

5 Hop Aroma Extraction and Analysis

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5.1 Introduction

Hops (*Humulus lupulus* L.) are dioecious (male and female flowers on separate plants), perennial, climbing plants of the hemp (*Cannabis*) family and Urticales order. As shown in Fig. 5.1, the female cone, of interest to brewers, is a close grouping of flowers arranged on a zigzagging central axis (strig). At each bend, there are florets with large covering bracts (leaves). Epidermal hair grows on the bract basis, forming a beaker-like gland, called the lupulin gland, secreting resins (bitter substances) and oils (hoppy flavours) (Davies 1960; Moerman 1982; O'Rourke 1994). Picked hops contain 75 to 80% water. Hops are carefully dried at a maximum temperature of 60°C to a water content of 10%. They are then stored in a cool, dark room until used within the year (Stevens 1966; Hughes and Simpson 1993). The composition of the whole hop cone is depicted in Table 5.1.

In the brewing industry, hops are processed in several different ways, yielding cones, pellets, stabilised or isomerised pellets, organic solvent extracts, CO₂ extracts (supercritical or liquid CO₂), or isomerised extracts. Each type of processing has its advantages and disadvantages (Hupe 1981; Moir 1988; Hughes and Simpson 1993; Lewis 1994; Wilson and Fincher 1995). Liquid CO₂ is the most selective solvent used commercially for hops, producing the purest whole resin and oil extract. It solubilises none of the hard resins or tannins, much lower levels of plant waxes, no plant pigments, and less water and water-soluble materials (Moir 1988; Hughes and Simpson 1993).

Mainly used in the boiling kettle, hop imparts bitterness to beer because of the isomerisation of humulones (α -acids) to isohumulones (Fig. 5.2) at this stage of the process (Tatchell 1955; Kuroiwa et al. 1972; Sandra 1976; Verzele and De Keukeleire 1991; Deinzer and Yang 1994). Since hop varieties contain bitter compounds in variable amounts and proportions, hop cones are usually classified into two categories (Table 5.2) on the basis of their α -acid content: (1) aromatic hops, containing low levels of α -acids (from 3.8 to 5.1%) (Moll 1991); and (2) bittering hops, essentially used to impart bitterness to beers (from 8.6 to 12% α -acids) (Kenny 1990).

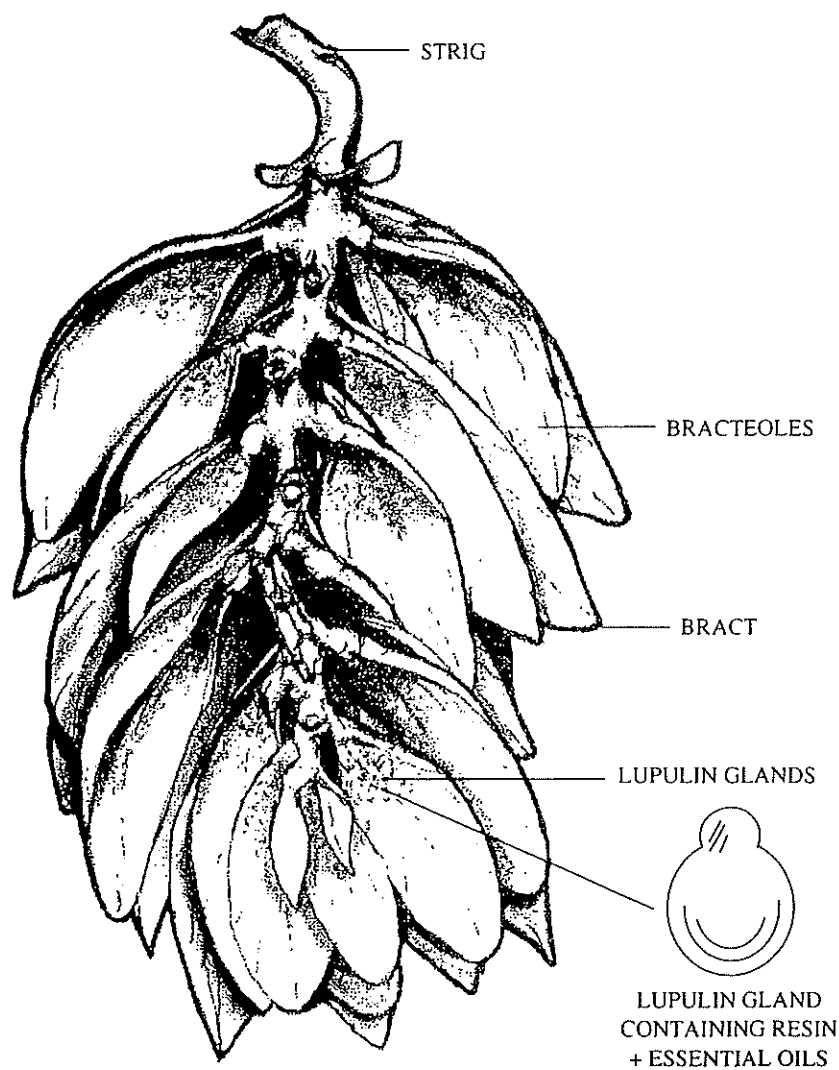


Fig. 5.1. Hop cone (O'Rourke 1994)

Table 5.1. Hop cone composition (in %; resin and oil content vary markedly with variety). (De Keukeleire 1993)

Substances	(w/w)%
Proteins	15
Total resins	
Soft resins	
α -acids	2-16
β -acids	2-10
Hard resins	3
Water	8-12
Essential oils	0.1-2
Tannins	4
Polyphenols	2-5
Monosaccharides	2
Amino acids	0.1
Lipids and waxes	<1-25
Pectin	2
Ash	10
Cellulose and lignin, etc.	40-50

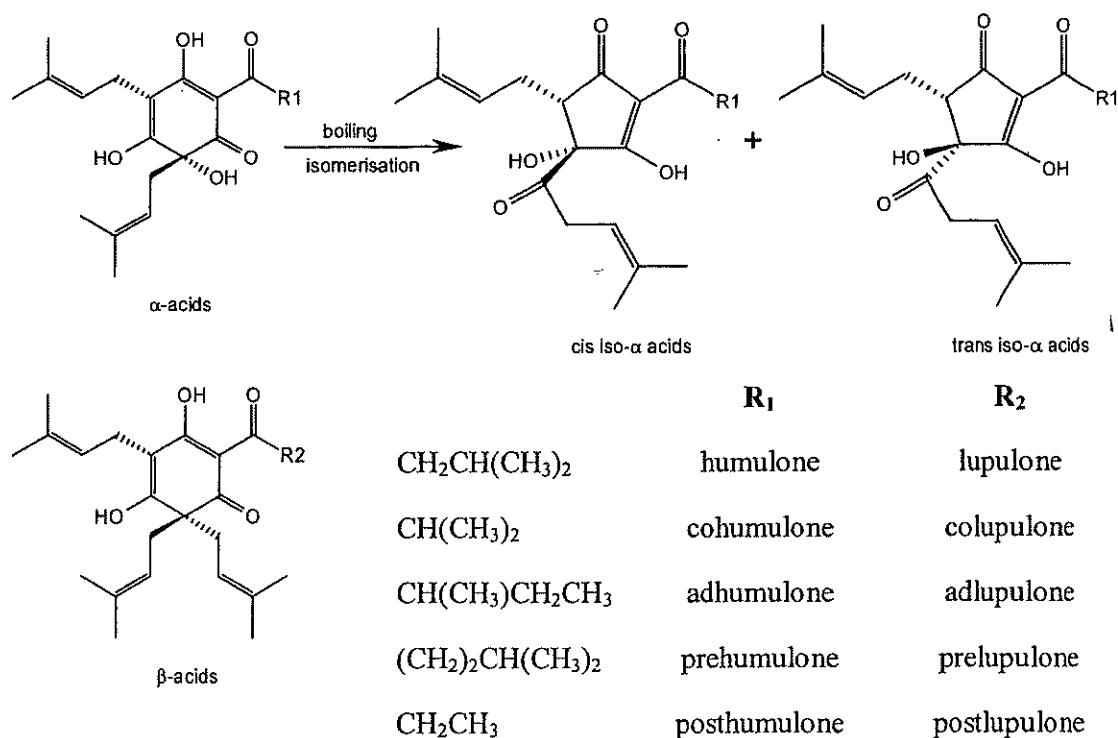


Fig. 5.2. Hop humulones and isohumulones

Table 5.2. Several "aromatic" (low-bitter) and bitter varieties. (Moll 1991; O'Rourke 1994)

Aromatic hops		Bitter hops	
Backe (E)	Progress (E)	Aquila (US)	Nugget (US)
Bramling (US)	Saaz (E)	Banner (US)	Olympic (US)
Cascade (US)	Spalt (E)	Bullion (US)	Orion (E)
Crystal (E)	Spalt Select (E)	Brewers Gold (E)	Pride (AUS)
East Kent Goldings (E)	Trisselspalt (E)	Centennial (US)	Pride of Ringwood (AUS)
Fuggle (E+US)	Styrian Goldings (E)	Challenger (E)	Record (E)
Golding (E)	Styrie (E)	Chinook (US)	Ringwood (AUS)
Hallertau Gold (E)	Tettnang (E+US)	Cluster (US)	Southern Brewer (AFR)
Hallertau Hersbrucker (E)	Whit bread Goldings (E)	Comet (US)	Star (E)
Hallertau Mittelfrüh (E+US)	Willamette (US)	Eroica (US)	Talisman (US)
Hallertau Tradition (E)		Galena (US)	Target (E)
Hersbruck Spät (E)		Hallertau Magnum (E)	Wye Target (E)
Hüller bitterer (E)		Hallertau Perle (E+US)	Wye Challenger (E)
Lublin (E)		Hueller (E)	Yeaman (E)
Mont Hood (US)		Northdown (E)	Yakima Cluster (US)
Perle (E+US)		Northern Brewer (E)	

E, European varieties; US, American varieties; AUS, Australian varieties; AFR, African varieties

Hop is also responsible for the appearance in beer of the lightstruck, sunstruck, or skunky flavour (3-methyl-2-buten-1-thiol) caused by photochemical degradation of iso-humulones in the presence of cysteine and riboflavin (Kuroiwa and Hashimoto 1961; Gunst and Verzele 1978; Goldstein et al. 1993; Lewis 1994). Other compounds derived from the isohumulone lateral chain can impart a cheesy (volatile fatty acids) or wine-like (the corresponding ethylic esters) flavour to beer. The soporific agents 2-methyl but-3-ene-2-ol and 3-methyl but-2-ene-1-ol also derive from humulone degradation. Lastly, bitter compounds exhibit high bacteriostatic activity, very useful in the brewing process, and contribute to beer foam stability (Derdelinckx and Maudoux 1992).

5.2 Hop Aroma

For brewers, qualitative and quantitative analyses of hop aroma are of prime importance in assessing hop quality (variety and freshness) (Moerman 1982; De Keukeleire 1993). To date, over 300 components have been positively or tentatively identified in hop oils: mainly hydrocarbons, ketones, aldehydes, esters, carboxylic acids, alcohols, oxygen heterocycles, and sulfur compounds (Buttery et al. 1965; Naya and Kotake 1972; Tressl et al. 1978b; Kralj et al. 1991; Moir 1992).

Probably the most reliable method for recovering hop oils is steam distillation liquid/liquid extraction (Fig. 5.3; Likens and Nickerson 1964; Nickerson and Likens 1966; Bouseta and Collin 1995; Perpète et al. 1998). The extraction time, the condenser temperature, and the flow rate of the nitrogen ensuring an inert atmosphere in the microextractor are crucial to good recovery (Bouseta and Collin 1995). With a 45-min extraction time, a temperature of -10°C in the cold finger, and a 2-mL/min nitrogen flow, recovery factors as high as 97 to 99% are obtained for terpenic compounds such as terpineol, verbenone, bornyl acetate, and *trans*-caryophyllene. After extraction, the Kuderna-Danish flask allows a high concentration factor without flavour loss (Bouseta and Collin 1995).

The above method has enabled us to determine easily more than a hundred molecules in hop pellets (Table 5.3 and Fig. 5.4).

5.2.1 Terpenic Compounds

Terpenic compounds are hydrocarbons representing 40 to 80% (by weight) of the total hop essential oils. Large amounts of three terpenes are present in all hop varieties (Fig. 5.5). The most abundant monoterpene ($\text{C}_{10}\text{H}_{16}$) is myrcene (about 30% of the total oil content) while α -humulene (18 to 33%) and β -caryophyllene (4 to 22%) are sesquiterpenes ($\text{C}_{15}\text{H}_{24}$) (Jenard 1966; Tressl et al. 1978b; Sharpe and Laws 1981; Moir 1992). According to Kralj et al. (1991), only eleven compounds repre-

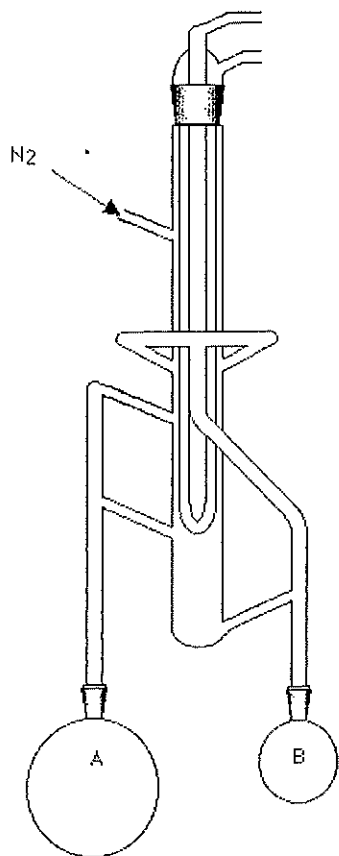


Fig. 5.3. Microextractor used for simultaneous steam-distillation solvent extraction (Perpète et al. 1998). A 50 ml ultrapure deoxygenated water + 0.5 g hop; B 1.5 ml dichloromethane

sent the fundamental hop oil composition: myrcene, α -humulene, β -caryophyllene, α -muurolene, β -farnesene, carvone, methyl-deca-4-enoate, 2-undecanone, and three unidentified compounds. Other hydrocarbon terpenes such as β -selinene, γ -cadinene, or tricyclic sesquiterpenes could be specific to some varieties (Davies and Menary 1982; Tressl et al. 1983).

Terpenic compounds are derived from isopentenyl diphosphate units also called activated isoprene. Located in the chloroplast, these units assemble to create unsaturated hydrocarbon chains of two or more units. The chains are further modified by oxidation, reduction, or carbon removal. The enzyme *isopentenyl diphosphatase- Δ -isomerase* (Fig. 5.6) catalyses the isomerisation of a first isopentenyl diphosphate molecule to 3,3-dimethyl allyl diphosphate.

The corresponding C_5 carbocation is further transferred to a second isopentenyl diphosphate molecule, yielding either geranyl diphosphate (*trans* compound) or its isomer, neryl-diphosphate (*cis* compound). The latter is a precursor of monoterpenes such as myrcene (Fig. 5.7). Cyclic monoterpenes are also usually created from neryl diphosphate or from linalyl diphosphate (Fig. 5.8).

Diphosphate removal from geranyl diphosphate again yields an allylic carbocation, allowing further isoprene additions. After removal of the diphosphate anion, farnesyl diphosphate is a precursor of various other sesquiterpenes such as α -humulene or β -caryophyllene (Fig. 5.9).

Figure 5.10 shows a series of cyclic sesquiterpenes also derived from farnesyl diphosphate.

Table 5.3. List of compounds detected in 11 hop varieties (Saaz, Lublin, Styrian Goldings, Hallertau, Mount Hood, Northdown, Northern Brewer, Galena, Nugget, Challenger, Pride of Ringwood). *n* Pic number, see Fig. 5.4; *RT* retention time (min); *I_k* retention index on a CP-Sil5 column; *Identification* mass spectrometric identification (*MS*) and/or pure compound elution (*GC*)

Compounds	<i>n</i>	<i>RT</i>	<i>I_k</i>	Identification
Furan,2,3-dihydro,4-methyl	1	7.70	659	MS
Unknown 95	95	12.76	805	MS
Unknown 96	96	13.30	813	MS
Isobutyl propanoate	2	15.15	844	GC
Isobutyl isobutyrate	3	18.56	898	GC/MS
Methyl hexanoate	4	19.03	904	GC/MS
3,3,6-Trimethyl,1,5-heptadiene	5	19.23	906	MS
Unknown 97	97	19.70	911	MS
Terpene 6 ^a	6	21.96	936	MS
α-Pinene	7	22.57	942	MS
2-Methylbutyl propanoate	8	23.20	949	GC/MS
β-Pinene	9	25.80	978	GC/MS
Myrcene	10	26.42	985	GC/MS
2,7-Dimethyl,2,6-octadiene	11	26.70	988	MS
3-Methylbutyl isobutyrate	12	27.42	996	GC/MS
2-Methylbutyl isobutyrate	13	27.88	1,001	GC/MS
Methyl heptanoate	14	28.37	1,005	GC/MS
Limonene	15	30.74	1,025	GC/MS
Unknown 16	16	31.33	1,030	MS
γ-Terpinene	17	31.95	1,036	MS
Heptanoic acid	18	32.84	1,044	GC/MS
1-Octanol	19	33.39	1,049	MS
Unknown 20	20	35.50	1,067	MS
Unknown 21	21	36.36	1,074	MS
Linalool oxide	22	36.78	1,078	MS
Nonanal	23	37.36	1,082	GC/MS
Linalool	24	37.46	1,084	GC/MS
3-Methyl,2-methylbutyl butanoate	25	38.04	1,089	MS
2-Methylbutyl pentanoate	26	38.35	1,092	MS
Methyl octanoate	27	39.90	1,104	GC/MS
Unknown 28	28	43.24	1,130	MS
3-Hexen-1-ol formate	29	43.93	1,136	MS
Octanoic acid	30	44.96	1,143	GC/MS
1,14-Tetradecanediol	31	47.43	1,162	MS
2-Decanone	32	48.48	1,171	GC/MS
Unknown 33	33	49.00	1,175	MS
α-Terpineol	34	49.55	1,179	MS
Octyl propanoate	35	50.23	1,184	MS
Methyl,4-nonenoate	36	51.12	1,191	MS
Methyl nonanoate	37	52.91	1,205	GC/MS
IST (carvone)		54.91	1,220	GC/MS
Unknown 38	38	56.24	1,230	MS
Geraniol	39	56.84	1,235	GC
Unknown 40	40	57.27	1,238	MS
Nonanoic acid	41	58.03	1,244	GC/MS
Unknown 42	42	59.64	1,256	MS
Unknown 43	43	60.79	1,265	MS
4,6-Dimethyl,methyl octanoate	44	61.65	1,272	MS
2-Undecanone	45	62.13	1,276	GC/MS
Unknown 46	46	63.72	1,288	MS
Methyl, deca,4-enoate	47	64.05	1,291	MS
Methyl, deca,4,8-dienoate	48	64.24	1,292	MS
Methyl geranate	49	65.45	1,302	GC/MS

Table 5.3. *Continued*

Compounds	<i>n</i>	RT	<i>I_k</i>	Identification
Methyl decanoate	50	65.84	1,306	GC/MS
Unknown 51	51	67.88	1,328	MS
Unknown 52	52	68.43	1,334	MS
Unknown 53	53	69.38	1,345	MS
Geranyl acetate	54	71.22	1,365	GC
Decanoic acid	55	71.76	1,371	MS
2-Dodecanone	56	72.38	1,378	GC/MS
Ylangene	57	72.79	1,382	MS
Copaene	58	73.18	1,387	MS
Unknown 59	59	73.61	1,391	MS
Unknown 60	60	73.94	1,395	MS
7-Methyl,methyl nonanoate	61	74.63	1,403	MS
β-Caryophyllene	62	76.76	1,435	GC/MS
Sesquiterpene 63 ^b	63	77.22	1,441	MS
Bergamotene	64	77.22	1,441	MS
β-Farnesene	65	78.18	1,455	GC/MS
Unknown 66	66	78.22	1,456	MS
α-Humulene	67	79.22	1,470	GC/MS
2-Tridecanone	68	79.82	1,479	GC/MS
α-Amorphene	69	80.09	1,483	MS
Methyl,3,6-dodecadienoate	70	80.40	1,488	MS
β-Selinene	71	81.08	1,498	MS
Sesquiterpene 72 ^c	72	81.36	1,503	MS
Sesquiterpene 73 ^d	73	81.46	1,504	MS
α-Selinene	74	81.57	1,505	MS
Sesquiterpene 75 ^e	75	81.98	1,513	MS
γ-Cadinene	76	82.46	1,522	MS
Unknown 77	77	82.79	1,527	MS
δ-Cadinene	98	82.92	1,529	MS
Sesquiterpene 78 ^f	78	83.05	1,532	MS
Sesquiterpene 79 ^g	79	83.50	1,540	MS
α-Muurolene	80	83.81	1,545	MS
1,13-Tetradecadiene	81	84.50	1,558	MS
Humuladienone	82	85.77	1,581	MS
Caryophyllene oxide	83	86.50	1,593	GC/MS
Humulene epoxide I	84	87.17	1,606	GC/MS
Humulene epoxide II	85	87.82	1,619	GC/MS
Humulene epoxide III	99	88.66	1,639	MS
Unknown 16	86	89.13	1,646	MS
Humulenol II	87	89.66	1,657	MS
Unknown 88	88	90.10	1,666	MS
Unknown 100	100	90.68	1,678	MS
Unknown 89	89	90.90	1,684	MS
Unknown 90	90	92.06	1,707	MS
Humulene diepoxide A	91	92.74	1,722	GC/MS
Humulene diepoxide B	92	93.34	1,736	GC/MS
Humulene diepoxide C	93	94.94	1,773	GC/MS
Humulene diepoxide D	94	95.46	1,785	GC/MS

^a Terpene 6: bicyclo [3.1.1] hep-2-ene,3,6,6-trimethyl

^b Sesquiterpene 63: 1H-cyclopenta [1,3] cyclopropano [1,2] benzene, octahydro-7-methyl-3-methylene-4-(1-methylethyl)-

^c Sesquiterpene 72: naphthalene,1,2,3,5,6,7,8,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-

^d Sesquiterpene 73: cyclohexene,1-methyl-4-(5-methyl-1-methylene-4-hexenyl)-

^e Sesquiterpene 75: naphthalene,1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-

^f Sesquiterpene 78: cyclohexene,6-ethenyl-6-methyl-1-(1-methylethyl)-3-(1-methylethylidene)-

^g Sesquiterpene 79: naphthalene,1,2,3,4,4a,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)-

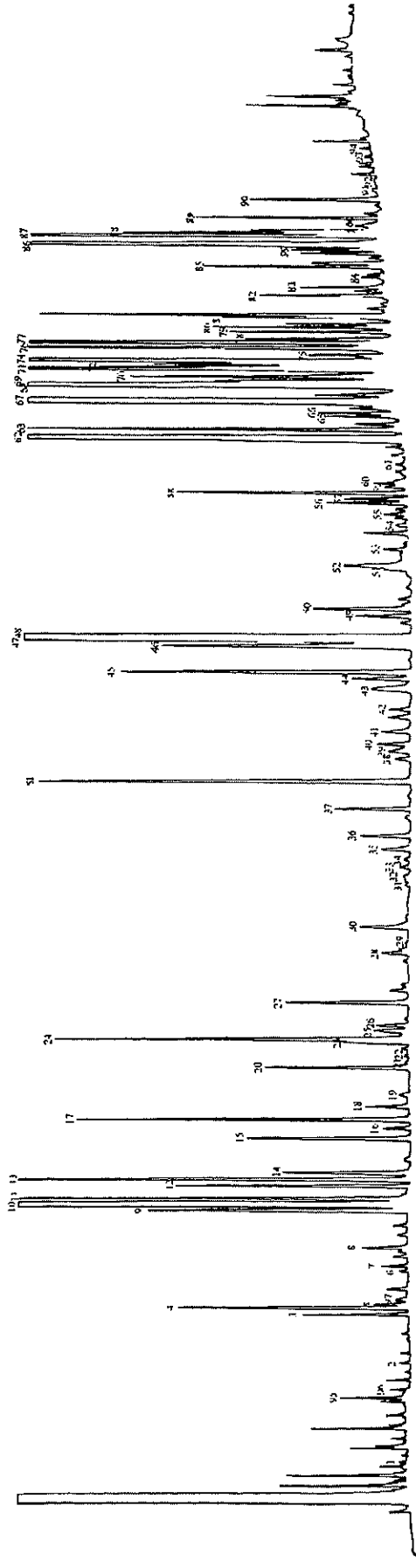


Fig. 5.4. Chromatographic profile corresponding to analysis of hop oil by GC

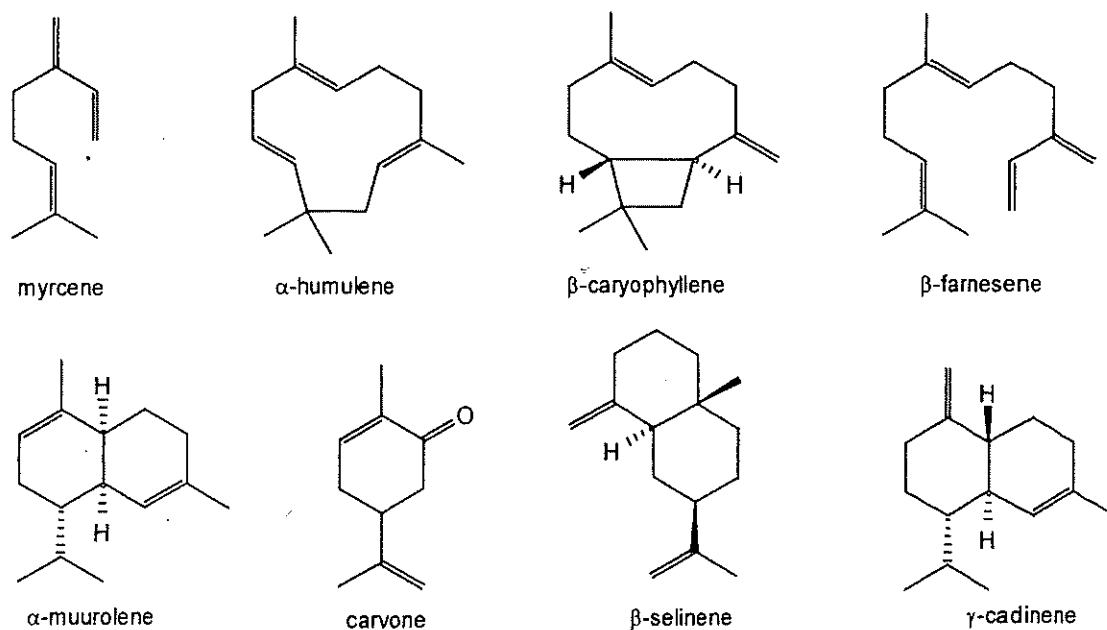


Fig. 5.5. Myrcene, α -humulene, β -caryophyllene, β -farnesene, α -muurolene, carvone, β -selinene, and γ -cadinene

5.2.2 Oxidation and Hydrolysis Products from Sesquiterpenes

Several authors (Tressl et al. 1978a, 1983; Peacock and Deinzer 1981) have shown that sesquiterpenes can be easily oxidised during hop storage to yield the corresponding epoxides (Fig. 5.11). Caryophyllene epoxide, three humulene epoxides, and five humulene di-epoxides have been evidenced in aged samples (Peacock et al. 1980; Sharpe and Laws 1981; Peacock and Deinzer 1989; Moir 1992). Subsequent hydrolysis during storage, boiling, or fermentation yields various alcohols and ketones such as humulol II, humulenol II, and humuladienone (Fig. 5.12; Tressl et al. 1978a; Fukuoka and Kowaka 1983; Lam et al. 1986).

The terpene oxidation rate depends on the storage temperature, light exposure, and hop reducing power (carotenoids, polyphenols, etc.) (Stevens 1966; Liégeois et al. 2000).

5.2.3 Alcohols, Carbonyles, Acids and Esters

As depicted in Fig. 5.13, geraniol, a monoterpene alcohol derived from geranyl diphosphate, can yield either geranial or esters such as geranyl acetate and geranyl isobutyrate. In the former case, an additional oxidation can occur, yielding geranic acid or methyl geranate. Hop esters can be hydrolysed or transesterified by yeast during beer fermentation, provided no α,β -unsaturated esters are concerned (e.g. methyl geranate; Palamand et al. 1971). Thus, geraniol resulting from yeast hydrolysis of geranyl acetate and geranyl isobutyrate may contribute to the floral

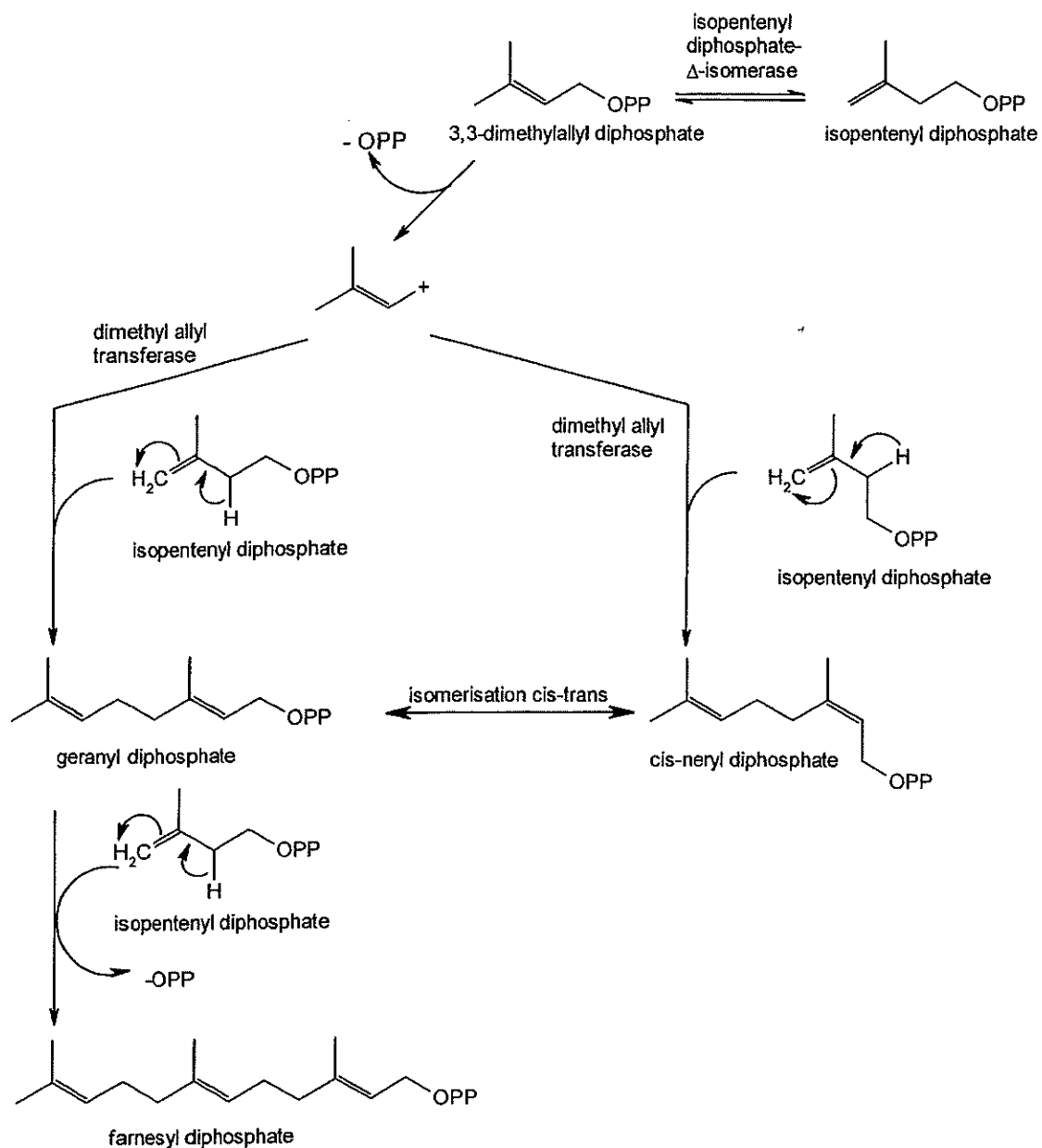


Fig. 5.6. Biosynthesis of monoterpene and sesquiterpene precursors

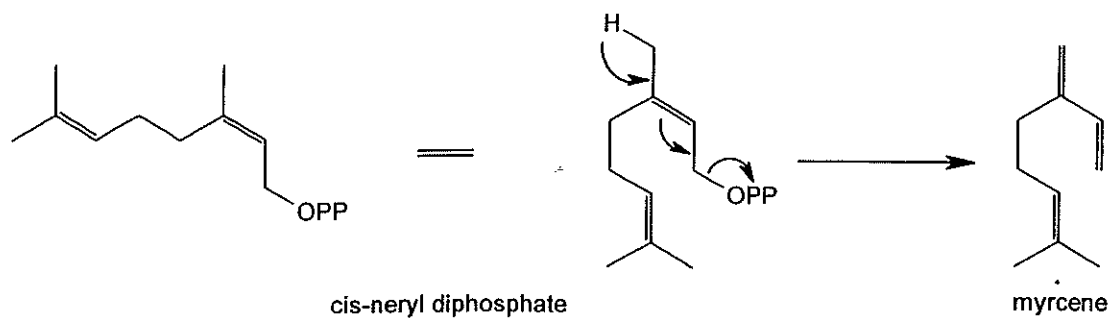


Fig. 5.7. Myrcene biosynthesis

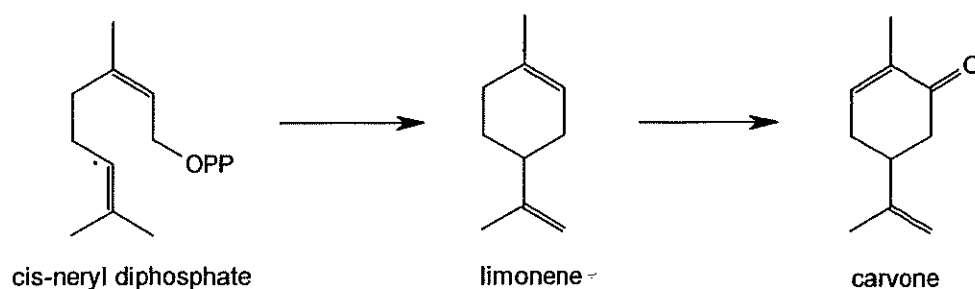


Fig. 5.8. Limonene and carvone synthesis from *cis*-neryl diphosphate

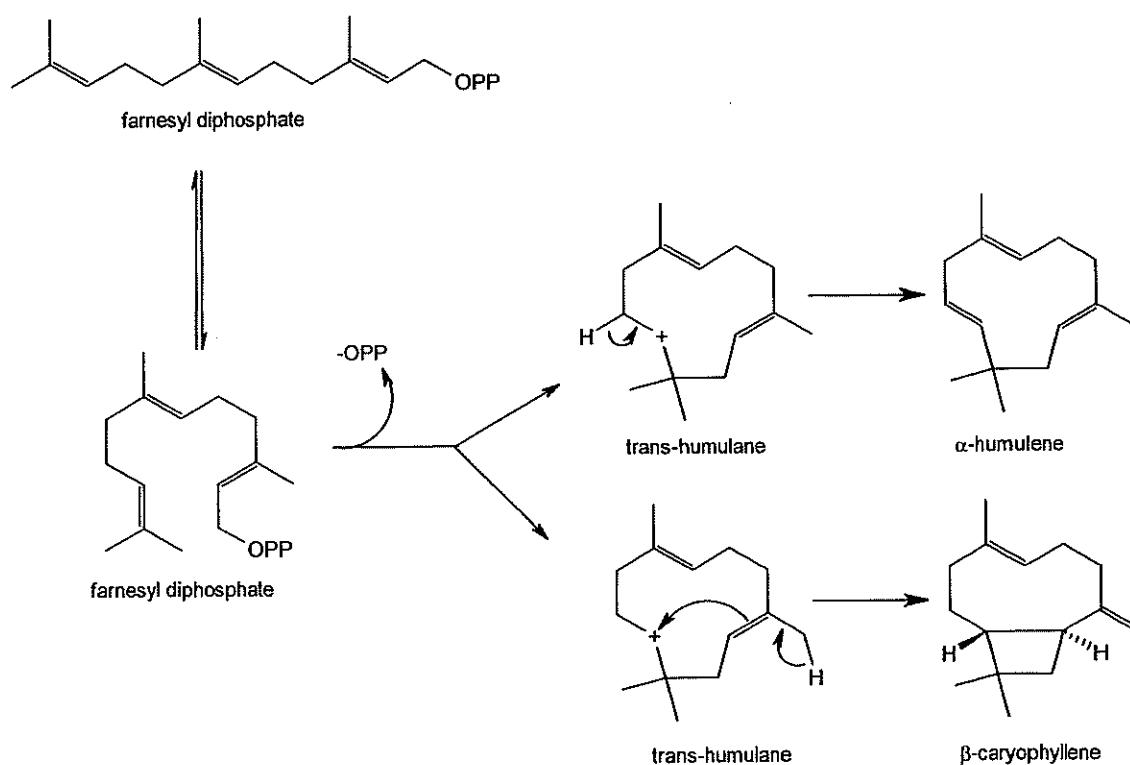


Fig. 5.9. α -Humulene and β -caryophyllene synthesis

hop aroma of beer (Peacock et al. 1981). Geraniol, nerol, and citronellol may also arise through yeast reduction of citral and citronellal.

Other terpenic alcohols such as linalool (the most abundant), α -terpineol, and farnesol are present in hop oils (Fig. 5.14). These terpenic alcohols can be viewed as end products of plant biosynthesis. Levels of most terpenic alcohols tend to drop during hop storage whereas allylic alcohol levels tend to increase (Tressl et al. 1978b; Moir 1992).

Linear ketones (10 to 13 carbon atoms) and 6-methyl-5-hepten-2-one (hoppy aroma) are present in hop essential oils (Maier 1966; Markl and Palamand 1973; Davies and Menary 1982; Kralj et al. 1991). Unsaturated linear esters have also been identified in hops (Fig. 5.15; Maier 1966; Shimazu et al. 1978; Haley and Peppard

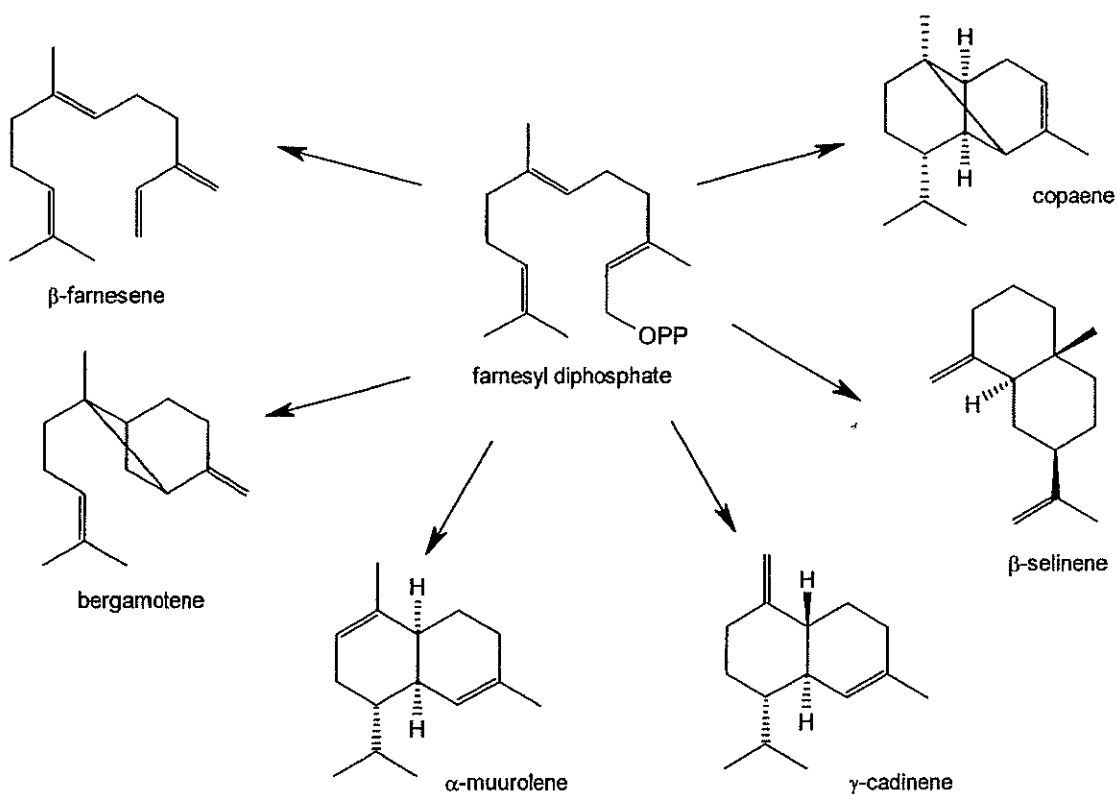


Fig. 5.10. Six sesquiterpenic compounds frequently present in hop essential oils

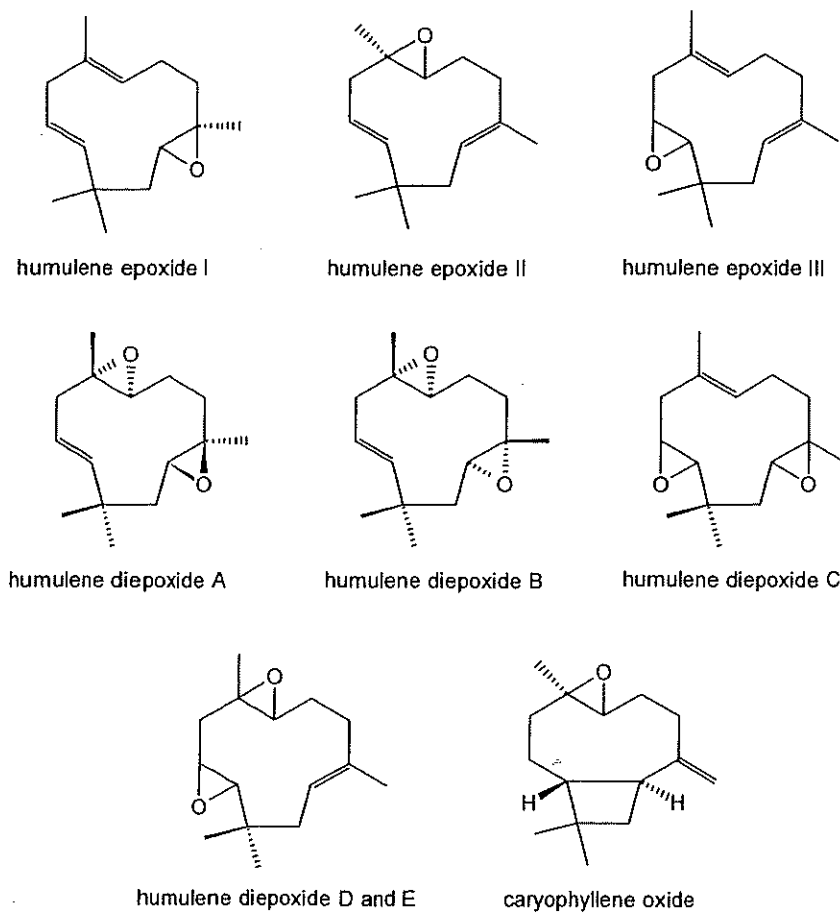


Fig. 5.11. Main epoxides and diepoxides in hop

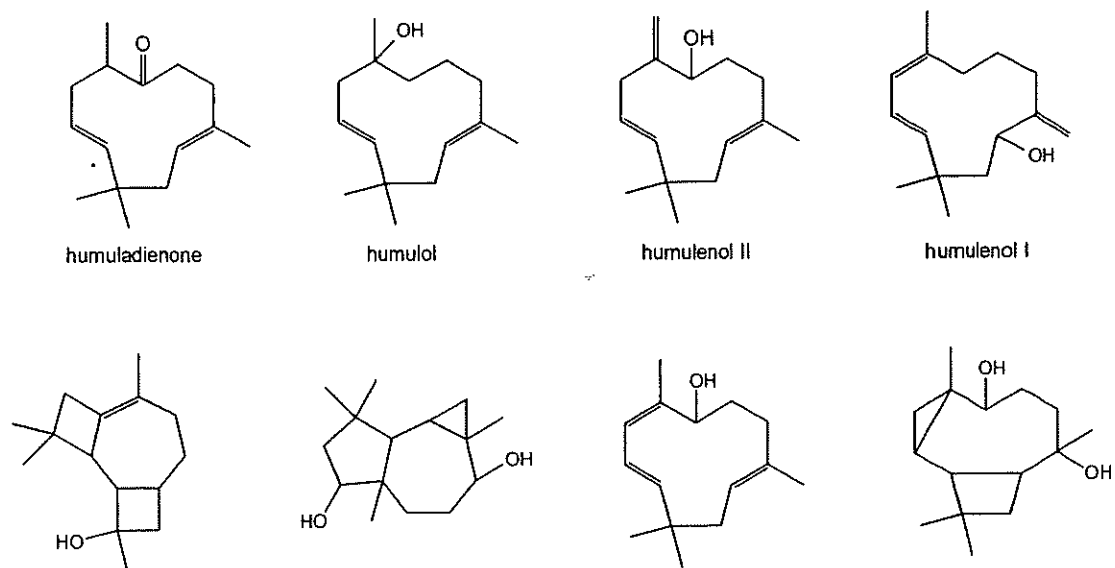


Fig. 5.12. Some humulene hydrolysis products. (Yang et al. 1991, 1993)

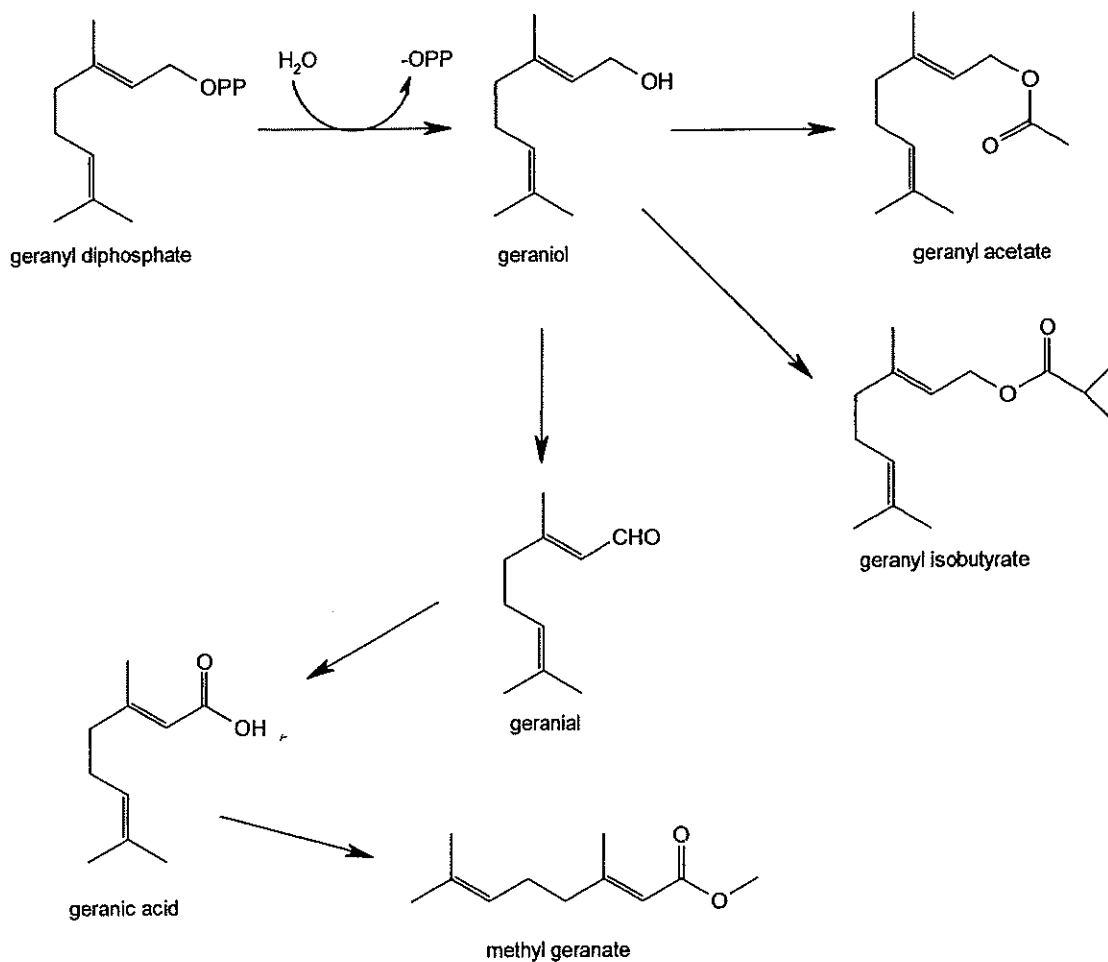


Fig. 5.13. Methyl geranate synthesis from geranyl diphosphate

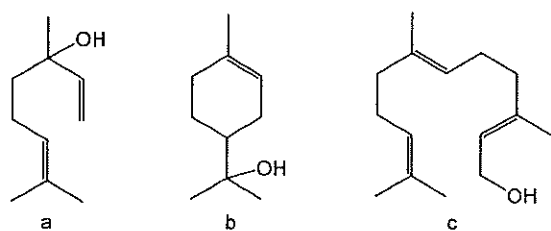
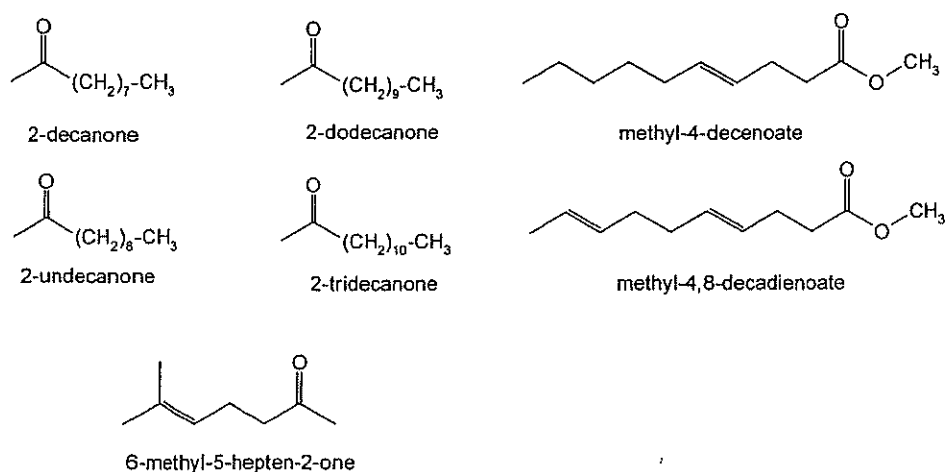
Fig. 5.14. a Linalool, b α -terpineol, c farnesol

Fig. 5.15. Other important ketones and esters present in hop oils

1983; Kralj et al. 1991). Ethyl lactate is another ester found in cones, mainly after ageing.

Tressl et al. (1978b) identified β -ionone and β -damascenone in hops. According to Strating and Van Eerde (1973), damascenone could impart a blackcurrant odour to aged beers. Both of these compounds are known as oxidative degradation products of β -carotene and analogues.

5.2.4 Hop Aroma Glycosides

After liquid carbon dioxide extraction, which removes essential oils and soft resins, hop solids still contain a water-soluble fraction with several aroma glycosides (Goldstein et al. 1999). Hydrolysis of hop solid with β -glucosidase releases a large number of aromatic compounds (Table 5.4). Direct LC-MS analyses of glycosides have confirmed the structures of several aglycones: grasshopper ketone, 3-methyl-2-pentanol, 4-methyl-2-pentanol, citronellol, aceto vanillonol, 2,6-dimethyl-2,7-octadiene-1,6-diol, and 3-hydroxy-7,8-dihydro- β -ionone.

Table 5.4. Identified molecules derived from treatment of hop solids with β -glucosidase (Goldstein et al. 1999)

2-Methyl-3-buten-2-ol	1-Phenylethanol	2-Hydroxy-5-methyl acetophenone
3-Methyl-2-butanol	2-Phenylethanol	Vanillyl acetone
2-Methyl-1-propanol	p-Hydroxyphenylethanol	1-Ethyl-2-pyrrolidone
3-Pentanol	4-Methyl-2-pentanone	2,4,5-Trimethyl acetophenone
2-Pentanol	3-Methyl-2-pentanone	2-Hexenal
4-Methyl-2-pentanol	4-Methyl-3-penten-2-one	Geraniol
3-Methyl-2-pentanol	2-Octen-4-one	α -Terpineol
3-Methyl-1-butanol	6-Methyl-5-hepten-2-one	Linalool
2-Methyl-1-butanol	3-Hydroxy-2-butanone	c- and t-Linalool oxide
1-Pentanol	Phenylacetaldehyde	Benzaldehyde
3-Methyl-2-buten-1-ol	Vanillin	Loliolide
1-Hexanol	4-Hydroxybenzaldehyde	2,6-Dimethyl-2,7-octadien-1,6-diol
3-Hexen-1-ol	Coumaran	4-Hydroxy-3-methoxy-acetophenone
2-Hexen-1-ol	Benzylic alcohol	2-Methyl-6-methylene-2,7-octadien-4-ol
1-Octen-3-ol	2-Methoxy-3-isopropyl-pyrazine	2-Methyl-6-methylene-3,7-octadien-2-ol
6-Methyl-5-hepten-2-ol	Raspberry ketone	2,2-Methylene bis[6-(1,1-dimethylethyl)-4-ethylphénol]
2-Ethyl-1-hexanol	4-Terpineol	5-Methyl-3-hexen-2-one
1-Octanol	5,5-Dimethyl-2-(5H)-furanone	
Ipsdienol	Acetophenone	

5.3 Varietal Discrimination of Hop Cultivars According to Their Oil Content

Buttery and Ling (1967) and Likens and Nickerson (1967) have shown that the chemical composition of hop essential oil, genetically determined, is only slightly influenced by external conditions. As this composition depends on the hop variety, some compounds can be taken as markers for varietal discrimination (Buttery and Ling 1967; Likens and Nickerson 1967; Naya and Kotake 1972; Kralj et al. 1991; Forster and Schmidt 1994; Perpète et al. 1998).

A first noteworthy difference between hop cultivars is their relative content in three terpenic hydrocarbons: α -humulene (H), β -caryophyllene (C) and myrcene (M) (Peacock et al. 1980).

- H > C > M in Saaz, Styrian, and Target
- M > H > C in Lublin, Galena, and Nugget
- H > M > C in Northern Brewer
- M > C > H in Pride of Ringwood

For Deinzer and Yang (1994), low humulene/caryophyllene (H/C) ratios are also typically associated with non-European hop varieties (e.g., H/C = 2.1 for Cluster) whereas high ratios (H/C = 3 for Hallertau Mittelfrüh and 2.9 for Tettngang) may be associated with the European hoppy aroma.

According to Davies and Menary (1982), the myrcene level is higher in bitter hops. Yet because myrcene is too volatile and too readily oxidised, it is hard to use it for varietal discrimination. Myrcene is usually not desired although partially responsible, once oxidised, for the hoppy aroma in beer.

Aromatic hops such as Saaz, Tettnang, Styrian Goldings, and Lublin can also be distinguished from bitter varieties by a higher β -farnesene content (150 to 1,140 ppm) (Moerman 1982; Perpète et al. 1998). As with myrcene, unfortunately, this conjugated diene readily undergoes Diels-Alder degradation, leading to a significant loss in aged hops or after pelleting (Peacock and McCarty 1992).

Bergamotene (Fig. 5.10) is closely associated with farnesene (Peacock and McCarty 1992; Perpète et al. 1998). In fresh cones, its concentration is usually about 5% of the level of farnesene. Perpète et al. (1998) found concentrations between 25 and 74 ppm in all tested pellets produced from aromatic cultivars and less than 5 ppm in bitter varieties. Bergamotene is much more stable than farnesene as it cannot undergo a Diels-Alder reaction. Hops nearly devoid of farnesene but containing 20 ppm bergamotene should thus be classified as high-farnesene hops.

Additional sesquiterpenes and their degradation products (α -amorphene, β -selinene, α -selinene, humulene epoxide I, humulene epoxide II, etc.) also prove very useful for varietal discrimination (Kralj et al. 1991; Perpète et al. 1998). In the "European bitter hops" group of Perpète et al. (1998) (Fig. 5.16), Northdown and Challenger are characterised by large amounts of α - and β -selinenes (>200 ppm, caryophyllene equivalent), as compared to Target and Northern Brewer. Northdown is distinguishable from Challenger by the concentration of a sesquiterpene that may be α -amorphene (>125 ppm, caryophyllene equivalent). The same terpene also occurs as a significant constituent distinguishing Mount Hood (>125 ppm, caryophyllene equivalent) from Hallertau in the "low bitterness" group. The most interesting marker of Northern Brewer hops emerging from their study is the humulene-to-farnesene ratio (above 220). All other cultivars, and especially Target with its low humulene content, show a ratio below 220. The compound 2-undecanone is an additional marker for distinguishing Target (>100 ppm) from Northern Brewer hops. High 2-undecanone concentrations can also occur in Pride of Ringwood samples (Perpète et al. 1998). This methylketone could give rise to an organoleptically active reduced compound in beer, where the estimated flavour threshold of 2-undecanol is 70 ppb (Meilgaard 1975).

Perpète et al. (1998) also used esters to establish their varietal classification flowchart (Fig. 5.16). Non-European and European bitter hops were discriminated from aromatic cultivars by quantification of 4-decenoic acid methyl ester (>150 ppm in the former) and 3-methylbutyl isobutyrate (<11 ppm in the latter). A high level of 3,6-dodecadienoic acid methyl ester, furthermore, can help to recognise the Galena cultivar.

Using 30 hop oil constituents as markers, Kralj et al. (1991) were able to classify 95 different hops in 14 groups. The European hoppy aroma correlates positively with the presence of 8 of these 30 compounds and negatively with the presence of the others, responsible for unwanted flavours (Kralj et al. 1991; Deinzer and Yang 1994; see Table 5.5). Among them, methyl decanoate, neryl acetate, α -copaene, α -humulene, and β -caryophyllene emerged as determining. According to Kralj et al. (1991), methyl decanoate, neryl acetate, and α -copaene are responsible for the non-European aroma.

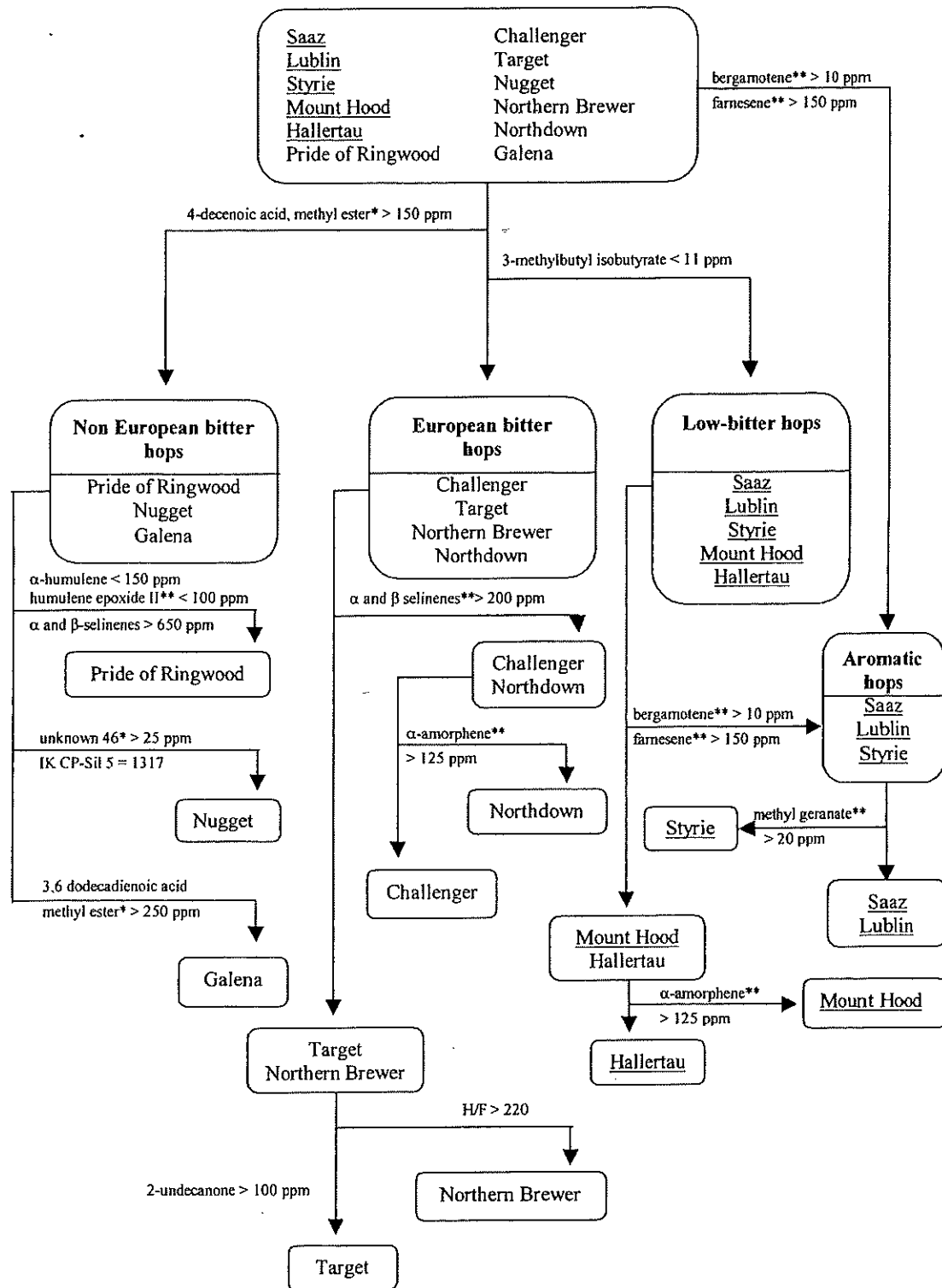


Fig.5.16. Discrimination flowchart proposed by Perpète et al. (1998) for distinguishing 12 hop cultivars. * Carvone equivalent for quantification; ** caryophyllene equivalent for quantification

Table 5.5. Correlations between some hop compounds [selection results from analysis of 95 local varieties and cultivars from different regions and grown in the ecological environment of Slovenia, 1986–1988 (Kralj et al. 1991)] and the European hoppy aroma. (Deinzer and Yang 1994)

Positive correlation	Negative correlation	
α -Humulene ^{a,b}	Myrcene ^c	Methyl decanoate
β -Caryophyllene ^b	α -Muuroolene	Neryl acetate
Carvone	Germacrene-D	γ -Copaene
Methyl, deca,4-enoate	Curcumene ^c	γ -Cadinene
2-Undecanone	β -Selinene	δ -Cadinene ^c
Farnesene ^a	α -Selinene	Selina-3,7(11)-diene ^c
Humulene epoxide I ^a	o-Cymene	Selina-3(14),7(11)-diene
Unidentified compound ^a	Methyl caprylate	Santalene ^c
	Geranyl acetate ^c	Calamenene
	Geraniol	Two unidentified compounds
	α -Phellandrene	

^aImproved European aroma with increasing concentration

^bHumulene/caryophyllene ratio must be greater than 3

^cIncreasing negative influence on aroma as concentration increases

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