4 Chemistry of Essential Oils

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4.1
What Is an Essential Oil?

Essential oil, also defined as essence, volatile oil, etheric oil or aetheroleum, is a complex mixture of volatile constituents biosynthesised by living organisms. Essential oils can be liberated from their matrix by water, steam and dry distillation, or expression in the case of citrus fruits [1–5]. Their occurrence and function in nature is still a question and the subject of ongoing research. However, there is evidence that organisms produce essential oils for defence, signalling or as part of their secondary metabolism. As a consequence essential oils comprise an important bioresource for renewable natural products [1–25].

Extracts of aromatic plant or animal materials obtained using organic solvents or fluidised gasses *are not* considered as essential oils [1, 23, 25–28]. Concretes, absolutes, spice oleoresins, *etc.* which can be classified as aromatic extracts are not covered in this chapter.

Essential oils, their fractions and their isolates are utilised in flavour and fragrance, food, perfumery, cosmetics and toiletries, fine chemicals, pharmaceutical industries and therapy. They are used as such or in diluted forms in the budding aromatherapy sector [1, 3, 5, 6, 8–14, 16–19, 21–35].

Essential oils may comprise volatile compounds of terpenoid or non-terpenoid origin. All of them are hydrocarbons and their oxygenated derivatives. Some may also contain nitrogen or sulphur derivatives. They may exist in the form of alcohols, acids, esters, epoxides, aldehydes, ketones, amines, sulphides, *etc.* Monoterpenes, sesquiterpenes and even diterpenes constitute the composition of many essential oils. In addition, phenylpropanoids, fatty acids and their esters, or their decomposition products are also encountered as volatiles [1–16, 21–33, 36–38].

Owing to their liquid nature at room temperature, essential oils are called as such. They should not be confused with fixed oils or fatty oils, which are composed of a naturally occurring mixture of lipids which may not necessarily be volatile. Therefore, essential oils differ entirely both in chemical and in physical properties from fatty oils. Essential oil evaporates completely when dropped on filter paper; however, fixed oil leaves a permanent stain which does not evaporate even when heated.

Essential oils occur mainly in aromatic plants. A few of them are found in animal sources, e.g. musk, civet and sperm whale, or are produced by microorganisms [1, 3, 6, 23, 25, 26, 29–33]. The Council of Europe describes "essential oil" as a product obtained from "vegetable raw material" [27]. Owing to a ban on animal-based flavour and fragrance materials, essential oils of trade are entirely of plant origin

Among many others, well-known families rich in essential oil bearing species are Apiaceae, Asteraceae, Cupressaceae, Hypericaceae, Lamiaceae, Lauraceae, Myrtaceae, Pinaceae, Piperaceae, Rutaceae, Santalaceae, Zingiberaceae and Zygophyllaceae [1–4, 8–11, 39].

In plants, essential oils occur in oil cells, secretory ducts or cavities, or in glandular hairs. In some cases, they are bound with carbohydrates in the form of glycosides [1–4, 8–14]. In such cases, they must be liberated by hydrolysis of the glycosidic bond. This is done by allowing enzymatic reactions to take place during wilting prior to distillation of fresh plant materials. Mosses, liverworts, seaweeds, sponges and fungi have also been shown to contain essential oils. Besides higher plants, some terrestrial and marine animals, insects, fungi and microorganisms are also known to biosynthesise volatile compounds [6–14, 30–33, 40, 41].

Essential oils are frequently associated with gums and/or resins. They are freed from such products by distillation.

Essential oil constituents can be classified as terpenoids and non-terpenoid hydrocarbons.

4.1.1
Non-terpenoid Hydrocarbons

Non-terpenoid hydrocarbons found in essential oils such as short chain alcohols and aldehydes are formed by metabolic conversion or degradation of phospholipids and fatty acids [12].

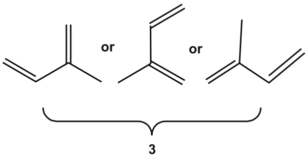
Hydrocarbons consist of carbon and hydrogen. They may also contain oxygen, nitrogen or sulphur. The simplest hydrocarbon is methane (CH_4), which is a colourless and odourless highly flammable gas. The carbons are connected by single, double or triple bonds to form higher molecular weight hydrocarbons. Saturated homologous straight-chain structures are called **alkanes**, while their unsaturated forms are called **alkenes**. Alkenes show isomerism owing to the

1 2

Structure 4.1

position of the hydrogen atoms attached to the double bond as in the examples *trans*-but-2-ene **1** and *cis*-but-2-ene **2** (Structure 4.1).

Molecules with three carbon atoms can only form a straight chain; however, with four carbons or more they can form both straight and branched chains. Then, their naming also changes accordingly. Isoprene is one such molecule; it is chemically 2-methyl-1,3-butadiene **3** (Structure 4.2).



Structure 4.2

4.1.2
Terpenoids

Terpenes, also called isoprenoids, are one of the largest classes of natural chemicals formed by head-to-tail rearrangement of two or more isoprene molecules. More than 30,000 terpenoids have been isolated from plants, microorganisms and animals [3, 7, 11, 37, 42]. They are important constituents of essential oils. Molecules formed from two isoprene **3** molecules are called **monoterpenes** ($C_{10}H_{16}$). C_5H_8 compounds are **hemiterpenes**. **Sesquiterpenes** contain three isoprene units; hence they have the formula $C_{15}H_{24}$. $C_{20}H_{32}$ compounds formed from four isoprene units are **diterpenes**. Heavier terpenes like diterpenes are generally not found in essential oils. Isoprene itself is considered the only hemiterpene, but oxygen-containing derivatives such as prenol and isovaleric acid are hemiterpenoids, too [3, 7–14].

Kekulé, in 1880, was the first scientist to name $C_{10}H_{16}$ compounds as "terpenes", because of their existence in turpentine. His assistant Wallach (1910 recipient of the Nobel Prize in Chemistry) hypothetically proposed in 1887 that terpenes were constructed via two or more isoprene units. Three decades later, Robinson (1947 recipient of the Nobel Prize in Chemistry) perfected Wallach's "isoprene rule" by suggesting that the isoprene units should be connected in a head-to-tail fashion. A few years later, Ruzicka (1939 recipient of the Nobel Prize in Chemistry) proposed in 1950 the "biogenetic isoprene rule", further developing Wallach's hypothesis. The rule reiterated the formation of terpenes by head-to-tail rearrangement of two or more isoprene units. This rule stipulates that the terpenoids are derived from aliphatic precursors such as geraniol for the formation of monoterpenes, farnesol for the sesquiterpenes, geranylgeraniol for the diterpenes and squalene for triterpenes. It is interesting to note that three terpene scientists received the Nobel Prize in Chemistry within a span of 37 years [3, 7–14, 38, 39, 42].

4.1.2.1
Biosynthesis of Terpenes

Terpenes, biogenetically, arise from two simple five-carbon moieties. Isoprenyldiphosphate (IPP) and dimethylallyldiphosphate (DMAPP) serve as universal precursors for the biosynthesis of terpenes. They are biosynthesised from three acetylcoenzyme A moieties through mevalonic acid (MVA) *via* the so-called *mevalonate pathway*. About 10 years ago, the existence of a second pathway leading to IPP and DMAPP was discovered involving 1-deoxy-*D*-xylulose-5-phosphate (DXP) and 2C-methyl-*D*-erythritol-4-phosphate (MEP). This so-called *non-mevalonate* or *deoxyxylulose phosphate pathway* starts off with the condensation of glyceraldehyde phosphate and pyruvate affording DXP. Through a series of reactions as shown in Fig. 4.1, IPP and DMAPP are formed, respectively [3, 7, 42, 43].

IPP and DMAPP lead to geranylpyrophosphate (GPP), which is an immediate precursor of monoterpenes. The formation of nerylpyrophosphate (NPP) from GPP gives rise to a wide range of acyclic, cyclic, bicyclic or tricyclic skeletons. Reactions like rearrangement, oxidation, reduction and hydration *via* various terpene cyclases result in the formation of numerous terpene derivatives. Condensation of GPP and IPP leads to farnesylpyrophosphate (FPP), the immediate precursor of sesquiterpenoids. Likewise, FPP and IPP are conducive to diterpenoids.

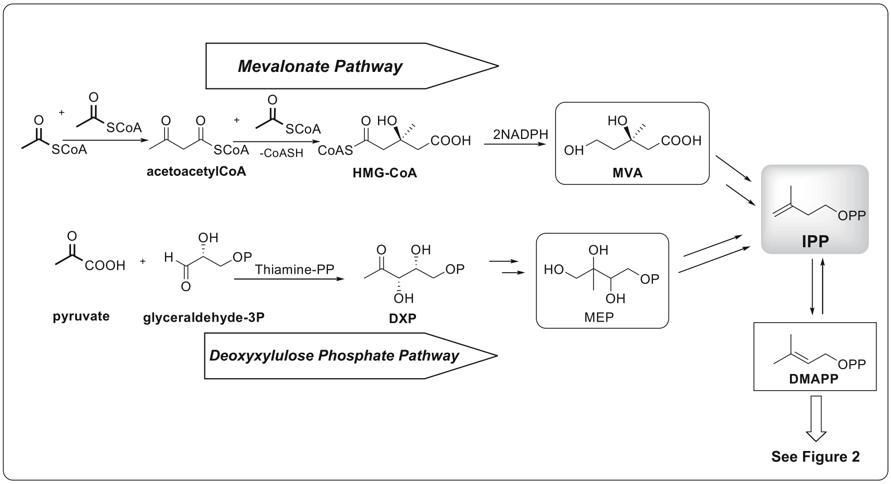
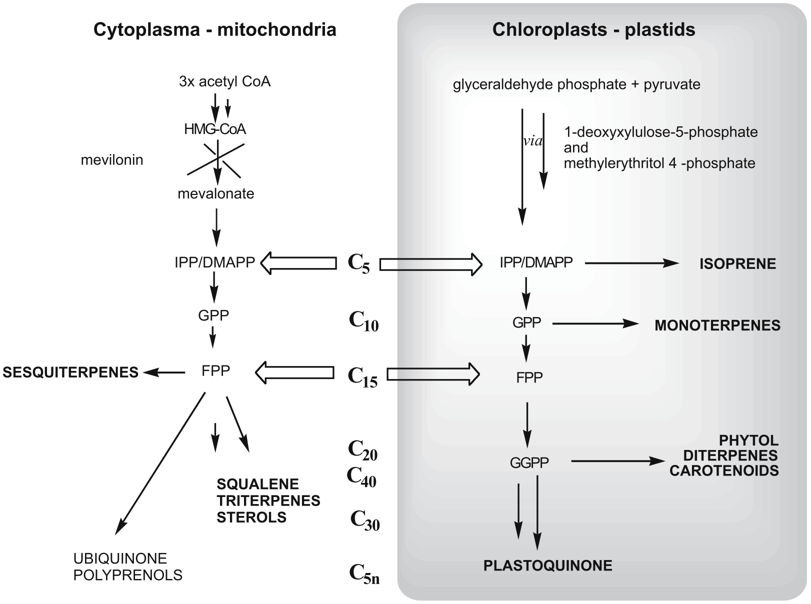


Fig. 4.1 Terpenoid biosynthesis: two independent pathways



Compartmentation of isoprenoid biosynthesis in higher plants. Arrows at the level of IPP (C5) and farnesyl diphosphate (C15) indicate possible exchanges between compartments. Dimethylallyl diphosphate (DMAPP), geranyl diphosphate (GPP), geranylgeranyl diphosphate (GGPP).

Fig. 4.2 Terpenoid biosynthesis sites and products (metabolites) (reprinted from Rohmer [46], copyright 2006, with kind permission from Elsevier)

The mevalonate-independent pathway is present in most bacteria and all phototropic organisms. In higher plants and most algae both pathways run independently. The mevalonate pathway is located in the cytoplasm and is responsible for the biosynthesis of most sesquiterpenoids. The mevalonate-independent pathway, in contrast, is restricted to the chloroplasts where plastid-related isoprenoids such as monoterpenes and diterpenes are biosynthesised via this pathway [43–45]. Figure 4.2 illustrates the interrelationships of both biosynthetic pathways connected to Fig. 4.1 [46].

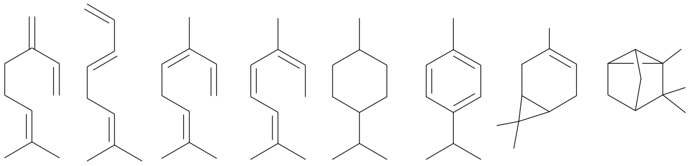
Monoterpenes

Monoterpenes are formed from two attached isoprene **3** units: 2,6-dimethyloctane as the simplest skeleton. Thus, they can be acyclic or linear like β-myrcene **4**, (E)-β-ocimene **5**, (Z)-β-ocimene **6**, and *allo*-ocimene **7** (Structure 4.3). Or they can be cyclic, meaning ring-forming, such as in the simplest form like p-menthane **8** or p-cymene **9**. Monocyclic **8**, **9**, bicyclic δ-3-carene **10** and tricyclic tricyclene **11** type monoterpenes are found in essential oils [1–4, 6–14, 16–23, 38, 39, 42, 47, 48].

Aromatic monoterpenes which contain a benzene ring like *p*-cymene **9**, carvacrol **12**, thymol **13** and phenylethyl alcohol **14** (Structure 4.4) are common constituents of many essential oils, e.g. oregano (*Origanum* sp.), thyme (*Thymus* sp.), savory (*Satureja* sp.) and rose (*Rosa* sp.) oils. Another important constituent class of essential oils is phenypropanoids [36]. They are not considered as terpenoids owing to their different biogenetic origins, which will be mentioned later.

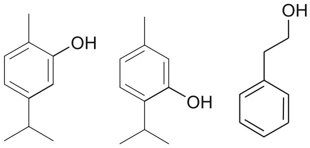
According to the *Dictionary of Natural Products* (DNP), there are 25 different classes of monoterpenes [37].

The biosynthesis of different classes of monoterpenes formed from α-terpinyl cation and respective precursors are illustrated in Fig. 4.3.



4 **5** **6** **7** **8** **9** **10** **11**

Structure 4.3



12 **13** **14**

Structure 4.4

4.1.2.1.1.1
Acyclic Monoterpenes

These regular monoterpenes constitute a small class which includes the trienes myrcene **4** and ocimenes (**5**–**7**) and the alcohols geraniol **15**, nerol **16**, citronellol **17**, linalool **18**, *etc* (Structure 4.5).

Citral is the naturally occurring mixture of the aldehydes geranial **19** and neral **20** (Structure 4.6). Citronellal **21** is another acyclic aldehyde within this grouping. Variation of the 2,6-dimethyloctane skeleton is easily noticeable.

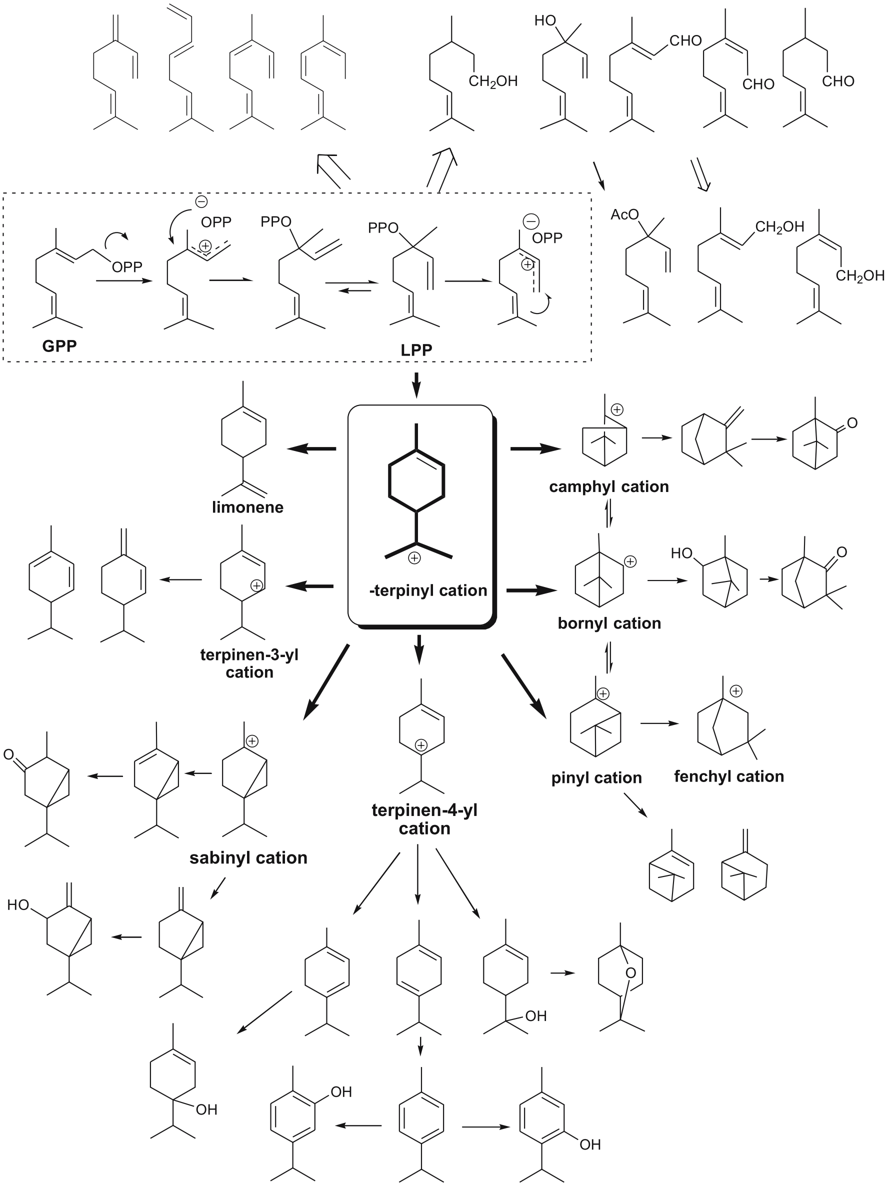
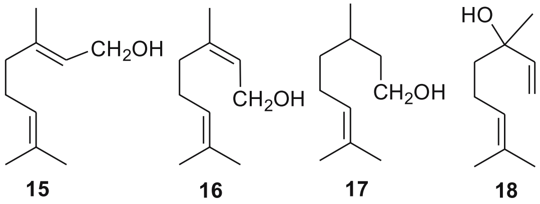
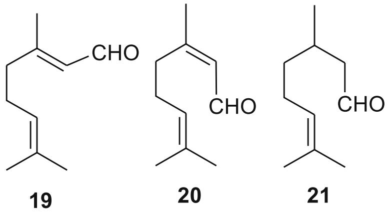


Fig. 4.3 Monoterpene (re)arrangements and important intermediates



Structure 4.5



Structure 4.6

Cyclic Monoterpenes

Cyclic monoterpenes can be classified in three subgroups according their ring size such as:

1. Monocyclic monoterpenes
2. Bicyclic monoterpenes
3. Tricyclic monoterpenes

Monocyclic Monoterpenes

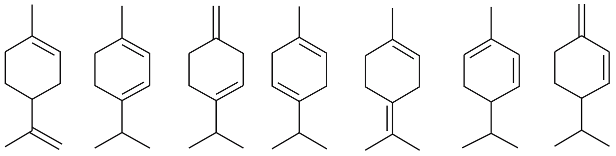
p-Menthane monoterpenes which possess the 1-methyl-4-isopropyl-cyclohexane **8** skeleton comprise the largest group of naturally occurring monoterpenes.

p-Menthadienes are limonene **22**, *α*-terpinene **23**, *β*-terpinene **24**, γ-terpinene **25**, terpinolene **26**, *α*-phellandrene **27** and *β*-phellandrene **28** (Structure 4.7) resulting from different rearrangements of the *α*-terpinyl cation (Fig. 4.3). This group is also classified among the monoterpene hydrocarbons.

Aromatic monoterpenes such as *p*-cymene **9** and its hydroxylated derivatives thymol **12** and its isomer carvacrol **13** always occur along with *α*-terpinene **23**, γ-terpinene **25** and terpinen-4-ol **29** (Structure 4.8). Metabolites, like *p*-cymene-8-ol **30** and cuminyl alcohol **31** may also be derived from *p*-cymene (Fig. 4.4).

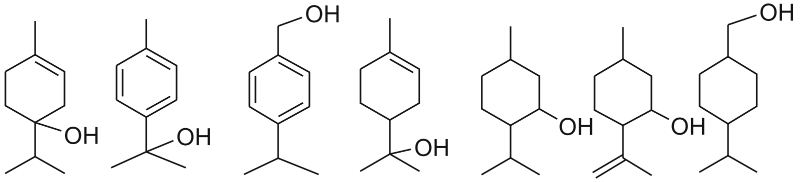
Other important members of this class include oxygenated derivatives such as *α*-terpineol **32**, menthol **33**, isopulegol **34** and *cis*-hexahydrocuminyl alcohol **35**, also classified as monoterpene alcohols.

Aldehydes in this group are as follows: carvone **36**, dihydrocarvone **37**, isomenthone **38**, piperitone **39**, pulegone (piperitenone) **40**, isopulegone **41** (Structure 4.9).



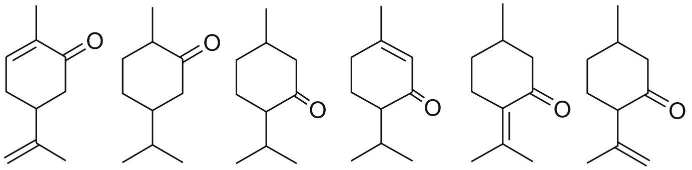
22 **23** **24** **25** **26** **27** **28**

Structure 4.7



29 **30** **31** **32** **33** **34** **35**

Structure 4.8



36 **37** **38** **39** **40** **41**

Structure 4.9

Bicyclic Monoterpenes

1,8-Cineole **42** as well as 1,4-cineole **43** are cyclic ethers (Structure 4.10). All including ascaridol **44** are bicyclic oxygenated monoterpenes. Their formation can be seen in Fig. 4.3.

Pinane monoterpenes are bicyclic monoterpenes resulting from intramolecular rearrangement of the *α*-terpinyl cation yielding the [3.1.1] bicyclic system (Fig. 4.3). *α*-Pinene **45** and *β*-pinene **46** (Structure 4.11) are the main constituents of turpentine oil from pines. They occur widely in essential oils.

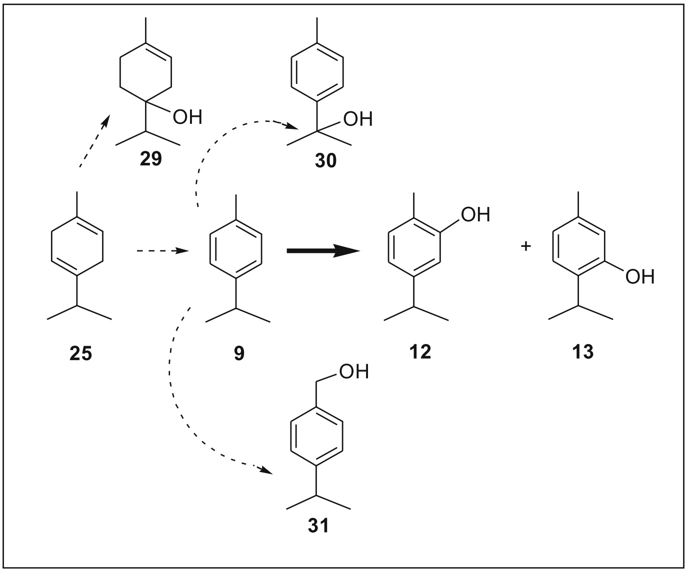
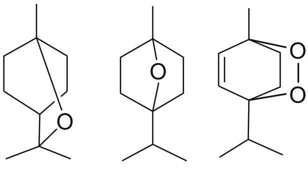


Fig. 4.4 Aromatic monoterpene biosynthesis

The bornane-, camphane- and fenchane-type monoterpenes possess the [2.1.1] bicyclic skeleton formed by different cyclisation of the terpinyl cation. Important members include borneol **47**, isobornyl acetate **48**, camphene **49**, camphor **50**, fenchone **51** (Structure 4.12).

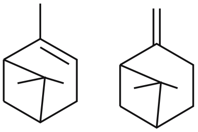
Thujane-type monoterpenes, unusual monoterpenes with a cyclopropane ring in a bicyclo[3.1.0] skeleton, are formed from the terpinen-4-yl cation directly or via the sabinyl cation. Important members include α-thujene **52**, sabinene **53**, the *cis* isomer **54** of sabinene hydrate, sabinol **55**, sabinylacetate **56**, α-thujone **57**, β-thujone **58** and isothujanol **59** (Structure 4.13).

Carane-type monoterpenes possess a cyclopropane ring in a bicyclo[4.1.0] skeleton. δ-3-Carene **10** is a common constituent in various essential oils.



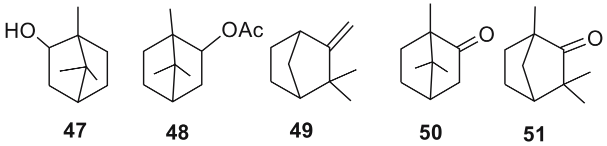
42 **43** **44**

Structure 4.10

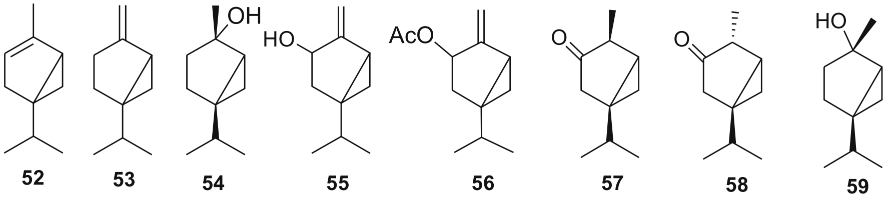


45 **46**

Structure 4.11



Structure 4.12



Structure 4.13

4.1.2.1.1.2.3
Tricyclic Monoterpenes

Tricyclene **11** or 1,7,7-trimethyltricyclo$[2.2.1.0^{2,6}]$heptane, is a good example which frequently occurs in various essential oils.

4.1.2.1.1.3
Irregular Monoterpenes

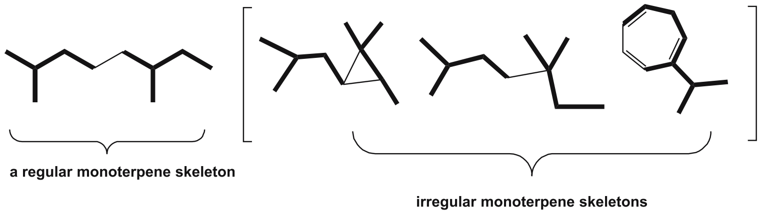
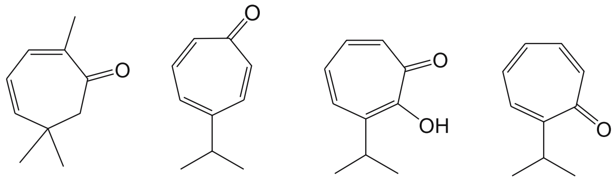


Fig. 4.5 Different classes of monoterpenes

There are two major types of irregular monoterpenes (Fig. 4.5):

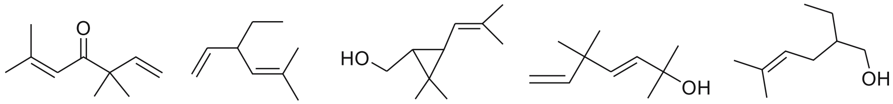
1. The substituted cycloheptane monoterpenes, also called tropones. Eucarvone **60**, nezukone (4-isopropyl-2,4,6-cycloheptatrienone) **61** and γ-thujaplicin **62** (Structure 4.14) most probably arise by an unknown ring expansion of the cyclohexane skeleton.



60 **61** **62** **63**

Structure 4.14

2. The other major group of irregular monoterpenes is formed by non-head-to-tail fusion of isoprene units. Important members include artemisia ketone **64**, santolinatriene **65**, chrysanthemol **66**, yomogi alcohol **67** and lavandulol **68** (Structure 4.15). Lavandulane-type compounds occur in the families Lamiaceae (Labiatae) and Apiaceae (Umbelliferae), while chrysanthemane, artemisane and santolinane types occur in the family Asteraceae (Compositae) [47, 48].

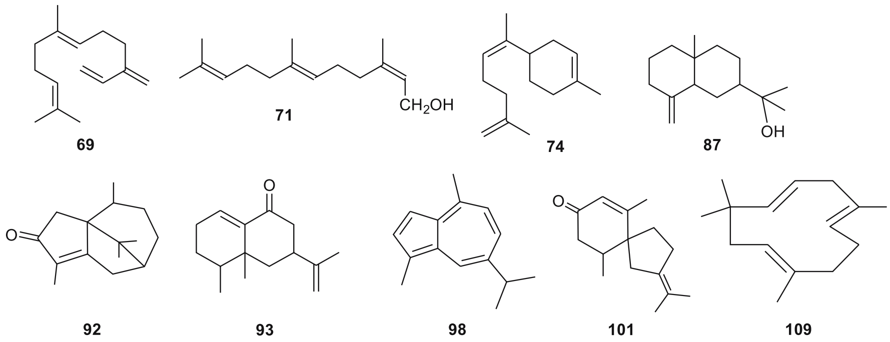


64 **65** **66** **67** **68**

Structure 4.15

4.1.2.1.2 Sesquiterpenes

Sesquiterpenes are formed by the addition of one more isoprene units to a monoterpene molecule, and thus have the molecular formula $C_{15}H_{24}$ (see also Fig. 4.2). There are linear, branched or cyclic sesquiterpenes. Sesquiterpenes are unsaturated compounds. Cyclic sesquiterpenes may be monocyclic, bicyclic or tricyclic. They are the most diverse group among the volatile terpenoids [2, 3, 7–11, 13, 14, 16, 20–24, 37–39, 49]. The DNP treats sesquiterpenoids in 147 different structural types [37]. Various types of sesquiterpenes (**69–109**) can also be seen in Structure 4.16.



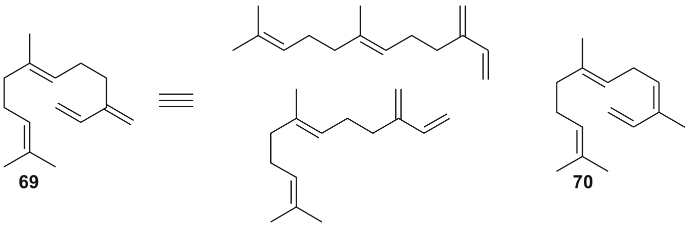
Structure 4.16

4.1.2.1.2.1
Acyclic Sesquiterpenes

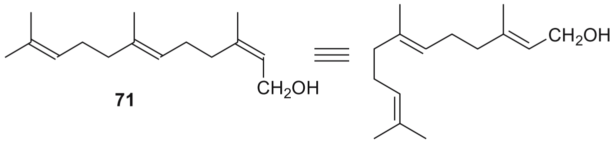
β-Farnesene **69** is a constituent of hops oil and many other oils. *α*-Farnesene **70** is the structural isomer. Structural representations of *α*-farnesene and *β*-farnesene are illustrated in Structure 4.17.

Farnesol **71** (Structure 4.18) is widely distributed in flower oils such as rose, acacia and cyclamen.

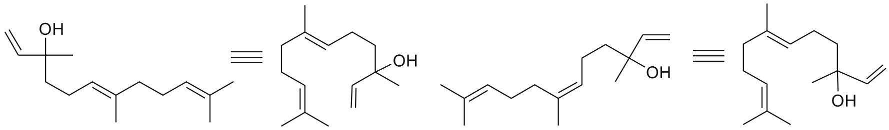
Nerolidol is isomeric with farnesol and is found in neroli oil and many other oils. Its *E* isomer **72** is more frequently found in nature than its *Z* isomer **73** (Structure 4.19).



Structure 4.17



Structure 4.18



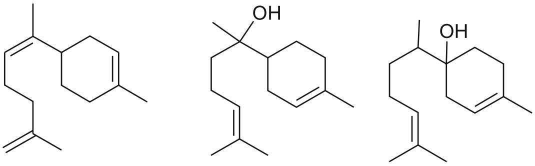
72 **73**

Structure 4.19

4.1.2.1.2.2

Monocyclic Sesquiterpenes

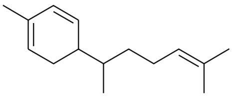
Bisabolene-type sesquiterpenes, e.g. *α*-bisabolene **74** (Structure 4.20), are widely distributed in nature. This sesquiterpene hydrocarbon is a constituent of bergamot, myrrh and a wide variety of essential oils. Its oxygenated derivatives *α*-bisabolol [6-methyl-2-(4-methyl-3-cyclohexen-1-yl)-5-hepten-2-ol] **75** and *β*-bisabolol [4-methyl-1-(6-methylhept-5-en-2-yl)cyclohex-3-enol] **76** are found abundantly in chamomile.



74 **75** **76**

Structure 4.20

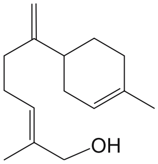
Zingiberene [5-(1,5-dimethyl-4-hexenyl)-2-methyl-1,3-cyclohexadien] **77** (Structure 4.21), is a constituent of ginger oil.



77

Structure 4.21

Lanceol or 2,7(14),10-bisabolatrien-12-ol **78** (Structure 4.22) is a primary alcohol found in the oil of sandalwood (*Santalum lanceolatum*). *Z* and *E* isomers exist.



78

Structure 4.22

4.1.2.1.2.3
Bicyclic Sesquiterpenes

Cadinene is a trivial name of a number of isomers which occur in a wide variety of essential oils e.g. cubeb oil. Actually, it is derived from the Cade juniper (*Juniperus oxycedrus* L.). The cadalane (4-isopropyl-1,6-dimethyldecahydronaphthalene) carbon skeleton is the base. Prominent stereochemical isomers are *α*-cadinene **79**, *γ*-cadinene **80** and *δ*-cadinene **81** (Structure 4.23). This group is also known as naphthalene-type sesquiterpenes.

α-Selinene **82**, *β*-selinene **83**, *γ*-selinene **84** and *δ*-selinenes **85** (Structure 4.24) are found in celery oil and many other oils.

α-Eudesmol **86**, *β*-eudesmol **87** and γ-eudesmol **88** (Structure 4.25) are tertiary alcohols found in many oils. They are practically the oxygenated forms of selinenes.

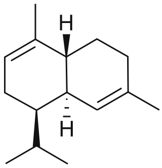
α-Cyperone **89** (Structure 4.26) is a sesquiterpene ketone found in the essential oil of the tubers of *Cyperus rotundus*. Further hydroxylated derivatives such as *α*-cyperol **90** and isocyperol **91** can be found along with another ketone with a tricyclic unusual skeleton, namely cyperenone **92**.

The bicyclic ketone eremophilone **93** (Structure 4.27) was first isolated from wood oil of *Eremophila mitchelii*. It is also found in many other oils. *allo*-Eremophilone **94** is also structurally related.

The azulenes are a group of bicyclic sesquiterpenes which are responsible for the blue colour of essential oils. They contain highly conjugated five- and six-membered aromatic carbon rings fused together. Chamazulene **97**, the blue-colouring principle of chamomile oil, is actually formed from matricine **95** during distillation, through the carboxylic acid **96** intermediate, as seen in Fig. 4.6 [1–4], whereas guaiazulene or 1,4-dimethyl-7-isopropylazulene **98** is found in geranium oil.

Vetivanes are sesquiterpene ketones occuring in vetiver oil. Vetivane is basically a spiro[4,5]decane **99** (Structure 4.28). Although structurally different as in the case of *α*-vetivone **100** and *β*-vetivone **101**, they are characteristic compounds present in vetiver oil. Analogues such as *α*-vetispirene **102** and *β*-vetispirene **103** may occur as well.

The tertiary alcohol guaiol **104** (Structure 4.29), also called 2-(1,2,3,4,5,6,7,8-octahydro-1,4-dimethylazulen-7-yl)propan-2-ol, is found in guaiacum wood oil.



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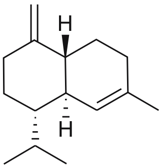

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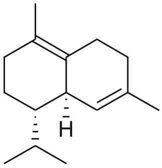

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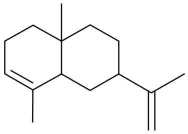
Structure 4.23



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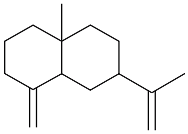

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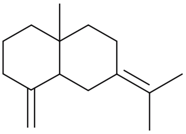

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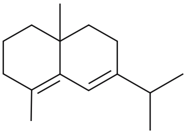

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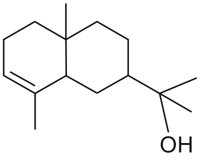
Structure 4.24



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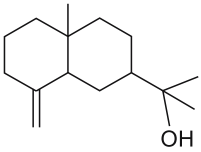

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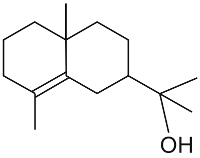

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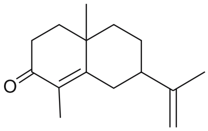
Structure 4.25



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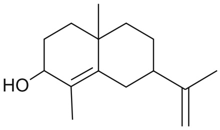

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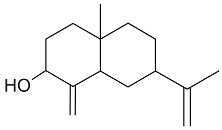

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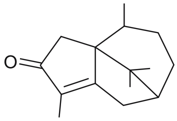

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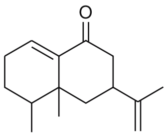
Structure 4.26



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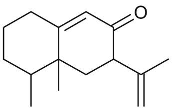

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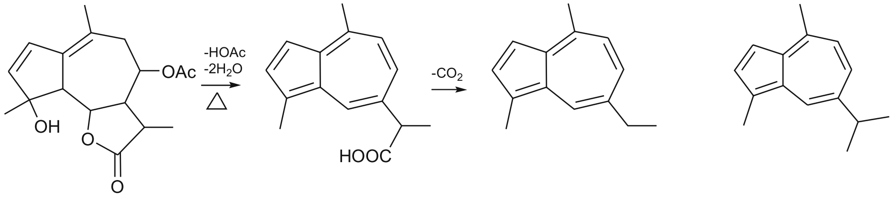
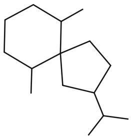
Structure 4.27



95 **96** **97** **98**

Fig. 4.6 Chamazulene chemistry



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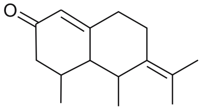

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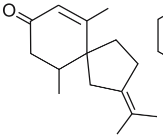

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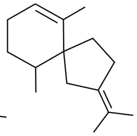

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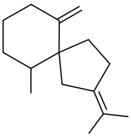

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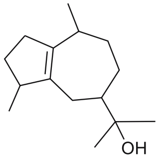
Structure 4.28



104

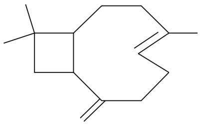
Structure 4.29

4.1.2.1.2.4

Miscellaneous Sesquiterpenes

Caryophyllene, a common constituent of essential oils, was first isolated from clove oil. *β*-Caryophyllene [(*E*)-caryophyllene] **105** (Structure 4.30) is the most widely encountered form of caryophyllenes. Caryophyllene derivatives (**106–108**) are characteristic constituents of most birch oils [49–51].

Humulene **109** (Structure 4.31) is isomeric with caryophyllene. First isolated from hops oil (*Humulus lupulus*), it is a common constituent of essential oils.



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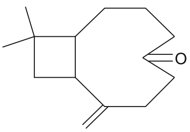

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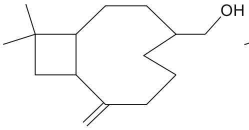

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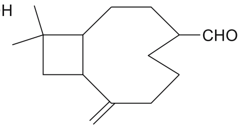

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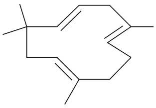
Structure 4.30

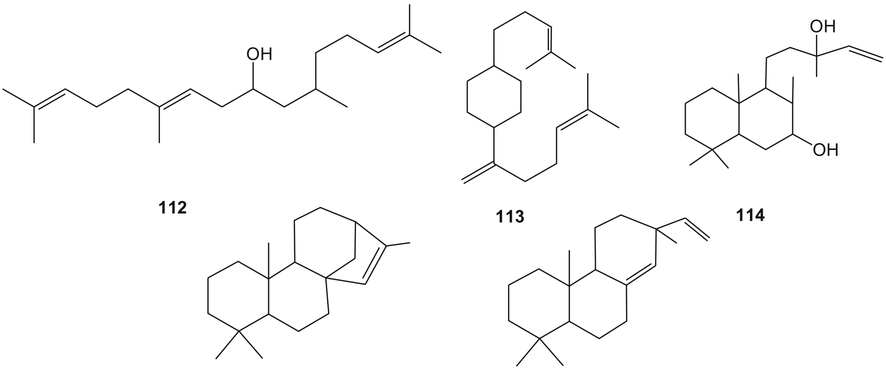


109

Structure 4.31

4.1.2.1.3
Diterpenes

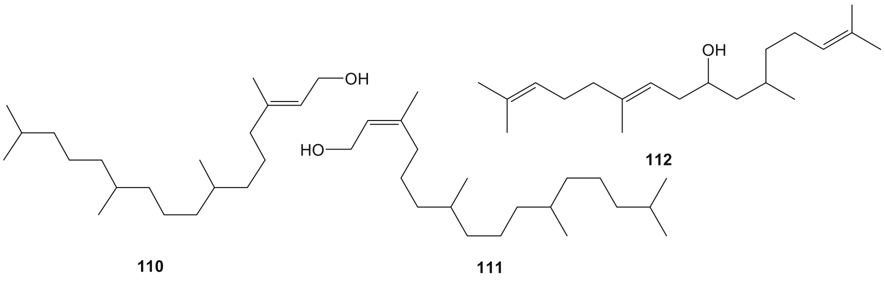
Head-to-tail rearrangement of four isoprene units results in the formation of diterpenes ($C_{20}H_{32}$), as seen also in Fig. 4.2. Diterpenes are generally found in resins, *e.g.* pimaric acid and abietic acid. Some diterpenoids are also constituents of essential oils, e.g. phytol [3, 7–14, 37, 52, 53]. Like sesquiterpenes, diterpenes are heavier than monoterpenes; therefore, they require more energy to go to the vapour phase. For this reason, longer distillation times are necessary for their recovery. The DNP lists 118 different structural types for diterpenoids [37]. Important diterpenes found in essential oils will be detailed. Some representatives of volatile diterpenes are as in Structure 4.32.



Structure 4.32

4.1.2.1.3.1
Acyclic Diterpenes

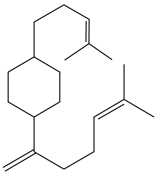
Phytol, a diterpene alcohol (3,7,11,15-tetramethyl-2-hexadecen-1-ol), occurs in two isomeric forms: *trans*-phytol **110** and *cis*-phytol **111** (Structure 4.33). Phytol was first isolated at the beginning of the nineteenth century during esterification of the chlorophyll molecule. It is a constituent of nettle and many essential oils. Another acyclic diterpene, geranylcitronellol **112**, also occurs in essential oils.



Structure 4.33

4.1.2.1.3.2
Cyclic Diterpene

Camphorene **113** (Structure 4.34), which is a constituent of camphor oil, is identical to dimyrcene. Several dimyrcene derivatives are constituents of pistachio oils [54]. The gum resin of *Commiphora mukul* furnishes essential oil (0.4 %) consisting chiefly of myrcene 4 and "dimyrcene" (camphorene 113) [55].



113

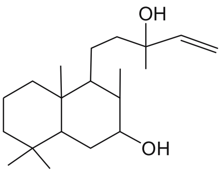
Structure 4.34

4.1.2.1.3.3
Bicyclic Diterpenes

Sclareol **114** (Structure 4.35), a ditertiary glycol, is a constituent of clarysage (*Salvia sclarea*) oil [56, 57]. The diterpene ketone sclareolide **115** and the lactone ambrox **116** are important (bio)synthetic derivatives found in clarysage extract.

Manool **117** and manoyl oxide **118** (Structure 4.36) are found in pine oils. They are common diterpenes encountered in many essential oils.

Labdane **119**, abienol **120** and labdanediol **121** (Structure 4.37) are representatives of volatile labdane derivatives.



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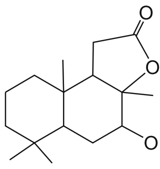

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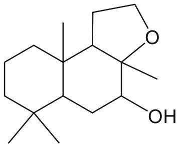

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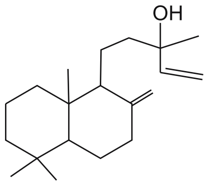
Structure 4.35



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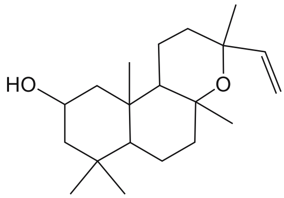

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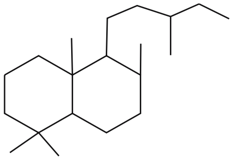
Structure 4.36



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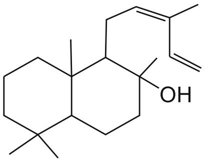

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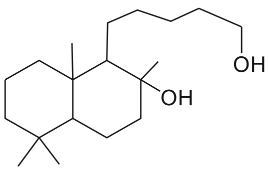


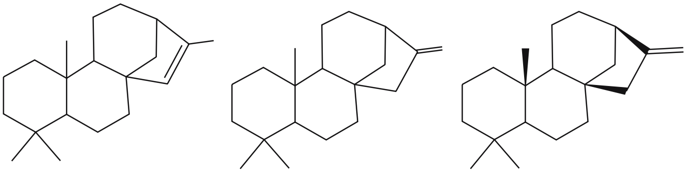
121

Structure 4.37

4.1.2.1.3.4
Tricyclic Diterpenes

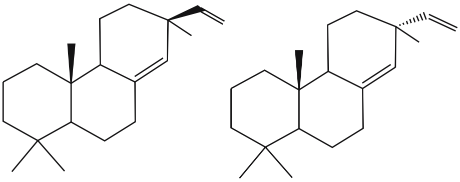
Kaur-15-ene **122**, kaur-16-ene **123** and phyllocladene **124** (Structure 4.38) are encountered in essential oils.

The diterpene pimaradiene **125** and sandaracopimaradiene (or isopimaradiene) **126** (Structure 4.39) are found in some essential oils.



122 **123** **124**

Structure 4.38

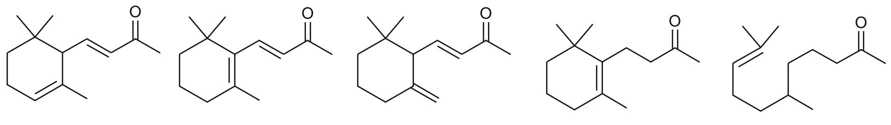


125 **126**

Structure 4.39

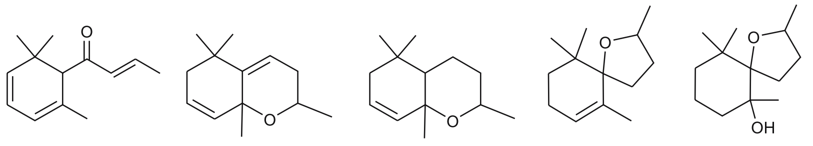
4.1.3
C$_{13}$ Norterpenoids

This is a fairly large group of C$_{13}$ compounds generally thought to be degraded carotenoids or catabolites of abscisic acid. α-Ionone **127**, β-ionone **128**, γ-ionone **129**, dihydro-β-ionone **130**, (*E*)-geranyl acetone **131** (Structure 4.40), pseudoionones such as β-damascenone (3,5,8-megastigmatrien-7-one) **132**, megastigmadienones, megastigmatrienes, edulans such as edulan I **133**, dihydroedulan II **134**, theaspirane **135**, 6-hydroxydihydrotheaspirane **136** (Structure 4.41) and related compounds are found in purple passiflora fruit (*Passiflora edulis*), tea (*Thea sinensis*) and many essential oils [1–4, 8–14, 18–23, 58].



127 **128** **129** **130** **131**

Structure 4.40

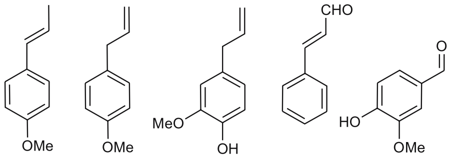


132 **133** **134** **135** **136**

Structure 4.41

4.1.4
Phenylpropanoids

Phenylpropanoids are biosynthesised by the *shikimic acid pathway* (Fig. 4.7) via the amino acid *l*-phenylalanine by the action of phenylalanine ammonia lyase (PAL), which removes the nitrogen function to generate *trans*-cinnamic acid through which *via* the action of various enzymes, including hydrolases, (ethyl)transferases, oxidoreductases and lygases, a wide range of phenylpropanoids are biosynthesised [12, 41, 59]. Phenylpropanoids contain one or more C_6–C_3 fragments, the C_6 unit being a benzene ring. Simple phenylpropanoids are constituents of essential oils [3, 8, 9, 36]. There is no widely accepted classification method for this class of compounds. Important phenylpropanoids include anethole **137**, methyl chavicol (estragol) **138**, eugenol **139**, cinnamic aldehyde **140** and vanillin **141** (Structure 4.42).



137 **138** **139** **140** **141**

Structure 4.42

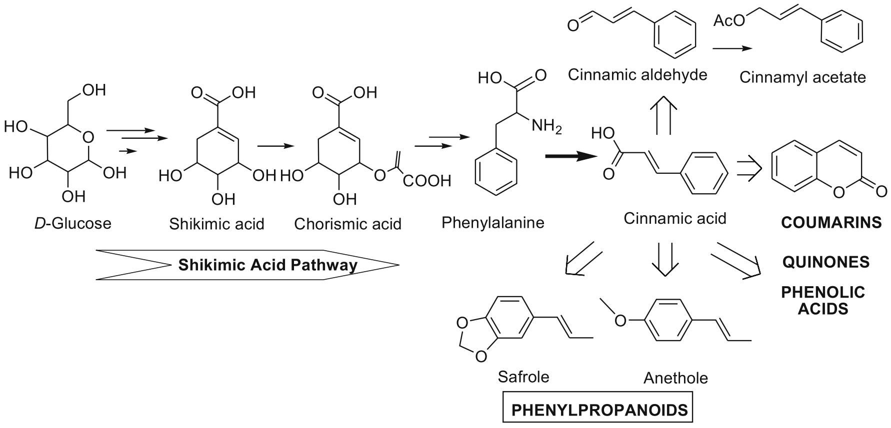
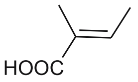


Fig. 4.7 Shikimic acid pathway and volatile phenylpropanoids

4.1.5 Esters

Esters of benzenoid and monoterpenic acids and alcohols as well as unsaturated carboxylic acids such as tiglic acid **142** and angelic acid **143** (Structure 4.43) are found in essential oils [60, 61].



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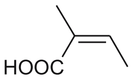
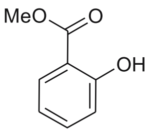


143

Structure 4.43

Methyl salicylate **144** (Structure 4.44), the main constituent of wintergreen oil, is derived from benzoic acid. Other important esters are linalyl acetate **145**, benzyl benzoate **146** and benzyl isobutyrate **147**.



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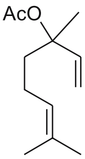

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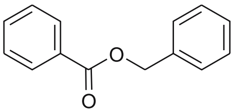

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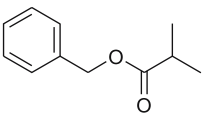


147

Structure 4.44

4.1.6
Lactones

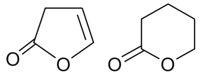
Lactones are cyclic esters derived from lactic acid ($C_3H_6O_3$). They are constituents of many essential oils and plant volatiles. They contain a heterocyclic oxygen next to a carbonyl function in a five or more membered ring that is saturated or unsaturated. Those with a five-membered ring are called γ-lactones, *e.g.* γ-angelica lactone **148**, whereas compounds containing a six-membered ring are called δ-lactones, *e.g.* δ-valerolactone **149** (Structure 4.45) [1–4, 6, 9, 22, 23, 29, 62].

Some representatives of γ-lactones are γ-valerolactone **150**, γ-decalactone **151** with peach-like flavour, (*Z*)-6-dodecen-4-olide **152**, 3-methyl-4-octanolide (whiskey lactone) **153** and 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (sotolone) **154** (Structure 4.46), found in fenugreek, coffee and sake [1–4, 21–23, 62].

Additional representatives of six-membered δ-lactones are δ-decalactone **155**, constituent of fruits, cheese and dairy products with creamy-coconut and peachy aroma, jasmolactone **156** as well as δ-2-decenolactone (2-decen-5-olide) **157** (Structure 4.47).

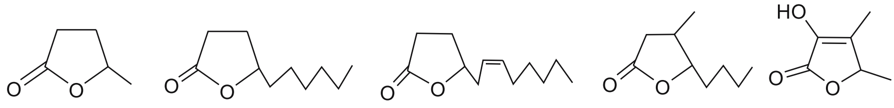
Macrocyclic lactones like ambrettolide (7-hexadecen-1,16-olide) **158**, 15-pentadecanolide (cyclopentadecanolide) **159**, hexadecanolide (cyclohexadecanolide) **160** and cyclohexadec-7-enolide **161** (Structure 4.48) are called musks. They are found in a variety of essential oils, e.g. ambrette seed oil and angelica root oil [1–4, 21–23, 62].

Coumarin **162** (Structure 4.49) is a naturally occurring lactone in crystal form found in hay and tonka beans. It is one of the most used fragrance materials and is responsible for spicy green notes. Dihydrocoumarine **163** is also present in various essential oils with a characteristic sweet herbal odour. Umbelliferone **164**, scopoletin **165**, bergaptene **166** and coumarin are found in Rutaceae, Apiaceae, Lamiaceae and Asteraceae oils. Nepetalactones **167** are confined to the oils of *Nepeta* species [1, 3, 21–23, 63].



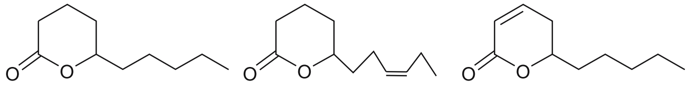
148 **149**

Structure 4.45



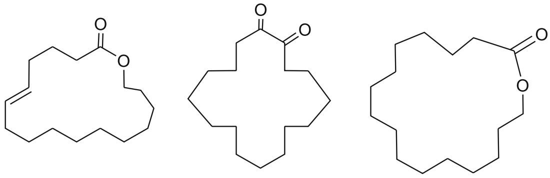
150 **151** **152** **153** **154**

Structure 4.46



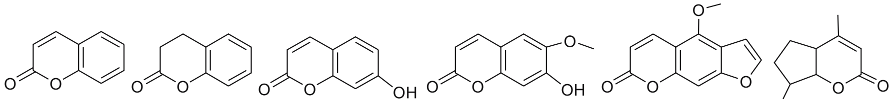
155 **156** **157**

Structure 4.47



158 **159** **160** **161**

Structure 4.48

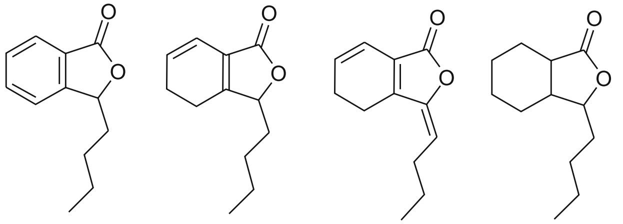


162 **163** **164** **165** **166** **167**

Structure 4.49

4.1.7 Phthalides

Phthalides are lactones of 2-hydroxymethyl benzoic acid. They are also called as benzofuran derivatives. Phthalides are found in some oils of Apiaceae, such



168 **169** **170** **171**

Structure 4.50

as celery, lovage and angelica [1–4, 21–23, 25]. Butylphthalides such as 3-butylphthalide **168** (Structure 4.50) are responsible for the celery aroma and odour in leaves, roots, tubers and seeds. The main compound in the oil is sedanolide (3-butyl-4,5-dihydrophthalide) **169**, together with its isomer *cis*-neocnidilide. (*Z*)-Ligustilide also known as 3-butylidene-4,5-dihydro-1(3*H*)-isobenzofuranone and 3-butylidene-4,5-dihydrophthalide **170** is also found along with 3-butylhexahydrophthalide **171** [1–4, 18, 21–23, 25].

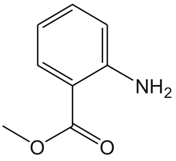
4.1.8
Nitrogen-Containing Essential Oil Constituents

Methyl anthranilate **172** (Structure 4.51) is found in the oils of sweet orange, lemon, mandarin, bergamot, neroli and ylang-ylang oils and jasmine and tuberose absolutes. Methyl *N*-methyl anthranilate **173** is the main constituent of mandarin petit grain oil, and occurs also in bitter orange, mandarin and rue oils.

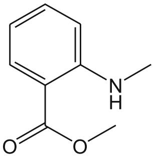
Indole **174** and 3-methyl indole (skatole) **175** (Structure 4.52) are cyclic imines and have a rather unpleasant faecal odour.

2-Methoxy-3-isobutylpyrazine **176** (Structure 4.53) is found in galbanum oil obtained from *Ferula galbaniflua*. 2,4-disubstituted pyridines **177**, N,N-dimethylated amino compounds **178**, alkyl pyrazines **179**, quinoline **180** and methyl quinolines **181** were isolated from fig leaf absolute [64].

Pyridines **177** and pyrazines **179** have been detected in black pepper, sweet orange and vetiver oils [1–4, 21–23, 54, 65].

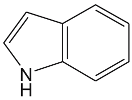


172



173

Structure 4.51



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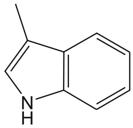
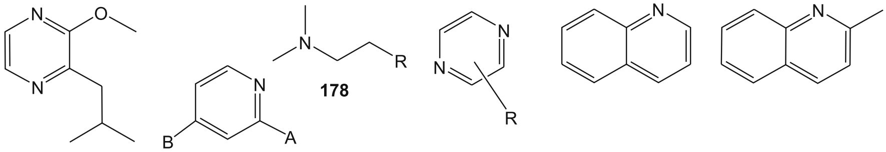


175

Structure 4.52



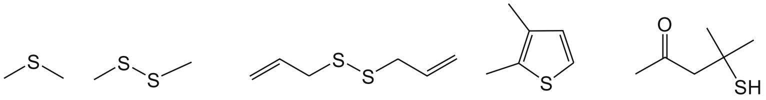
176 **177** **178** **179** **180** **181**

Structure 4.53

4.1.9
Sulphur-Containing Essential Oil Constituents

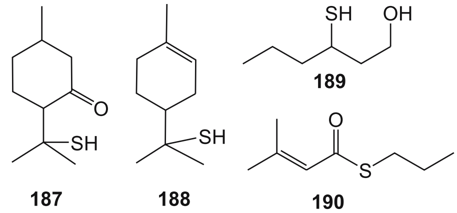
Several sulphides and thiophenes such as dimethyl sulphide **182**, dimethyl disulphide **183**, diallyl disulphide **184**, and 3,2-dimethylthiophene **185** (Structure 4.54) are volatile constituents of garlic, onion, leek and shallot oils. 4-Mercapto-4-methyl-pentanone **186** is the characteristic component of blackcurrant (*Ribes nigrum*) oil. It has an obnoxious cat-urine smell but in proper dilutions it acquires cassis-like floral and fruity-green aspects [1–4, 21–23, 25, 66]. 8-Mercapto-*p*-menthan-3-one **187** (Structure 4.55), a sulphur derivative of pulegone, is a major constituent of buchu (*Agathosma betulina*) oil together with methylthio and acetylthio derivatives of pulegone and other *p*-menthane molecules [67]. 1-*p*-Menthene-8-thiol **188** is an extremely potent component of grapefruit, orange, yuzu and must oils. 3-Mercaptohexanol **189** derivatives are found in passion fruit flavour. Several *S*-prenylthioesters **190** have been detected in essential oils of Rutaceae genera like *Agathosma* and *Diosma*.

Thiazols **191** (Structure 4.56) were identified in the essential oil of coriander. Sulphur compounds such as dimethyl disulphide, its analogues, rose thiophene (3-methyl-2-prenylthiophene) **192**, the S-analogue of perillene, cyclic disulphides, thiodendrolasin **193**, epithiosesquiterpenes **194**, mint sulphide **195** and isomintsulphide **196** (Structure 4.57) have been detected in rose oil. Mint sulphide occurs in the essential oils of peppermint, spearmint, pepper, ylang ylang, narcissus, geranium, chamomile and davana. Sulphides of humulene **197** and caryophyllene **198** were found in rose and hops oils [1–4, 21–23]. There is a recent review on the comprehensive coverage of sulphur-containing flavour constituents [66].



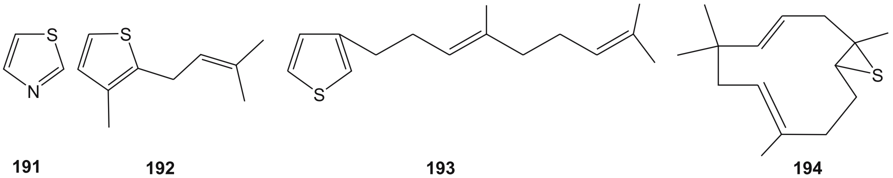
182 **183** **184** **185** **186**

Structure 4.54



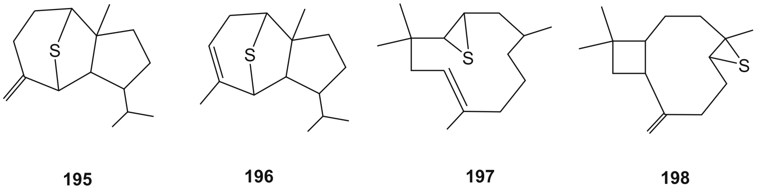
187 188 189 190

Structure 4.55



191 192 193 194

Structure 4.56



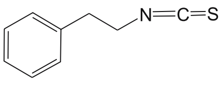
195 196 197 198

Structure 4.57

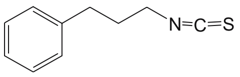
4.1.10
Isothiocyanates

Isothiocyanates are sulphur- and nitrogen-containing phytochemicals with the general formula R-NSC, *e.g.* phenylethyl isothiocyanate **199**, 3-phenylpropyl isothiocyanate **200** and benzyl isothiocyanate **201** (Structure 4.58). Isothiocyanates occur naturally as glucosinolate conjugates mainly in cruciferous vegetables. Isothiocyanates are also responsible for the typical flavour of these vegetables [1–4, 21–23, 25, 54].

Isothiocyanates can be found in cruciferous vegetables such as mustard, broccoli, cauliflower, kale, turnips, collards, Brussels sprouts, cabbage, radish, turnip and watercress. Glucosinolates are precursors of isothiocyanates along with other metabolites such as thiocyanates, as seen in Fig. 4.8. When the raw vegetables containing glucosinolates are chewed, the plant cells are broken and an enzyme (myrosinase) hydrolyses the glucosinolates into isothiocyanates [1–4, 21–23, 25, 54].



199



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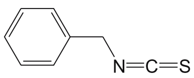


201

Structure 4.58

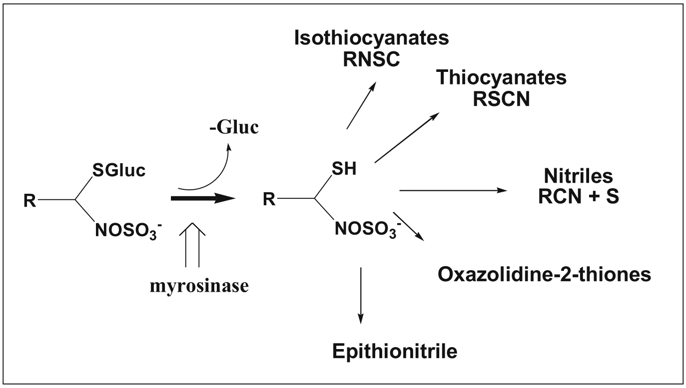
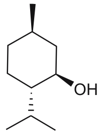


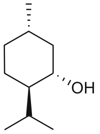
Fig. 4.8 Formation of glucosinolate-derived metabolites

4.2
Impact of Chirality: Enantiomers

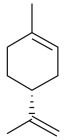
Chirality is an important aspect of aroma chemicals since enantiomers of the same compound may possess different organoleptic characters. Chirality means the occurrence of one or more asymmetric carbon atoms in an organic molecule. Such molecules exhibit optical activity and therefore have the ability to rotate plane-polarised light by equal amounts but in opposite directions. In other words, two stereoisomers which are mirror images of each other are said to be enantiomers. If two enantiomers exist in equal proportions, then the compound is called racemic. Enantiomers can be laevorotatory ($^{\text{L}}$, *l*, -, *S*), meaning rotating the plane of the polarised light to the left; or dextrorotatory ($^{\text{D}}$, *d*, +, *R*), that is,



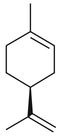
L-menthol **8**
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanol
Minty, fresh, cool



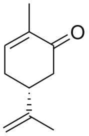
D-menthol **8'**
(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexanol
Minty, medicinal, camphor-like



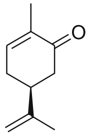
L-limonene **22**
(*R*)-1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene
Turpentine



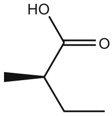
D-limonene **22'**
(*S*)-1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene
Orange



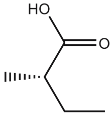
L-carvone **36**
(*R*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enone
Spearmint, costmary



D-carvone **36'**
(*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enone
Caraway, dill



L-2-methylbutanoic acid **201**
(*R*)-2-methylbutanoic acid
Cheesy, sweet



D-2-methylbutanoic acid **201'**
(*S*)-2-methylbutanoic acid
Fruity, sweet

Fig. 4.9 Effect of stereochemistry on flavour and fragrance

rotating the plane of the polarised light to the right. Racemic compounds show zero rotation [1–4, 9, 10, 14, 22, 68–71].

Many natural compounds originating from essential oils which are used in perfumes, flavours and fragrances are optically active. Each enantiomer may display entirely different organoleptic properties. Each enantiomer may be characteristic for a particular essential oil source. Some examples are given in Fig 4.9, illustrating frequently used compounds.

The pattern of distribution of enantiomers may serve as fingerprints to prove the authenticity of a certain essential oil or its adulteration. As high ratio of stereospecificity is achieved in enzyme-catalysed reactions; high enantiomeric purity is expected in chiral natural products. Essential oils generally possess chiral compounds with high enantiomeric purity [70]. “Enantiotaxonomy” can use enantiomeric chemotypes or “enantiotypes” in order to recognise the chemical differences between closely related aromatic plants [72].

Capillary gas chromatography (GC) using modified cyclodextrins as chiral stationary phases is the preferred method for the separation of volatile enantiomers. Fused-silica capillary columns coated with several alkyl or aryl α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin derivatives are suitable to separate most of the volatile chiral compounds. Multidimensional GC (MDGC)–mass spectrometry (MS) allows the separation of essential oil components on an achiral normal phase column and through heart-cutting techniques, the separated components are led to a chiral column for enantiomeric separation. The mass detector ensures the correct identification of the separated components [73]. Preparative chiral GC is suitable for the isolation of enantiomers [5, 73].
The formula for chiral purity is as follows:

$$\frac{A_R}{A_S + A_R} \times 100$$

where A_S is the area of the peak due to the *S* enantiomer and A_R is the area of the peak due to the *R* enantiomer.

4.3
Analysis of Essential Oils

Several techniques and criteria are used for the assessment of the quality of essential oils. These are:

1. Sensory evaluations
2. Physical tests
3. Chemical tests
4. Instrumental techniques

Sensory evaluation is carried out by the use of sensory organs and most importantly by the nose. It is considered crucial for the acceptance of an essential oil in perfumery houses. A perfumer or a panel of fragrance experts often have the last word on the acceptance criteria; however, their assessment should be verified and documented by experimental proof [1, 2, 4, 5, 69–73].

Physicochemical tests are required in essential oil monographs published in standards, pharmacopoeias and codices. Chromatospectral techniques are modern methods used to assess the quality of essential oils. The most important technique for the analysis of essential oils is GC. Several detectors may be used in combination with GC. A flame ionisation detector is necessary for quantitative analysis of essential oil constituents. A quadrupole mass detector or an ion-trap detector is indispensable for the characterisation of essential oil constituents. This combination is commonly called GC/MS [1, 2, 4, 5]. This technique is more useful if it is used in conjunction with a reliable computerised library. Several commercial GC/MS libraries exist. Wiley, National Bureau of Standards [74] and National Institute of Standards and Technology libraries [75] contain authentic or keyed-in mass spectra of volatile constituents which may or may not exist in essential oils. The major drawback of such libraries is the lack of retention data; therefore, compounds with identical mass spectra cannot be differentiated. The retention time is the time a compound remains in the column during analysis. The retention index is calculated by a formula and varies with the polarity of a column. Libraries like Adams [76] and MassFinder [77], on the other hand, are specialised libraries for essential oils. They contain the retention index of each compound measured on a non-polar column. Such libraries are more reliable. In case of doubt, coinjection with the suspected compound, checking the retention times in columns with different polarities or isolation and structure elucidation of the compound in question using other spectral techniques may be necessary. The ideal situation is to create a home library if essential oil analysis becomes a major activity. In such a case, mass spectra of known compounds can be entered along with their retention data. It takes several years to create a home library but once created it is more reliable than any other library. We use our own in-house Baser Library of Essential Oil Constituents which contains MS and retention data of over 3,500 genuine compounds found is essential oils.

An atomic emission detector when coupled with GC is capable of separating compounds according to their atoms, such as carbon, hydrogen, oxygen, nitrogen, sulphur and halogens; therefore, it is very useful in detecting compounds containing atoms other than carbon and hydrogen.

MDGC is useful for separating compounds of an essential oil using two columns in line with different polarities. Through column-switching techniques, selected impure compounds in the first column can be diverted to the second column to ensure their complete separation. If the second column is chiral, then enantiomers potentially can be separated. The selected chiral stationary phase affects the resolution and separation drastically [73].

GC/isotope ratio MS and site-specific natural isotope fractionation deuterium NMR spectroscopy are useful more recent tools for detecting sophisticated adulterations [3–5].

Another technique is ^{13}C NMR, which can be successfully utilised in the direct analysis of essential oils without need to separate them by GC [5, 78].

4.4
Conclusions

Essential oils are important natural products used for their flavour and fragrances in food, pharmaceutical and perfumery industries. They are also sources of aroma chemicals, particularly of enantiomers and useful chiral building blocks in syntheses. Biological and pharmacological activities of essential oils and their constituents have been gathering momentum in recent years [79, 80]. Essential oils therefore will continue to be indispensable natural ingredients. The *European Pharmacopeia* contains monographs on 25 essential oils [81]. Many essential oils enjoy generally recognized as safe (GRAS) status. The budding aromatherapy sector is expected to expand the market in coming years.

The compositions of some important essential oils of trade are listed in Table 4.1.

Table 4.1 Composition of important essential oils of trade

Oil	Plant source	Important constituents (%)
Terpene hydrocarbons		
Cade	*Juniperus oxycedrus* L.	Sesquiterpene hydrocarbon (cadinene), guaiacol, cresol
Copaiba	*Copaifera* spp.	Sesquiterpene hydrocarbons: β-caryophyllene (min. 50)
Cypress	*Cupressus sempervirens* L.	Monoterpene hydrocarbons, car-3-ene
Elemi	*Canarium luzonicum* Miq.	Monoterpene hydrocarbons, limonene (40–72), α-phellandrene (10–24) and sesquiterpene alcohol elemol (1–25)
False pepper	*Schinus molle* L.	Fruit oil: Monoterpene hydrocarbons, α-phellandrene (5–26), β-phellandrene (5–7), limonene (4–9) Leaf oil: β-pinene (14), sabinene (13), terpinen-4-ol (11), and sesquiterpene hydrocarbons, bicyclogermacrene (29), germacrene D (12)
Ginger	*Zingiber officinale* Roscoe	Sesquiterpene hydrocarbons, zingiberene (34), β-sesquiphellandrene (12)

CT chemotype

Table 4.1 *(continued)* Composition of important essential oils of trade

Oil	Plant source	Important constituents (%)
Terpene hydrocarbons *(continued)*		
Gurjun balsam	*Dipterocarpus* spp.	Sesquiterpene hydrocarbons, α-gurjunene (min. 60), calarene, α-copaene
Indian curry leaf	*Murraya koenigii* (L.) Spreng.	Sesquiterpene hydrocarbons, β-caryophyllene (29), β-gurjunene (21), α-selinene (13)
Juniper berry	*Juniperus communis* L.	Monoterpene hydrocarbons, pinenes, sabinene, myrcene
Kumquat	*Fortunella japonica* (Thunb.) Swingle	Rind oil: Monoterpene hydrocarbons, limonene (92–95)
Nutmeg	*Myristica fragrans* Houtt.	Monoterpene hydrocarbons, sabinene, pinenes
Opopanax	*Commiphora erythraea* Engl var. *glabrescens* Engl.	Sesquiterpene hydrocarbons, α-santalene, (*E*)-α-bergamotene, (*Z*)-α-bisabolene
Pepper	*Piper nigrum* L.	Monoterpene hydrocarbons (about 80), sabinene (20–25)
Pine silvestris	*Pinus silvestris* L.	Monoterpene hydrocarbons, pinenes, car-3-ene, limonene, myrcene
Sweet orange	*Citrus sinensis* (L.) Osbeck	Monoterpene hydrocarbon, limonene (92–97)
Turpentine	*Pinus* spp.	Monoterpene hydrocarbons, pinenes, camphene
Alcohols		
Ajowan	*Trachyspermum ammi* Spraque	Thymol (4–55)
Amyris	*Amyris balsamifera* L.	Cadinol (50), valerianol (22), cadinene (11), 7-*epi*-γ-eudesmol (11), 10-*epi*-γ-eudesmol (10)
Basil (European type)	*Ocimum basilicum* L.	Linalool (45-62), estragol (trace-30), eugenol (2-15)
Carrot seed	*Daucus carota* L.	Carotol (min. 50)
Cedarwood oil, Chinese	*Cupressus funebris* Endl.	Cedrol (10–16), α-cedrene (13–29), thujopsene (18–31)
Cedarwood oil, Texas	*Juniperus mexicana* Schiede	Cedrol (min. 20), α-cedrene (15–25), thujopsene (25–32)
Cedarwood oil, Virginia	*Juniperus virginiana* L.	Cedrol (5–30), α-cedrene (22–53), thujopsene (10–25)

CT chemotype

Table 4.1 *(continued)* Composition of important essential oils of trade

Oil	Plant source	Important constituents (%)
Alcohols *(continued)*		
Coriander	*Coriandrum sativum* L.	(+)-Linalool (65–78)
Dementholised mint oil	Japanese mint oil	(-)-Menthol (30–50), menthone (17–35), isomenthone (5–13)
Geranium	*Pelargonium* spp.	Citronellol, geraniol
Japanese mint	*Mentha canadensis* L.	(-)-Menthol (about 70)
Matricaria	*Matricaria recutita* L.	(-)-α-Bisabolol (10–65) and bisabolol oxides (29–81) types exist
Neroli	*Citrus aurantium* L. subsp. *aurantium*	(+)-Linalool (28–44), (E)-nerolidol, (E,E)-farnesol, esters
Oregano	*Origanum onites* L., *O. vulgare* L. subsp. *hirtum* (Link) Ietsw. or other *Origanum* spp., *Thymbra spicata* L., *Coridothymus capitatus* Rechb. fil., *Satureja* spp., *Lippia graveolens* Kunth	Carvacrol (min. 60 according to [81])
Palmarosa	*Cymbopogon martini* (Roxb.) W. Wats.	Geraniol (up to 95%)
Patchouli	*Pogostemon cablin* (Blanco) Benth.	(-)-Patchoulol (27–35), norpatchoulenol (0.4–1)
Peppermint	*Mentha* × *piperita* L.	(-)-Menthol (30–55), menthone(14–32)
Pine, white	*Pinus palustris* Mill.	α-Terpineol (53)
Rose oil	*Rosa* × *damascena* Miller	Citronellol, geraniol, nerol, phenylethyl alcohol
Rosewood	*Aniba rosaeodora* Ducke	(-)-Linalool (up to 86)
Sandalwood, East Indian	*Santalum album* L.	(+)-α-Santalol (45–55), (-)-β-santalol (18–24)
Sweet marjoram	*Origanum majorana* L.	Terpinen-4-ol (min 20), *cis*-sabinene hydrate (3–18)
Tea tree	*Melaleuca alternifolia* (Maiden et Betch) Cheel, *M. linariifolia* Smith, *M. dissitiflora* F. Mueller and other species	Terpinen-4-ol (min. 30), 1,8-cineole (max. 15), γ-terpinene (10–28), α-terpinene (5–13), α-terpineol (1.5–8)
Thyme	*Thymus vulgaris* L., *T. zygis* Loefl. ex L.	Thymol (36–55)

CT chemotype

Table 4.1 *(continued)* Composition of important essential oils of trade

Oil	Plant source	Important constituents (%)
Alcohols *(continued)*		
Vetiver	*Vetiveria zizanoides* (L.) Nash	Sesquiterpene fraction: khusimol (15), α-vetivone and β-vetivone (10)
Esters		
Bergamot	*Citrus aurantium* L. subsp. *bergamia* (Risso et Poit.) Engl.	Linalyl acetate (22–36), linalool (3–15)
Cardamom	*Elettaria cardamomum* Maton	α-Terpinyl acetate (30), 1,8-cineole (30)
Clarysage	*Salvia sclarea* L.	Linalyl acetate (56–78), linalool (6.5–24)
Dwarf pine needle	*Pinus mugo* Turra	Esters calculated as bornyl acetate (1.5–5)
Fir needle, Canadian	*Abies balsamea* Mill.	Esters calculated as bornyl acetate (8–16)
Fir needle, Siberian	*Abies sibirica* Ledeb.	Esters calculated as bornyl acetate (32–44)
Lavandin, abrialis	*Lavandula angustifolia* Mill. × *L. latifolia* Medik.	Linalyl acetate (20–29), linalool (26–38)
Lavandin, grosso	*Lavandula angustifolia* Mill. × *L. latifolia* Medik.	Linalyl acetate (28–38), linalool (24–35)
Lavandin, super	*Lavandula angustifolia* Mill. × *L. latifolia* Medik.	Linalyl acetate (35–47)
Lavender	*Lavandula angustifolia* Miller	Linalyl acetate (25–46), linalool (20–45)
Linaloe	*Bursera* spp.	Linalyl acetate (40–70)
Peru balsam	*Myroxylon pereirae* (Royle) Klotzsch	Benzyl benzoate, benzyl cinnamate
Petitgrain oil, Bigarade	*Citrus aurantium* L. subsp. *Aurantium*	Leaf and twig oil. French: linalyl acetate (51–71), linalool (12–24); Italian: linalyl acetate (51–63), linalool (22–33); Paraguayan: linalyl acetate (40–60), linalool (15–30)
Pine-needle	*Pinus silvestris* L., *P. nigra* Arnold	Esters calculated as bornyl acetate (1.5–5)
Silver fir, European	*Abies alba* Mill.	Esters calculated as bornyl acetate (4–10)
Tolu balsam	*Myroxylon balsamum* (L.) Harms	Benzyl and cinnamyl esters of benzoic and cinnamic acid

CT chemotype

Table 4.1 *(continued)* Composition of important essential oils of trade

Oil	Plant source	Important constituents (%)
Esters *(continued)*		
Valerian	*Valeriana officinalis* L.	(-)-Bornyl acetate
Wintergreen	*Gaultheria procumbens* L.	Methyl salicylate (96-99)
Ylang-ylang	*Cananga odorata* Hook. f. et Thoms.	Benzyl acetate (6–18), geranyl acetate (3–14), *p*-cresyl methyl ether (15–16), methyl benzoate (4–9)
Aldehydes		
Bitter almond	*Prunus amygdalus* Batsch. var. *amara* (DC.) Focke	Benzaldehyde (min. 98)
Cinnamon bark, Ceylon	*Cinnamomum zeylanicum* Nees	Cinnamaldehyde (55–75)
Cinnamon bark, Chinese	*Cinnamomum cassia* Blume	Cinnamaldehyde (70–88), 2-methoxycinnamaldehyde (3–15)
Citronella, Ceylon	*Cymbopogon nardus* (L.) W. Wats.	Citronellal (3–6), geraniol (15–23), citronellol (3–9)
Citronella, Java	*Cymbopogon winterianus* Jowitt.	Citronellal (30–45), geraniol (20–25), citronellol (9–15)
Cumin	*Cuminum cyminum* L.	Cuminaldehyde (20–40), *p*-mentha-1,4-dien-7-al (20–45), *p*-mentha-1,3-dien-7-al (4–12)
Lemon oil	*Citrus limon* (L.) Burman fil.	Geranial (0.5–2), neral (0.2–1.2), limonene (60–80)
Lemongrass, Indian	*Cymbopogon flexuosus* (Nees ex Steud.) W. Wats.	Geranial (35–47), neral (25–35)
Lemongrass, West Indian	*Cymbopogon citratus* (DC.) Stapf	Geranial (40–50), neral (31–40)
Lemon-scented eucalyptus	*Eucalyptus citriodora* Hook.	Citronellal (75)
Litsea cubeba	*Litsea cubeba* C.H. Persoon	Geranial (38–45), neral (25–33)
Ketones		
Armoise	*Artemisia herba-alba* Asso	β-Thujone CT (43–94), camphor CT (40–70); chrysanthnone CT (51), davanone CT (20–70), cis-chrysanthenyl acetate CT (38–71), 1,8-cineole/α-thujone CT (50/27), 1,8-cineole/β-thujone CT (13/12), 1,8-cineole/camphor CT (38/25), *cis*-chrysanthenol CT (25), *cis*-chrysanthenyl acetate CT (25)

CT chemotype

Table 4.1 *(continued)* Composition of important essential oils of trade

Oil	Plant source	Important constituents (%)
Ketones *(continued)*		
Caraway	*Carum carvi* L.	(+)-Carvone (50–65), limonene (30–45)
Common mugwort	*Artemisia vulgaris* L.	α-Thujone (56), 1,8-cineole (27), camphor (20), borneol (19), sabinene (16)
Davana	*Artemisia pallens* Wall.	*cis*-Davanone (38), *trans*-davanone (5)
Dill	*Anethum graveolens* L.	(+)-Carvone (30–40), limonene (30–40), α-phellandrene (10–20), (+)-dill ether (up to 10)
Orris root	*Iris pallida* Lam., *I. germanica* L.	*cis*-γ-Irone (30–40), *cis*-α-irone (20–30) [*I. pallida* oil contains (+) enantiomers; *I. germanica* oil contains (-) enantiomers]
Pennyroyal	*Mentha pulegium* L.	(+)-Pulegone (40–84)
Roman mugwort	*Artemisia pontica* L.	Artemisia ketone (23–46), α-thujone (14–30), 1,8-cineole (12–23)
Sage, Dalmatian	*Salvia officinalis* L.	α-Thujone (18–43), β-thujone (3–9), 18-cineole (6–13), camphor (3–9)
Spearmint	*Mentha spicata* L.	(-)-Carvone (50–80)
Tansy	*Tanacetum vulgare* L.	Thujones (70)
Wormwood	*Artemisia absinthium* L.	There are several chemotypes: (*Z*)-epoxy-ocimene CT (26–54); sabinyl acetate CT (32–85); chrysanthenyl acetate CT (42); β-thujone CT (18–60); β-thujone/(*Z*)-epoxy ocimene CT (21–41/22–29); *cis*-chrysanthenol CT (16–69)
Ethers		
Cajuput	*Melaleuca leucadendron* L.	1,8-Cineole (50–60)
Eucalyptus	*Eucalyptus globulus* Labill.	1,8-Cineole (min. 70); *Eucalyptus globulus* Labill. ssp. *globulus* oil: 1,8-cineole (62–82); *Eucalyptus globulus* Labill. ssp. *maidenii* oil: 1,8-cineole (69–80)
Laurel leaf	*Laurus nobilis* L.	1,8-Cineole (30–70)
Sage, Turkish	*Salvia fruticosa* Mill.	1,8-Cineole (35–51), camphor (7–13)

CT chemotype

Table 4.1 *(continued)* Composition of important essential oils of trade

Oil	Plant source	Important constituents (%)
Phenyl propanoids (phenyl ethers)		
Anis	*Pimpinella anisum* L.	(*E*)-Anethole (87–94)
Basil (Reunion type)	*Ocimum basilicum* L.	Estragol (methyl chavicol) (75–87), linalool (0.5–3)
Bay	*Pimenta racemosa* Moore	Eugenol (44–56), myrcene (20–30), chavicol (8–11)
Bitter fennel	*Foeniculum vulgare* Mill. subsp. *vulgare* var. *vulgare*	(*E*)-Anethole (55–75), fenchone (12–26), limonene (1–5)
Calamus	*Acorus calamus* L.	β-Asarone: diploid variety (0), triploid variety (0–10), tetraploid variety (up to 96%)
Chervil	*Anthriscus cerefolium* (L.) Hoffm.	Estragol (75–80), 1-allyl-2,4-dimethoxy benzene (16–22)
Cinnamon leaf, Ceylon	*Cinnamomum zeylanicum* Nees	Eugenol (70–85)
Clove	*Syzygium aromaticum* (L.) Merill et L.M. Perry	Eugenol (75–88)
India dill	*Anethum sowa* Roxb.	Dill-apiole, limonene, carvone
Parsley seed	*Petroselinum crispum* (Mill.) Nym. ex A.W. Hill	Myristicine (methoxy safrole) (25–50), apiole (dimethoxy safrole) (5–35), 2,3,4,5-tetramethoxy allylbenzene (1–12)
Piper aduncum	*Piper aduncum* L.	Dill-apiole (32–97)
Sassafras, Brazilian	*Ocotea pretiosa* (Nees) Mez.	Safrole (84)
Sassafras, Chinese	*Cinnamomum camphora* Sieb.	High boiling fraction: safrole (80–90)
Star anis	*Illicium verum* Hook fil.	(*E*)-Anethole (86–93)
Sweet fennel	*Foeniculum vulgare* Mill. subsp. *vulgare* var. *dulce*	(*E*)-Anethole (more than 75), fenchone (less than 5)
Tarragon	*Artemisia dracunculus* L.	French tarragon or Italian tarragon oil: β-pinene and sabinene (24–47); Russian tarragon or German tarragon: sabinene(11–47), methyl eugenol (6–36), elemicin (1–60)

CT chemotype

Table 4.1 *(continued)* Composition of important essential oils of trade

Oil	Plant source	Important constituents (%)
Peroxides		
Chenopodium	*Chenopodium ambrosioides* L. var. *anthelminticum* (L.) A. Gray	Ascaridole (60–77)
N- and/or S-containing oils		
Asafoetida	*Ferula foetida* Regel	*R*-2-Butyl-1-propenyl disulphide (a mixture of *E* and *Z* isomers), 1-(1-methylthiopropenyl)-1-propenyl disulphide, 2-butyl-3-methyl-thioallyl disulphide (both as a mixture of diasteromers)
Buchu leaf	*Agathosma betulina* (Bergius) Pillans, *A. crenulata* (L.) Pillans	*trans*-*p*-Menthane-8-thiol-3-one and its *S*-acetate (characteristic minor components), (+)-limonene (10)
Galbanum	*Ferula galbaniflua* Boiss., *F. rubricaulis* Boiss.	2-Methoxy-3-isobutyl pyrazine, 5-*sec*-butyl-3-methyl-2-butenethioate, 1,3,5-undecatriene as minor components, and monoterpene hydrocarbons (75), sesquiterpene hydrocarbons (10), lactones umbellic acid, umbelliferone
Garlic	*Allium sativum* L.	Diallyl disulphide (over 50%)
Mandarin	*Citrus reticulata* Blanco	Methyl *N*-methyl anthranilate (0.3–0.6), limonene (65–75), γ-terpinene (16–22)
Mustard	*Brassica* spp.	Allyl isothiocyanate (over 90)
Onion	*Allium cepa* L.	Methylpropyl disulphide, dipropyl disulphide, propenylpropyl disulphide, 2-hexyl-5-methyl-3(2*H*)-furanone
Lactones		
Ambrette seed	*Hibiscus abelmoschus* L.	(*Z*)-7-Hexadecan-16-olide, ambrettolide (8–9), 5-tetradecen-14-olide, (2*E*,6*E*)-farnesyl acetate (39–59)
Angelica root	*Angelica archangelica* L.	15-Pentadecanolide, 13-tridecanolide as characteristic minor components in addition to terpenoids and sesquiterpenoids (about 90)
Celery seed	*Apium graveolens* L.	3-Butylphthalide and sedanenolide (1.5–11), (+)-limonene (58–79), β-selinene (5–20)

CT chemotype

Table 4.1 *(continued)* Composition of important essential oils of trade

Oil	Plant source	Important constituents (%)
Lactones *(continued)*		
Holy grass	*Hierochloe odorata* L.	Coumarin (10–60)
Lovage root	*Levisticum officinale* Koch	3-Butyl phthalide (32), ligustilide (24), ligusticum lactone
Diterpenes		
Labdanum	*Cistus ladaniferus* L.	Labdane diterpenes and monoterpene hydrocarbons

CT chemotype

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