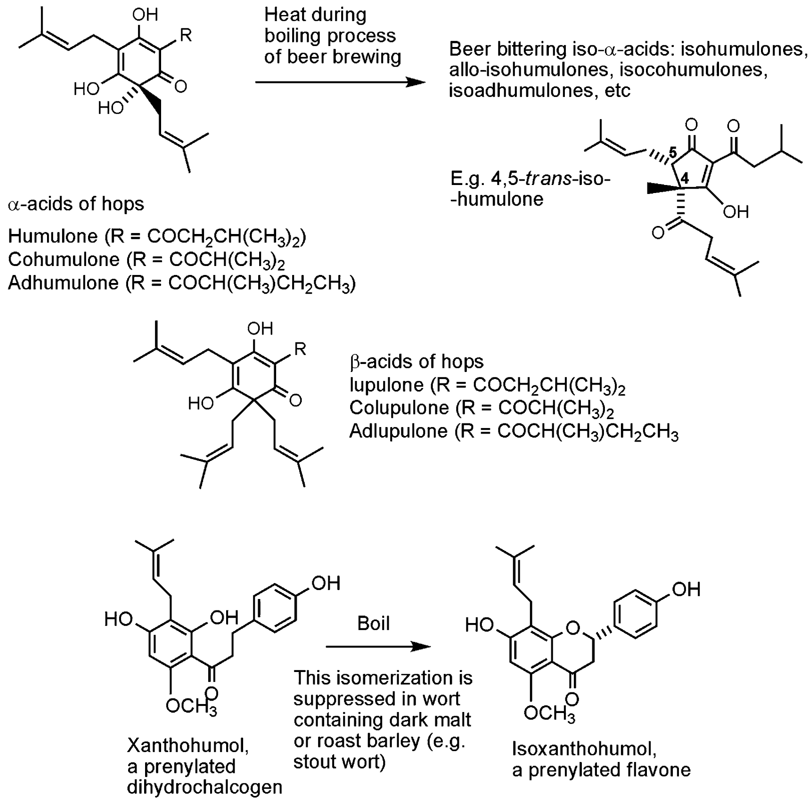


Fig. 19 Major bittering substances in beer and their origins

Table 26 Iso-α-acid content of Pilsner beers[a]

Iso-α-acid	*c*-ich	*t*-ich	*c*-ih	*t*-ih	*c*-iah	*t*-iah
Content (mg/L)	9.7	2.7	7.9	2.2	2.5	0.7

c cis, *t trans*, *ich* isocohumulone, *ih* isohumulone, *iah* isoadhumulone
[a]Data from Jaskula et al. (2007): liquid–liquid extraction of isoacids from beer, followed by quantitation by HPLC. Mean of replicate values for three beers

with *cis*-isocohumulone and *cis*-isohumulone being the most abundant of all (Table 26), and the cohumulones are the most intensely bitter. Because of high variations in α-acid and volatile terpenoid content of hop varieties, hops are divided into three categories: aroma or noble (low α-acid; ~5 % w:w), intermediate or dual purpose, and bittering (high α-acid; 8–15 % w:w).

Volatile Compounds

Also released into the wort from hops during the boil are numerous volatile compounds, many of which are important contributors to beer hop aroma. These

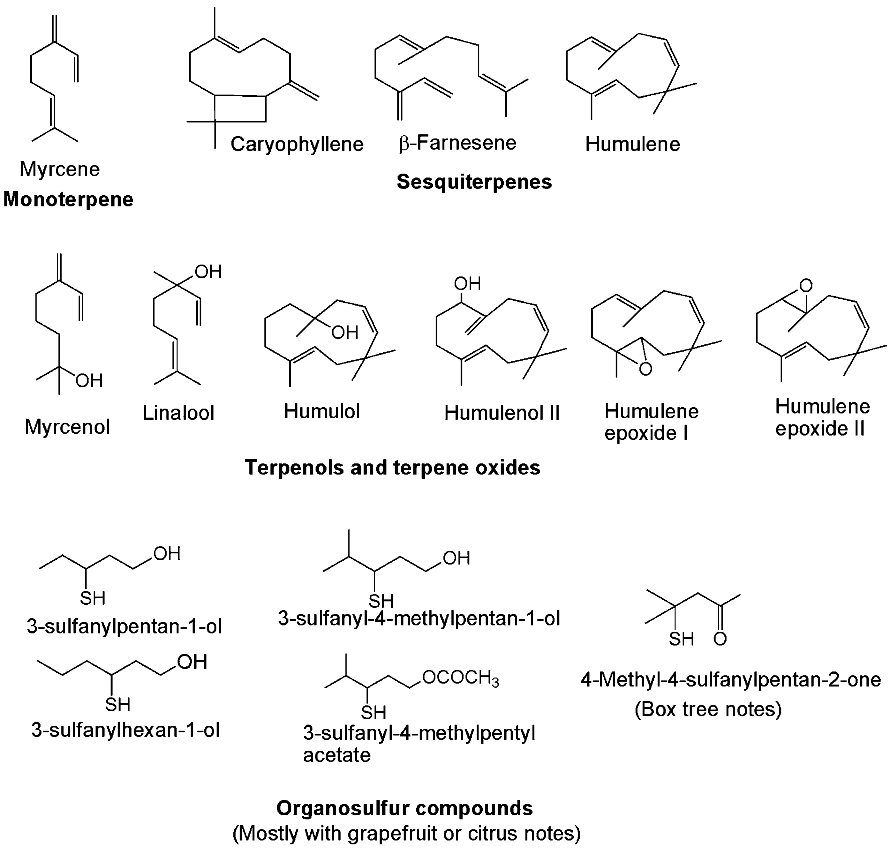


Fig. 20 Some volatile compounds of hops

include large numbers of fatty acids, carbonyl compounds, esters, and furans, but of special interest are the terpenoids (particularly oxygenated sesquiterpenoids) and sulfur compounds (Fig. 20), since these are thought to be the biggest contributors.

During the boil, some of these terpenoids undergo a variety of transformations and some will be lost via evaporation, so to compensate for this, some brewers add a portion of hops late in the boil or hop oil at later stages of the process. The most abundant terpenoids in Bavarian beer (in μg/L) were humulenol I (1150), linalool (450), humulol (220), and humulene epoxide I (125), followed by Karahana ether (60), 7,7-dimethyl-6,8-dioxabicyclo[3,2,1]octane (50), T-cadinol (45), humulene epoxide II (40), β-fenchyl alcohol (40), and α-terpineol (40) (Hough et al. 1982, pp. 422–453 and references therein).

Although much of the primary beer aroma is derived from hops, some volatile compounds originating from wort or produced by yeast alcoholic fermentation also make important contributions. These include ethanol, CO_2, some lower alcohols, some esters, lower carboxylic acids, and caramelization/Maillard and related products (various *O*- and *N*-heterocycles). The latter have special importance if caramalts, crystal malts, roast malts, or roast barley are used in the brew, but they are also present generally, as a result of the boiling stage. A summary of typical beer volatile compounds is given in Table 27.

Amino Acids, Peptides, Proteins, and Other Nitrogen Compounds

Beer generally contains a rather greater quantity and wider range of these compounds than cider or wine, even though much is lost during boiling (as "trub") and fermentation. The total nitrogen (*N*) content of beer is in the range 300–4,000 mg/L (mostly up to ca. 2,000 mg/L), with α-amino *N* content making up about 6–15 % of this, the remainder being ammonium, peptides, polypeptides, proteins, nucleic acid *N* components, biogenic amines, and *N*-heterocycles (see "Volatile Components"). They originate mostly from wort (cereal) and yeast. Table 28 displays the range and mean values of amino acids in 35 beers (Kabelová et al. 2008), where it can be seen that L-proline is easily the most abundant, because of its resistance to metabolism during fermentation.

Around 30 proteins or polypeptides have been found in beer, mostly glycopeptides or glycoproteins in the molecular weight range 5,000–12,000 Da, but also some of ~40,000 Da, one of which is related to "barley protein Z" (which binds β-amylase), and a few in the range 100,000–150,000 Da. The latter are thought to have a positive influence on foam quality, whereas some of the smaller glycoproteins are believed to have a negative influence on beer clarity. The small quantities of hordeins (the prolamins of barley gluten, with molecular weights of 30,000–50,000 Da) that are also present (especially in less refined beers) are of interest because of their potential effect on gluten-sensitive individuals. Biogenic amines, especially histamine and tyramine, in beer (3.02–3.23 mg/L and 3.61–7.4 mg/L, respectively – similar levels to red wine) are likewise of interest, because of their potentially allergenic nature (Fuller et al. 2011, pp. 1093–1110).

Individual nucleotides, nucleosides, and their nitrogenous bases (pyrimidines and purines) are present in the ranges (mg/L) 1.1–73.3, 7.0–139.0, and 0.2–41.0, respectively, the total content of these species being much higher than in cider or wine.

Phenolic Compounds

According to the predominant brewing methods, phenolic compound levels in beer are low, even though malt and hops are rich in polyphenols and certain volatile phenols are formed during fermentation. This is largely because too high a phenolic content in the finished beer can lead to hazes (polyphenol–protein colloids) and premature staling, which produces unacceptable aroma and flavor (Table 29).

Much of the malt polyphenols exist as cross-links between the polymeric carbohydrate chains that form the grain cell walls. Some of these, and much of the free polyphenols (some from hops), are lost in the boiling step as "trub," along with proteinaceous material and lipids. One important hop-derived prenylated polyphenol, xanthohumol, partially survives the brewing processes, some of it being isomerized to isoxanthohumol during boiling (Fig. 13). Xanthohumol levels in beer are in the range (0.126–0.200 mg/L), and both compounds have been shown

Table 27 Typical volatile compounds in beer[a]

Compound	Typical or range of concentrations (μg/L)	Odor threshold value (OTV)[b] (μg/L)	Odor activity value (=concn/OAV)[c]	Comments
Ethanol	$3.5–6.5 \times 10^7$	1.0×10^5	350–650	
CO_2	Tr.–37.2×10^3	150	0.72	
Acetaldehyde	20–580	0.5	0.40–2.41	
Diacetyl	0.36	7.0×10^4	0.29–0.85	Highest levels in ales
Hex-2-enal	$0.5–6.0 \times 10^4$	6.5×10^4	0.24–2.1	
1-Propanol	$0.6–9.8 \times 10^4$	33	0.25–3.1	
2-Methylpropanol	$0.8–4.1 \times 10^4$	3.3×10^4	0.05–0.8	
2-Methylbutanol	$0.28–1.69 \times 10^5$	1.6×10^3	0.33–0.88	
3-Methylbutanol (isoamyl alcohol)	$1.9–5.5 \times 10^4$	2.0×10^4	0.87	
2-Phenylethanol	0.1–0.4	1.75×10^5		
Dimethyl sulfide	345–3,175	1.5×10^3		Highest level in lagers
Methionol	$0.8–6.9 \times 10^4$			
Ethyl acetate	$0.4–4.9 \times 10^3$			
Isoamyl acetate	$0.1–1.6 \times 10^4$			
SO_2	$0.57–1.45 \times 10^5$			
Acetic acid	1.3×10^3			Lambic and Gueuze beers have higher levels
3-Methylbutanoic acid	$0.41–9.63 \times 10^2$			
4-Vinylphenol[d]	$0.053–3.76 \times 10^3$			Higher values for blond ales and wheat beers
4-Vinylguaiacol[d]				
Humulenol I	1,150			
Linalool	450			
Humulol	220			
Humulene epoxide I	125			
2-Acetylfuran	$0.4–9.7 \times 10^4$	8.0×10^4	0.05–1.2	Higher levels in dark beers
5-Hydroxymethylfurfural	$0.5–7.8 \times 10^3$	1.0×10^6		None have OAV > 1, but collectively they give burnt/coffee aroma
2-Methylpyrrole	1.8×10^4	$20–10^3$		
Pyrazines[e]	Tr.–4.19×10^2			

[a]Data from Hough et al. (1982, pp. 776–838), unless stated otherwise
[b]In water or beer: these values can vary enormously according to experimental design and hence should be used as a guide to odor potency
[c]OAV > 1 indicates individual contribution to aroma, but values lower than 1 for family groups of compounds (e.g., pyrazines) can be important
[d]Data from Vanbeneden et al. (2008)
[e]Methylpyrazine, tetramethylpyrazine, pyrazine, and 2-ethyl-3,5-dimethylpyrazine, in particular

Table 28 L-Amino acid content of beers[a]

L-Amino acid	ASP	ARG	ALA	GLU	GLY	HIS	ILEU	LEU	LYS
Range (mg/L)	1.5–26.4	3.8–92.2	11.1–63.6	0.3–32.9	6.2–130	2.2–33.9	1.5–21.3	2.5–41.9	1.8–36.2
Mean (mg/L)	9.2	33.5	40.2	10.9	22.3	14.9	8.9	15.4	12.2
L-Amino acid	MET	PHE	PRO	SER	THR	TYR	VAL		
Range (mg/L)	1.1–10.4	2.9–46.4	31.8–250.4	0.6–25.7	1.5–59.2	2.9–50.6	2.7–39.9		
Mean (mg/L)	4.1	19.3	146.3	9.4	10.1	22.0	21.6		

[a]Data from Kabelová et al. (2008) from analysis of 35 European beers

Table 29 Compound giving rise to aged aromas and other organoleptic perceptions of stale beer[a]

Compound	Aroma (other)	Major origin and comments
trans-2-Nonenal	Cardboard (astringent mouthfeel)	From oxidation of linoleic acid and aldol condensation of lower aldehydes (from oxidation of lower alcohols). Detected at low levels because of low odor threshold value (OTV) (0.1 mg/L)
Oxidized flavonoid phenols (*o*-quinones)	Grassy, metallic	Flavonoids may be oxidized by oxidized melanoidins (Maillard reaction products)
3-Methylpropanal (isovaleraldehyde)	Grassy	The *o*-quinone groups can cause hazes via polyphenol–protein colloids
Hexanal	Cheesy, goaty	General oxidation of 3-methylpropanol (a fusel alcohol)
3-Methylpropanoic acid	Grassy, currant	Oxidation of unsaturated long-chain fatty acids
Strecker aldehydes (e.g., phenylacetaldehyde)		Oxidation of isohumulone (from hops)
		Reaction between amino acids and 4,5-epoxy-2-alkenols (breakdown products of oxidized unsaturated long-chain fatty acids)

[a]Information from McKay et al. (2011, pp. 132–210), and references therein

to have highly estrogenic and anti-inflammatory properties. Also of health benefit are the small quantities of tumor-inhibiting isoflavones (biochanin A, daidzein, formononetin, and genistein) found in beer.

Volatile phenols, such as 4-vinylphenol (smoky, phenolic notes) (Table 27), can be found at beneficially low levels in ales (especially wheat beers) fermented at relatively high temperatures and in beers produced from smoked malt (Rauchbier and some porter beers).

Lipids

Beer contains only trace amounts of lipids (glyceride esters, fatty acids up to C_{18}, and steroids), since much of the original lipid content of malt is removed in the trub at the boiling stage. High lipid content reduces foam quality and oxidation of unsaturated long-chain fatty acids, like linoleic acid, can ultimately give *trans*-2-nonenal, a major "staling" compound of beer (cardboard notes) (Table 29).

Minerals and Vitamins

The mineral content of beer is very variable, since in practice many different brewing liquors are used, and there are many water treatments available to transform the liquor into one that is more suitable for brewing a particular beer style, including boiling, ion exchange, and reverse membrane osmosis (all performed prior to mashing). Nevertheless, beer is a rich source of minerals and some typical mineral contents are shown in Table 17.

Beer is generally rather richer in vitamins than cider or wine (Table 14). In particular, it is a rich source of folate, containing up to 68.2 μg/L (as 5-MTHF) (Owens et al. 2007).

Some Other Components

Malt and hops contain a wide range of both volatile and nonvolatile weak carboxylic and phenolic acids, while others are formed during fermentation, but usually at lower levels than those in cider or wine so that the total acidity of beer is normally not more than 1–2 g/L (as sulfuric acid), corresponding to pH 3.9–4.6. High concentrations of D- and/or L-lactic acid, along with a higher than normal level of acetic acid (and ethyl acetate), are indicative of the involvement of lactic acid bacteria and yeasts such as *Hansenula* and *Pichia* spp. during fermentation. Lambic and Gueuze beers, produced by spontaneous fermentation by such organisms, contain up to 3,500 mg/L lactic acid and 1,200 mg/L acetic acid. If *Brettanomyces* spp. are involved in fermentation (as in some Belgian ales, like Lambic beers), then short-chain fatty acids are produced in significant concentrations, giving pleasant cheesy notes.

A number of malodorous products are produced during the "staling" of beer, toward the end of its shelf life. This can happen prematurely if the levels of O_2, polyphenols, and/or lipids are too high in the new beer, so modern brewing processes strive to keep the levels of these substances low, especially in the later production stages. Oxidation is the basic cause of staling and occurs by a variety of routes, many being catalyzed by Cu^{2+}/Cu^{+}, Fe^{3+}/Fe^{2+}, and Mn^{3+}/Mn^{2+} redox systems. The major compounds associated with stale beer are shown in Table 29.

Many beers do not have added sulfite (preservative), but those that do are subject to national regulations regarding maximum total allowed sulfite levels (e.g., 200 mg/L in the EU and 80 mg/L in the USA).

Rice Wine

Rice wine, in its many variations, is enjoyed all over eastern Asia, and some forms of it (like Japanese sake) have some popularity in the USA and Europe. Rice wine production is more like that of beer than wine, but hops are not used in rice wine manufacture and the saccharification of starch and fermentation steps occur in the same vessel (occurring either simultaneously or sequentially) (McKay et al. 2011, pp. 211–230 and references therein). As a typical example, Fig. 21 shows the outline of the traditional production process for makkoli (makgeolli), a popular Korean cloudy rice wine. In all cases, a mash of cooked milled rice and water (porridge) is treated with certain amylolytic and fermentative fungi and lactic acid bacteria (LAB) growing on a suitably nutritious medium (the "starter"). Details of the starter are given in Fig. 21.

Rice wine can be cloudy or clear, usually unflavored but sometimes flavored with fruit juice or syrup, flowers, herbs, or mushrooms. The cloudy drinks, in particular, are a rich source of carbohydrate (including dextrins and fibrous β-glucans), amino acids, proteins, and minerals (Tables 14 and 17). The ethanol content of rice wine (Table 14) varies from 6 % to 7 % ABV for cloudy versions, like makkoli, to 16–20 % ABV for most clarified types, including Chinese "yellow wine" and sake. Ethanol (brewer's alcohol) may be legally added to some kinds of

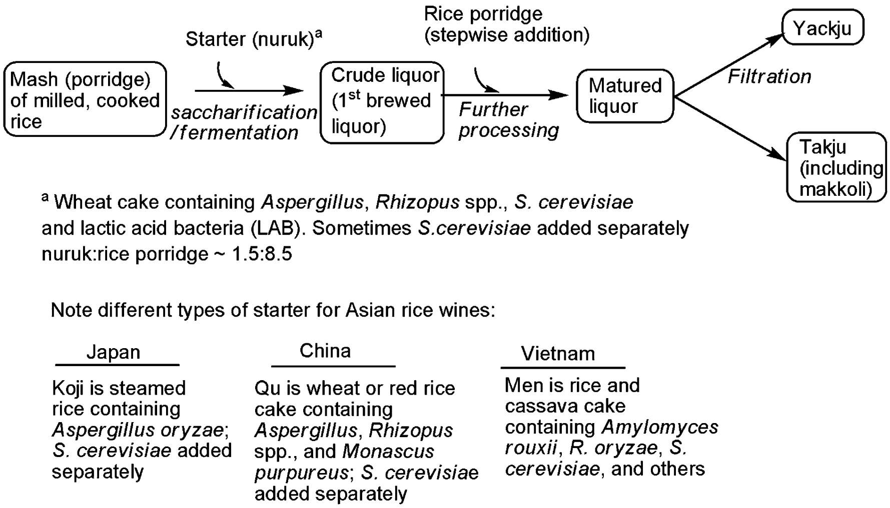


Fig. 21 Outline scheme for the manufacture of traditional Korean rice wine (Based on McKay et al. 2011, pp. 211–230)

sake. Also, because of the activities of LAB, rice wine generally possesses high levels of lactic acid (D- and/or L-isomers) – indeed in many modern styles of sake, lactic acid may be added with the starter.

The spectrum of microorganisms in the starter influences the flavor of rice wine (superimposed on a cereal-like alcoholic taste) via its volatile compound composition, as does the degree of polishing of the rice: highly polished rice gives a fruity product (e.g., much sake), whereas unpolished rice yields a product with earthy, grainy notes as well as fruity notes (e.g., some Chinese rice wine). The volatile compounds of rice wine are typified by two examples. Table 30 demonstrates the fruity-wine character of makkoli made from polished rice, while Table 31 shows the more aromatic characters of some Chinese rice wines, where benzenoid compounds, furans, *N*-heterocycles, phenols, and sulfur compounds are in evidence, as well as acids, alcohols, carbonyl compounds, and esters.

Spirits

If any alcoholic beverage (5–12 % ABV) is boiled, and if its vapor is condensed, then the result will be a crude distilled spirit containing ~22–30 % ABV. Most of the nonvolatile components in the wine (pigments, polyphenols, carbohydrates, acids, amino acids, peptides, proteins, and minerals) are left behind in the still, whereas the distillate is composed of ethanol, water, and many volatile flavorants ("congeners"; Fig. 22). The volatiles of most spirits (irrespective of identity) generally fall into the categories: esters, aromatic compounds, terpenoids, alcohols, acetals, aldehydes, phenols, ketones, furans, carboxylic acids, other heterocyclic

Table 30 Volatile compounds in makgeolli (makkoli), a Korean rice wine[a]

Alcohols	Acetate esters	Ethyl alkanoate esters
Isobutanol (24.2–43.4)	Isobutyl (0.2–0.6)	Hexanoate (0.63–1.08)
Isoamyl alcohol (196.2–365.5)	Isoamyl (10.3–17.2)	Octanoate (1.07–2.17)
2-Methylbutanol (66.4–123.1)	2-Methylbutyl (0.9–1.8)	Decanoate (1.21–2.98)
2-Phenylethanol (134.6–156.3)	2-Phenylethyl (2.4–4.1)	

[a]Data from Kang et al. (2014), in mg/L

Table 31 Volatile compounds of Chinese rice wines[a]

Compound	Concentration (μg/L)	Compound	Concentration (μg/L)
Alcohols		*Esters, continued*	
2-Methylpropanol	n.d.–945	Ethyl 2-phenylacetate	24.7–630
2-Methylbutanol	n.d.–2,158	Ethyl 3-pyridine carboxylate	n.d.–477
3-Methylbutanol	n.d.–2,295	Isoamyl acetate	
1-Hexanol	n.d.–102	2-Phenylethyl acetate	n.d.–222
3-Ethoxypropanol	n.d.–173	*Carbonyl compounds*	
2,3-Butanediol	n.d.–297	3-Hydroxy-2-butanone	n.d.–64.4
1-Octanol	n.d.–91.6	Nonanal	n.d.–59.5
Acids		*Aromatics (not esters)*	
Acetic	42.9–503	Benzaldehyde	139–3,540
3-Methybutanoic	n.d.–47.8	Acetophenone	n.d.–137
Hexanoic	n.d.–173	Benzyl alcohol	0.48–130
Octanoic	7.89–174	2-Phenylethanol	1,333–16,711
Decanoic	n.d.–18.9	*cis*-2-Phenyl-2-butenal	n.d.–968
Esters		*Lactones*	
Ethyl acetate	303–3,352	γ-Butyrolactone	n.d.–67.5
Ethyl benzoate	13.5–432	γ-Nonalactone	n.d.–220
Ethyl 3-methylbutanoate	n.d.–9,827	*Phenols*	
Ethyl hexanoate	n.d.–299	Phenol	n.d.–53.0
Ethyl lactate	77.0–4,560	4-Ethyphenol	n.d.–48.1
Ethyl octanoate	n.d.–115	*Sulfur compounds*	
		Dimethyl trisulfide	n.d.–70.2
		Furans	
		Furfural	117–2,831
		N-Heterocycles	
		Tetramethylpyrazine	n.d.–73.0

[a]Data from Luo et al. (2008): 10 different rice wine types. Values have been rounded off to 3–5 significant figures (*n.d.* not determined); only compounds that are present in a majority of samples are included

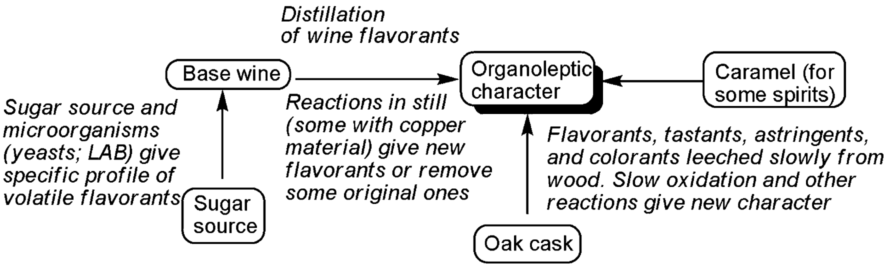


Fig. 22 Some origins of spirit organoleptic character (not including "flavored spirits" (like gin) or liqueurs)

compounds, and organosulfur compounds. Table 32 outlines the basic production methods for some important distilled spirits.

Ethanol and Water Content in Relation to Distillation Method

Distillation is performed in stills (Fig. 23), the simplest being pot stills (alembics or alambics), where at least two distillations (in batches) are needed to achieve a 65–75 % ABV distillate (with "heads" and "tails" management). Most pot still spirits are double or triple distilled. The same results can be reached using a columnar still (fitted with a fractionator or rectifier) in a single batch distillation. A continuous still (e.g., a Coffey still) can give a highly rectified spirit (~95 % ABV) in a continuous single distillation: a continuous flow of wine gives a continuous flow of spirit. However, the purer the spirit, the lower the concentrations of its volatile flavorants and the weaker the flavor. For this reason, the European Union specifies that rectified spirit should be less than 86 % ABV, but in practice most "new make" spirits are collected at much lower ethanolic strengths (e.g., ~68 % ABV for Scotch whisky; ~57 % ABV for Bourbon).

The alcoholic strengths of spirits are shown in Table 14: these figures refer to finished spirits, as purchased. Most spirits have ethanol contents in the range 37.5–46 % ABV; they are diluted with pure water to these values before bottling. In cask or maturation vessel, their ethanol contents would be ~60 % ABV or higher: Scotch malt whiskies bottled without dilution are called "cask strength" (57–63 % ABV). Liqueurs (USA: cordials) are usually of 16–40 % ABV, and eastern Asian spirits are normally of 20–40 + % ABV, whereas highly rectified vodka or similar can be of 86 % + ABV.

Spirit Production Process and Chemical Composition of Spirit

The three aspects of production that have the greatest influence on the spirit composition (and hence organoleptic character) are summarized in Table 33. They are:

- Nature of raw materials and nature of fermentation (e.g., active microorganisms)
- Distillation (equipment, method, and reactions)
- Cask aging (extraction of compounds from wood, slow reactions, adsorption of some compounds on wood)

Table 32 Fermented beverage origin, type of still, distillation method, and maturation method for selected spirits

Spirit	Fermented beverage origin	Still type[b]	Distillation method	Maturation (min. aging in cask in years)
Armagnac	White wine	Continuous	Continuous	Oak cask (2)
Calvados[a]	Cider	Alambic charentais	Double	Oak cask (3)
Cognac	White wine	Alambic charentais	Double	Oak cask (2.5)
Fruit	Fruit wine	Pot or column	Double or single	Glass or porcelain mostly, but also oak or ash cask
Gin	Cereal wine (called "wash")	Pot or column	Double or single	None usually; sometimes glass or cask
Pomace[c]	Grape or fruit pomace	Pot or column	Double or single	Oak cask (2)
Rum/ cachaça	Cane sugar wine or similar (called "beer")	Pot or column or continuous	Double or single or continuous	Oak cask (1) or none
Soju/ shochu/ Chinese liquor	Rice wine (trad.)/wine from various sugar/ starch sources	Mostly continuous, pot (trad.)	Continuous or double	Earthenware or none
Tequila/ mezcal	Maguey (*Agave*) pine wine	Pot	Double	Oak cask (2)
Vodka	Cereal wash/potato wine	Continuous	Continuous	None usually
Whisk(e)y	Cereal wash[d]	Pot, column, or continuous	Double/triple, single, or continuous	Oak cask[e] (3 for Scotch, 2 for Bourbon)

[a]A kind of pot still. Other apple spirits are made using column or continuous stills
[b]Pot and column stills are batch stills, the latter having some kind of fractionator in the still head, giving a more refined spirit. Continuous (e.g., Coffey stills) give a continuous flow of usually highly refined spirit: Armagnac is an exception
[c]Pomace is the residual fruit pulp left behind when the fermenting wine is pressed from it
[d]Bourbon wort (51–75 % maize, remainder barley, rye) is fermented with crushed grains and distilled off the porridge wine. Scotch whisky wort (all barley for malt whisky, barley and wheat or maize for grain whisky) is filtered off the grains before fermentation and distillation
[e]Charred oak casks for Bourbon, used Bourbon casks, ex-sherry casks, and others for Scotch whisky

Table 34 (Scotch whisky and Bourbon whiskey) shows how volatile composition depends on type of cereal, fermentation method, and distillation method, whereas Table 35 (*Agave* spirits) demonstrates how different species of the raw material can influence volatile composition, given similar distillation and other processing techniques. Concentrations of selected congeners in a particular spirit type (cider spirit) are given in Table 36. Table 37 (pear spirit) shows how the presence of wine lees (yeast and other deposits) can influence the distillate volatile composition.

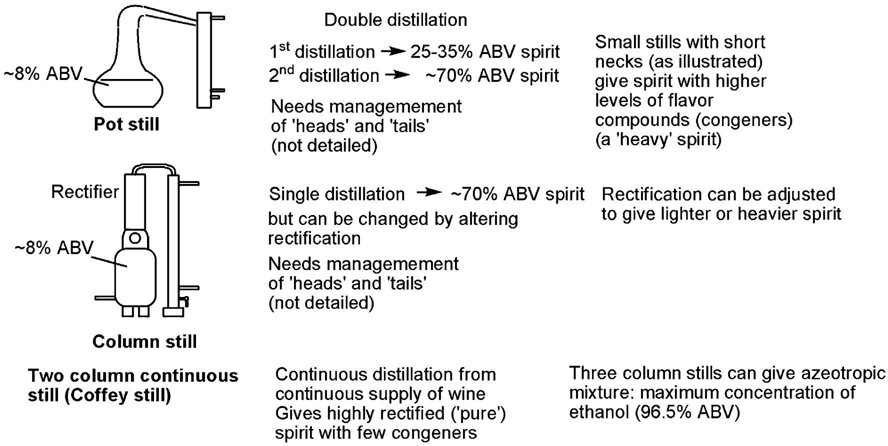


Fig. 23 Influence of still type and distillation method on chemical composition (and hence organoleptic character) of spirit

Generally, the greater the number of evaporation/condensation cycles during distillation, the lower is the congener level of the spirit (a "light" or "pure" spirit), hence, in general, continuous stills give the "lightest" spirits, while pot stills produce the "heaviest." See Table 32 for examples of kinds of stills and distillation modes used to produce various well-known spirits.

For very good practical, as well as historical reasons, pot and columnar stills are usually constructed of copper (or at least have copper inner surfaces), in which case high (malodorous) levels of organosulfur compounds in the wine are much depleted to positive odor levels in the spirit, through reaction with the copper surface, giving nonvolatile copper sulfide. However, copper also catalyzes reaction between hydrogen cyanide (from urea in the wine) and ethanol to give ethyl carbamate, although its production can be limited by using high reflux rates and lower distillation temperatures.

Flavored Spirits

These are usually diluted highly rectified spirit or grain neutral spirit (GNS) either redistilled with flavoring agents (raw materials, essential oils, essences, etc.) or simply infused with flavoring agents (Buglass and Caven-Quantrill 2012 and references therein). The following are the best-known types (flavorings or "botanicals" in parentheses):

Gin (juniper berry, coriander, citrus peel, orris root, and others)
Vodka (fruit, such as cranberry, or herbs)
Akvavit (caraway, dill, and others)
Arak, tsipouro, ouzo, pastis, and others (aniseed and star anise mainly)
Rum, cachaca (fruit or spices)
Soju (herbs, flowers, roots, bark)

Table 33 Influence of steps in production process on chemical composition and organoleptic character of spirits[a]

Raw materials and fermentation step	Distillation step	Cask aging
Raw materials (e.g., cereals, fruit, vegetables sugar cane juice, etc.), along with fermentative microorganisms and fermentation conditions define wine and hence spirit flavor profile: – Acidic wine tends to give better brandy (higher levels of esters) (fruity, sweet) – Peat-smoked malted barley gives malt whisky with higher levels of volatile phenols (smoky, spicy, medicinal) – Slow "spontaneous" fermentations tend to give spirit with higher level of flavor compounds – Brewer's yeast gives more fruity esters, furanones (sweet, caramel), and methional (cooked potato) in spirit than distiller's yeast – Activities of LAB give higher levels of ethyl lactate, volatile phenols and γ-lactones (from γ-hydroxy acids)	Type of still and method of distillation – see Fig. 18. A lower number of evaporation/condensation cycles tends to produce spirits with higher levels of acetaldehyde, acetals, ethyl acetate, and long-chain fatty acid ethyl esters, whereas a higher number of evaporation/condensation cycles tends to give a spirit richer in fusel alcohols, isoamyl acetate, 2-phenylethanol, and 2-phenylethyl acetate Reactions: – Acetaldehyde and acetal formation – Isomerization of terpenoids – Formation of norisoprenoids from carotenes – Maillard reactions (to give furans and *N*-heterocycles). Lower distillation temperature gives fewer furans (less caramel character) – Depletion of some sulfur compounds in copper still	Extraction of compounds from wood: lactones[b] (coconut, sweet), furans (toasty, nutty), *trans*-2-nonenal (woody), phenols[c] (smoky, spicy), maltol and cyclotene[d] (sweet, caramel), terpenoids (floral, herbaceous), pyrazines (coffee, chocolate, burnt) Also hydrolyzable tannins[e] (bitter, astringent) and coumarins (bitter) Slow reactions: esterifications, hydrolyses, oxidations (e.g., aldehydes to acids) Adsorption on to wood: Cu^{2+} (from copper still) and some sulfur compounds Slow overall loss of ethanol or water, depending on original strength of spirit in cask For Scotch malt whisky: flavor compounds from the cask's previous occupant (e.g., oloroso sherry, port, Sauternes)

[a]From Buglass et al. (2011, pp. 469–594) and references therein. For further information on distillation method, see Fig. 23
[b]For example, *cis*- and *trans*-whisky lactone
[c]For example, cresols, eugenol, guaiacol, phenol, vanillin, and others (lignin hydrolysis products and charring pyrolysis products)
[d]Wood toasting products
[e]Ellagitannins and gallic acid tannins mainly

Many of these flavored spirits have added sucrose syrup before bottling, giving about 20–50 g sucrose/L spirit, about 10 % of the sugar content of liqueurs (next subsection). Low-calorie sweeteners, like steviol derivatives, or occasionally maple syrup can be used in place of sucrose.

In these spirits, the flavorant, tastant, and bitter/astringent agents tend to dominate the organoleptic character of the drink; the volatile component profile reflects

Table 34 Volatile compounds of aged Scotch whisky and Bourbon whiskey

Scotch whisky[a] (aroma descriptor)	Bourbon whisky[b] (aroma descriptor)
Key odorants[c]	
Ethyl esters: cyclohexanoate, decanoate, dodecanoate, hexanoate, 2-methylpentanoate, 3-methylpentanoate, octanoate (all fruity or waxy)	Norisoprenoid: *trans*-β-damascenone (fruit)
Acetate ester: isoamyl acetate (fruity)	Lactones: γ-nonalactone (peach), γ-decalactone (coconut), *cis*-whisky lactone (coconut)
Alcohols: 3-methylbutan-1-ol (malt), 2-methylpropan-1-ol (winey)	Phenols: eugenol (cloves), vanillin (vanilla)
Acids: decanoic (fat), hexanoic (cheese), octanoic (waxy)	
Other important odorants	
Phenols: *o*-,*p*-cresols (phenolic), 4-ethylphenol (smokey), phenol (phenolic), guaiacol (coffee), vanillin (vanilla)	Alcohols: 3-methylbuan-1-ol (malt), 2-phenylethanol (rose),
Aldehydes: *trans*, *trans*-2,4-nonadienal, *trans*-2-nonenal, hexanal (all green)	Aldehydes: *trans*-2-decenal, *trans*-2-heptenal, *trans*, *trans*-2,4-nonadienal (all green/fatty)
Alcohols: 4-hepten-1-ol, 1-octen-3-ol, 2-nonenol (all mushroom, earthy)	Ester: ethyl 2-methylbutanoate (fruit)
Sulfur compounds: dimethyl trisulfide (onion), methyl (2-methyl 3-furyl) disulfide (meaty)	Lactone: *trans*-whisky lactone (coconut)
	Norisoprenoid: β-ionone (violet)
	Plus ethanol and other alkanoate esters

[a]Buglass et al. (2011, pp. 469–514) and references therein
[b]Poisson and Schieberle (2008)
[c]Key odorants allocated on basis of odor activity values and/or by reconstitution/omission studies

the composition of the flavoring mixture. Thus gin made with a high proportion of juniper berries has a high α-terpineol, oxygenated sesquiterpenoid, and oxygenated diterpenoid (Fig. 24) content, whereas that made with a greater quantity of coriander has a higher level of linalool (Tables 19 and 38). Anethole is the dominant volatile of aniseed flavored spirits, having a mean concentration of ~2.5 g/L (Buglass et al. 2011, pp. 554–573 and references therein).

Liqueurs

Liqueurs (USA: cordials) are flavored and sweetened spirits of ethanol content 15–40 + % (v:v) and sugar content of at least 10 % (w:v). GNS is often the spirit base, but others, such as brandy, fruit spirit, or gin, are used in some liqueurs (e.g., cherry spirit in cherry liqueurs, gin in sloe gin). Sugar is added mostly as sucrose syrup (usually 200–300 g/L liqueur) but honey is also used for some liqueurs. Like flavored spirits, the combination of botanicals competes well with the ethanol and sugar for organoleptic attention and tends to dominate the taste of most liqueurs. The following are the major categories of liqueurs:

Table 35 Selected volatile compounds in *Agave* (maguey) spirits – tequila, mezcal, sotol, and bacanora[a]

Compound conc. (mg/L)	Acetaldehyde	1-Butanol	2-Butanol	2/3-Methyl-1-butanol
Tequila (mixed)	80	10	600	1,350
Tequila (100 %)	80	5.5	695	2,450
Mezcal	90	9.5	630	1,800
Sotol	150	23	295	200
Bacanora	470	17	490	1,700

Compound conc. (mg/L)	2-Phenylethanol	Ethyl lactate	Methanol
Tequila (mixed)	18	235	1,450
Tequila (100 %)	63	170	2,150
Mezcal	56	180	1,500
Sotol	18	40	1,300
Bacanora	47	35	2,700

[a]Data from Lachenmeier et al. (2006). Mean values. Tequila made from *Agave tequilana* Weber var. *azul*; mezcal made from *A. angustifolia* Haw, A. *potatorum* Zucc., A. *salmiana* Otto, and others. Sotol made from *Dasylirion* spp.; bacanora made from *A. angustifolia*. "Mixed" tequila is 51 % agave spirit. These were all produced using pot stills, but the fermentative microorganism profile probably differed throughout the samples

Table 36 Selected volatiles in cider spirit from Asturias (N. Spain)[a]

Compound	Acetaldehyde	Acetal	Ethyl acetate	Methanol	2-Butanol	1-Propanol
Conc. range (mg/L)	231–339	72–140	513–893	764–1,430	24–124	415–550
Compound	2-Methyl-1-propanol	2-Propen-1-ol	1-Butanol	2-Methyl-1-butanol	3-Methyl-1-butanol	Furfural
Conc. range (mg/L)	253–354	21–493	80–147	433–523	2,190–2,573	12–23

[a]Data from Madrera et al. (2006), p. 5 commercial samples distilled in "alquitara," traditional pot stills, usually used for grape marc spirits. Similar levels of these compounds have been found in other cider spirits, such as calvados

Fruit liqueurs (e.g., "cherry brandy," sloe gin, curaçao)
Herb liqueurs (Kümmel, "monastery liqueurs," ginseng, flower petal liqueurs)
Cocoa, coffee, and tea liqueurs
Nut liqueurs
Cream liqueurs

As well as flavorant herbs and spices, specific bittering agents, such as citrus peel, elecampane, gentian roots, cascarilla, cinchona, quillaja bark, and others, play an important role in the organoleptic impact of liqueurs, and some, like saffron, are added for color. Examples of flavor and bitter chemical components of herbs,

Table 37 Dependence of volatile composition of pear spirit on presence of wine lees during distillation[a]

Compound		Methanol	Ethanal	Furfural	Ethyl acetate	2-Phenylethanol
Concentration (mg/L)	With lees	185	19	113	22	208
	Without lees	238	30	109	36	219
Compound		**1-Hexanol**	**1-Butanol**	**2-Methyl-1-butanol**	**3-Methyl-1-butanol**	**1-Propanol**
Concentration (mg/L)	With lees	12	29	141	1,381	331
	Without lees	49	72	160	1,700	386

Compound		2-Methyl-1-propanol	Ethyl decanoate	Ethyl 2- *trans*- 4-*cis*-decadienoate
Concentration (mg/L)	With lees	314	6	14
	Without lees	374	0	7

[a]Data from García-Llobodanin et al. (2007) for heart fraction of single distillation of wine made from pear juice concentrate and distilled in a copper alembic

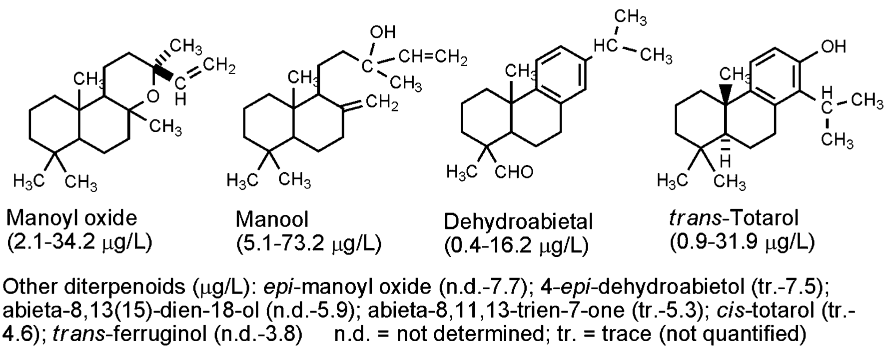


Fig. 24 Juniper diterpenoids in commercial gin (Vichi et al. 2008)

spices, and bitter agents can be found in Table 19, and Fig. 25 displays structures and botanic origins of some prominent bitter compounds.

Conclusion and Future Directions

Today, the identities and, in most cases, at least approximate concentrations of many hundreds of chemical components in a wide range of beverages are known, thanks largely to advances in analytical technology (particularly chromatography and spectroscopy) and associated supporting methods, such as separation/focusing techniques ("sample preparation") and chemometric/statistical methods. Inevitable further advances in these fields should give an even greater scope of knowledge,

Table 38 Concentrations of selected volatile components of commercial gin[a]

Compound	Concentration (mg/L) [mean]		
	London dry	Plymouth	Mahon
Monoterpenoids:			
α-Pinene	1.95–3.60 [2.56]	6.12	5.65
Sabinene	0.66–1.02 [0.94]	0.09	2.53
β-Myrcene	2.38–5.01 [4.00]	6.17	11.09
β-Phellandrene	0.20–0.54 [0.31]	0.46	0.64
γ-Terpinene	1.16–1.37 [1.26]	2.87	1.51
Citronellol	0.05–0.22 [0.13]	0.10	1.97
Myrtenol	0.02–0.04 [0.03]	0.02	0.37
Citronellal	0.08–0.17 [0.12]	0.06	0.41
Camphor	0.83–1.54 [1.17]	1.19	0.85
Linalool	10.96–36.99 [22.37]	16.83	1.93
α-Terpineol	1.13–1.89 [1.51]	3.80	9.03
Geranyl acetate	0.70–2.09 [1.38]	1.53	0.25
γ-Eleme	0.22–0.42 [0.35]	0.65	0.92
Sesquiterpenoids:			
Caryophyllene oxide	0.15–0.39 [0.23]	0.09	5.13
Torreyol	0.08–0.19 [0.13]	0.14	1.52
Spathulenol	0.05–0.08 [0.06]	0.04	1.29
Elemol	0.01–0.02	0.01	0.32
trans-Cadinol	0.03–0.07 [0.05]	0.08	0.97
trans-Muurol	0.03–0.08 [0.05]	0.12	1.27
Eudesmol	0.01–0.02	0.01	0.18
α-Cadinol	0.06–0.12 [0.09]	0.18	1.45
Total monoterpenoids	45.84	62.24	71.34
Total sesquiterpenoids	4.18	7.01	19.76

[a]Data from Vichi et al. (2005)

allowing greater opportunities for manufacturers to more effectively monitor their production processes at all stages and to improve their products. Over the past two or three decades, consumers and governments alike have become increasingly interested in health issues relating to beverages. Labeling legislation with regard to content and health warnings have been in force throughout the food industry for many years, and although there is considerable variation between countries and between food types, it is in general likely that legislation will be tightened over the next decades. At the same time it is likely that the trend toward the greater use of natural ingredients (which contain unidentified compounds or some of unknown or uncertain physiological activities) will continue. Also, data on physiological activity or toxicity of chemical components of beverages will be become more complete and more reliable. Hence knowledge of chemical composition of beverages will maintain its importance.

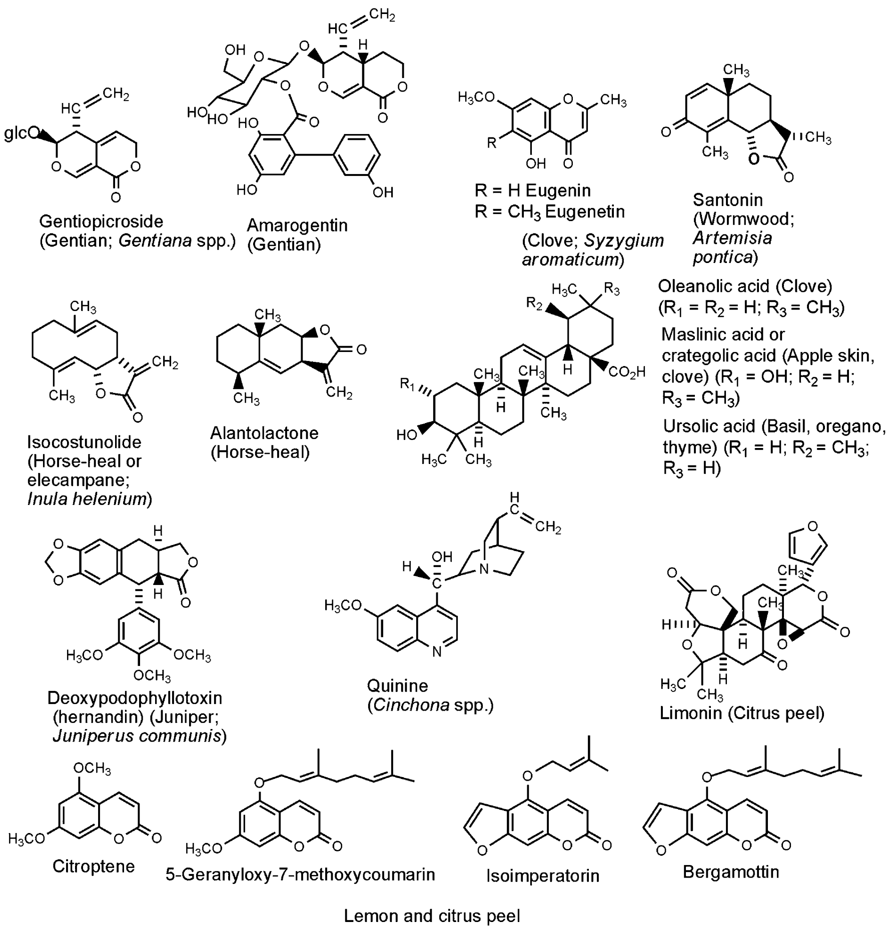


Fig. 25 Some bitter or astringent compounds of fruit and herb liqueur flavorings

Cross-References

- ► Classical Wet Chemistry Methods
- ► Nutritional and Toxicological Aspects of the Chemical Changes of Food Components and Nutrients During Drying
- ► Nutritional and Toxicological Aspects of the Chemical Changes of Food Components and Nutrients During Freezing
- ► Nutritional and Toxicological Aspects of the Chemical Changes of Food Components and Nutrients During Heating and Cooking

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