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Chirospecific analysis of plant volatiles

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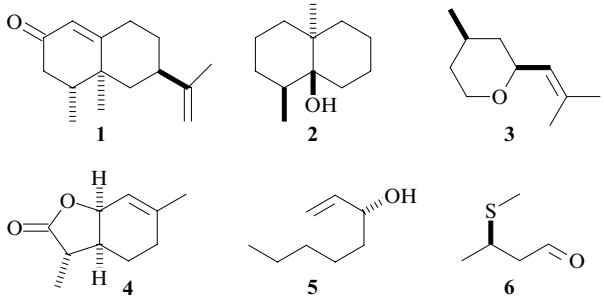
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Abstract. Characteristic features of the analysis of plant volatiles by enantioselective gas (gas-liquid) chromatography and gas chromatography/mass spectrometry are discussed. The most recent advances in the design of enantioselective stationary phases are surveyed. Examples of the preparation of the most efficient phases based on modified cyclodextrins are given. Current knowledge on the successful analytical resolution of different types of plant volatiles (aliphatic and aromatic compounds and mono-, sesqui- and diterpene derivatives) into optical antipodes is systematically described. Chiral stationary phases used for these purposes, temperature conditions and enantiomer separation factors are summarised. Examples of the enantiomeric resolution of fragrance compounds and components of plant extracts, wines and essential oils are given. The bibliography includes 157 references.

I. Introduction

The enantiodifferentiation, *viz*., the recognition of enantiomers (optical isomers), plays an important role in the functioning of living systems and the appearance of biological activity. Numerous examples concerning differences in biological activity of optical antipodes have been documented. An analysis of the optical purity is of great importance in chemistry of natural compounds, fine organic synthesis, pharmacognosy, drug technology, analytical chemistry and environmental analytical chemistry. Enantioselective gas (gas-liquid) chromatography and GLC-mass spectrometry are the main tools of investigation of enantiomeric composition of natural volatile compounds.

The differences in properties of optical isomers result in the difference in recognition at the molecular level. Many remarkable examples of the recognition of plant volatiles responsible for the characteristic aroma of plants and products of their processing can be given taking into account that the ability to perceive odours is also associated with the molecular recognition of enantiomers as a result of their interaction with olfactory chemoreceptors. For example, the sesquiterpenoid (+)-nootkatone (**1**), which has the bitter taste of grapefruit, has the characteristic grapefruit flavour, which is 2200 times more intense than that of its (−) enantiomer.[1] (−)-Geosmin (**2**) isolated from grape wines has a much stronger flavour (at least ten times stronger) than (+)-geosmin. Grape wines produced from Cabernet Sauvignon grapes contain only (−)-geosmin.[2] Of four isomeric rose oxides, only (2*S*,4*R*)-rose oxide (**3**) has a pleasant strong rose aroma, whereas other stereoisomers have no flavour. Natural (3*S*,3a*S*,7a*R*)-lactone **4** has a sweat flavour with a coconut undertone, which is 25 million (!) times more intense than that of its (3*R*,3a*R*,7a*S*) isomer.[3,4] Oct-1-en-3-ol is one of the major components responsible for the mushroom flavour, but only (*R*)-(−) enantiomer **5** has the intense mushroom aroma.[5] (*R*)-3-Methylthiobutanal (**6**) has the characteristic aroma of potato products, whereas the (*S*) enantiomer has no flavour at all.[6]



1 **2** **3** **4** **5** **6**

The above-considered examples are not arbitrary because the development of methods of enantioselective analysis is to a large extent associated with investigations of fragrant substances; their enantiomeric composition often determines a particular characteristic flavour.

Different plants produce terpenes of different optical purity, whose enantiomeric composition depends on numerous factors. For example, studies on the essential oil of the dill herb *Anethum graveolens* L. showed that the enantiomeric ratio of the major components (dill ether,† limonene, α- and β-phellandrenes and carvone) changes with the age of plants and is

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† The systematic name is (3*S*,3a*S*,7a*S*)-3,6-dimethyl-2,3,3a,4,5,7a-hexahydrobenzo[*b*]furan.

different in different parts of the plants.[7] The enantiomeric purity of camphor in essential oils from different plants of the Lamiaceae and Compositae families varies from 0% to 100%, with either the (+) or (−) enantiomer predominating in different plants.[8,9] As was demonstrated with extracts from roots and seeds of angelica (*Angelica archangelica* L.), the enantiomeric excess of monoterpenes can vary depending on the place of vegetation.[10] An analysis of the enantiomeric composition of the essential oil components allows the determination of the authenticity of essential oils available in the market, for example, of melissa (*Melissa officinalis* L.).[11,12]

As a rule, sesquiterpene hydrocarbons are present in plant extracts in the optically active form, with a particular enantiomer predominating, whereas derivatives, which are artefacts and are produced in non-enzymatic secondary processes in the course of processing of plant materials, are detected in the optically inactive form (as racemates).[13]

The chirospecific analysis (analysis of the enantiomeric composition of the components) is of great importance in studies of foodstuff, as well as of flavour and fragrance compounds. For example, the quality of grape wines can be determined from the enantiomeric ratio of ethyl lactates.[14] Only one of the enantiomers of octane-1,3-diol and some its derivatives were found in different varieties of apples.[15] With a knowledge of the enantiomeric composition of the strawberry flavour components, it is possible to distinguish between products prepared from strawberry and those flavoured with synthetic strawberry flavourants.[16] (*R*)-3-Mercapto-2-methylpropanol makes a major contribution to the flavour of red grape wines produced from Cabernet Sauvignon and Merlot grapes.[17] Particular enantiomers of branched carboxylic acids are important contributors to the flavour of Parmesan cheese and the characteristic flavour of lamb meat.[18,19]

Modern methods of chirospecific analysis allowed studies of racemic forms of compounds, which have long been used as fragrance compounds. For example, the characteristic lilial flavour was demonstrated to be mainly due to the presence of the (*R*) isomer, which is hundred times more flavouring than the (*S*) isomer.[20] Numerous synthetic derivatives of campholenic and fencholenic aldehydes were investigated, which is associated with their unusual wood or sandal flavour.[21,22] The enantioselective separation of enantiomers of α-ionone, which is an important fragrance compound, by gas chromatography was documented.[23]

The analysis of the enantiomeric composition of plant metabolites has numerous applications. This method plays an important role in the determination of the origin of plant extracts and the authenticity of essential oils and flavour and taste components, as well as in the elucidation of the biosynthesis pathways of particular compounds.

Enantiomers of various chemical compounds can be separated by such methods as gas chromatography, high-performance liquid chromatography, capillary electrophoresis, supercritical fluid chromatography, capillary electrochromatography, thin-layer chromatography, *etc*.[24] Gas-liquid chromatography (GLC) is most often used for the analysis of the enantiomeric composition of plant volatiles and fragrance compounds.

Enantiomers can be resolved by GLC either directly or indirectly. The indirect approach is based on the preparation of derivatives of the analyte with an enantiomerically pure reagent[25,26] to transform the enantiomeric pair into the diastereomeric pair and the subsequent separation of the diastereomers by GLC on a usual, *i.e*., achiral, stationary phase. As an example, let us mention the enantiomeric resolution of (−)-menthol esters and hydroxy acids in the form of *O*-trifluoroacetyl derivatives.[27] As a rule, this method is used to analyse polar compounds (alcohols, amines, acids, amino alcohols, *etc*.), because it is difficult, if at all possible, to study these compounds directly by gas chromatography.

The direct enantiomeric resolution on enantioselective stationary phase columns (chiral GLC) is a much more appealing method. In this case, there is no need to transform analytes into derivatives, and the separation is achieved due to the formation of diastereomeric associates between enantiomers of the analyte and a chiral selector ‡ of the stationary phase.

The history, advances and trends in the development of chiral GLC were covered in the reviews.[28,29]

II. Chiral gas-liquid chromatography

1. Types of chiral stationary phases

In spite of a large variety of stationary phases used in gas chromatography, there are no universal phases for the separation of all types of compounds. The selectivity of each phase is limited to particular groups of compounds. However, though certain usual achiral stationary phases are suitable for the separation of several groups of organic compounds, no more or less universal chiral stationary phases are presently known.

Enantioselective stationary phases used in chiral GLC can be divided into three groups depending on the character of interactions between the analyte (selectand) and the chiral selector:

— derivatives of optically active amino acids (analytes form hydrogen bonds with the stationary phase);

— optically active metal complexes (analytes form coordination compounds with components of the stationary phase);

— natural and modified cyclodextrins, optically active crown ethers and calixarenes (analytes form inclusion compounds with components of the stationary phase[30]).

The general methodology, the mechanism of separation, the scope and examples of the use of chiral GLC were considered in detail in the reviews.[31–34] In the present review, only chiral selectors and stationary phases belonging to the third group, to be more precise, stationary phases based on modified cyclodextrins, will be considered. These stationary phases are most widely used in the analysis of natural volatile compounds, flavour and fragrance compounds, and they are employed in about 90% of examples of the successful enantiomeric resolution.[35] In particular, there are reviews on the use of such chiral stationary phases for the analysis of the enantiomeric composition of the components of essential oils and fragrance compounds,[36–40] fragrant monocyclic monoterpenes[41] and flavour components of cheeses.[42]

Derivatives of natural amino acids suitable for the application in specific cases[43] and polysiloxane-based stationary phases containing optically active metal complexes§ {for example, 3-(perfluoroacyl)camphorate complexes of metals [Ni(II), Co(II), Mn(II), Rh(I) and Eu(III)], which were used for the enantiomeric resolution of various compounds, including some terpenes[34]} as chiral selectors are beyond the scope of the present review.

a. Cyclodextrins in enantioselective analysis

Cyclodextrins are cyclic oligomers consisting of α-D-glucopyranosyl residues, which are linked to each other by α-(1 → 4) glycosidic bonds. Nowadays, α-, β- and γ-cyclodextrins containing 6, 7 and 8 α-D-glucopyranosyl residues, respectively,

‡ The chiral selector is an enantiomerically pure component of the stationary phase responsible for the recognition of optical isomers.

§ According to the data presented in the review,[43] phases containing chiral metal complexes are losing in popularity because of the universal use of cyclodextrin derivatives, as evidenced by a dramatic decrease (almost to zero in 2001–2004) in the number of publications on the use of phases based on chiral metal complexes.

are commercially available. Cyclodextrin molecules have a truncated cone shape. The outer surface of the molecules is hydrophilic, while the inner surface is hydrophobic. Due to this structural feature, cyclodextrins readily form inclusion complexes with organic molecules belonging to different classes of compounds.[44] It is the ability of cyclodextrins to form inclusion complexes that makes them attractive as agents in various applications ¶ associated with the molecular recognition.[46]

The formation of host – guest complexes is believed to play a major role in the mechanism of recognition of enantiomeric molecules by cyclodextrins and their derivatives.[47] Complexes of hydrophobic molecules with cyclodextrins are formed through interactions between the substrate (selectand) and the hydrophobic cyclodextrin cavity; the complexation can lead to a change in the conformation of the guest molecule.[48] As a rule, less polar molecules form more stable complexes than higher-polarity molecules. Since the cavity volumes in α-, β- and γ-cyclodextrins are different, stability of complexes of hydrophobic molecules with a particular cyclodextrin depends on the matching of the size of the guest molecule to the cyclodextrin cavity size.[45] The formation of such complexes was detected by GLC analysis.[49]

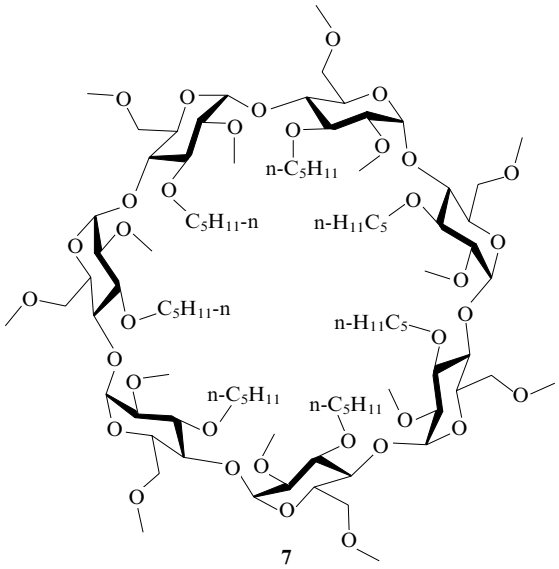
The mechanism of enantiomeric recognition with the use of cyclodextrin stationary phases remains unclear. An analysis of a wide range of model racemic mixtures revealed no relationship between the retention and the thermodynamic characteristics of interactions between selectands and chiral selectors.[50] However, in spite of the absence of detailed data on the recognition mechanism, cyclodextrin-based stationary phases are used with advantage for the enantiomeric resolution of various compounds. Enantioselective chromatography on cyclodextrin stationary phases plays an important role in the analysis of essential oils for the determination of their quality and authenticity,[51] in the stereochemical analysis of terpenoids, in the determination of the absolute configurations and enantiomeric purity of components of complex natural mixtures,[52] *etc*.

b. Chiral stationary phases based on modified cyclodextrins

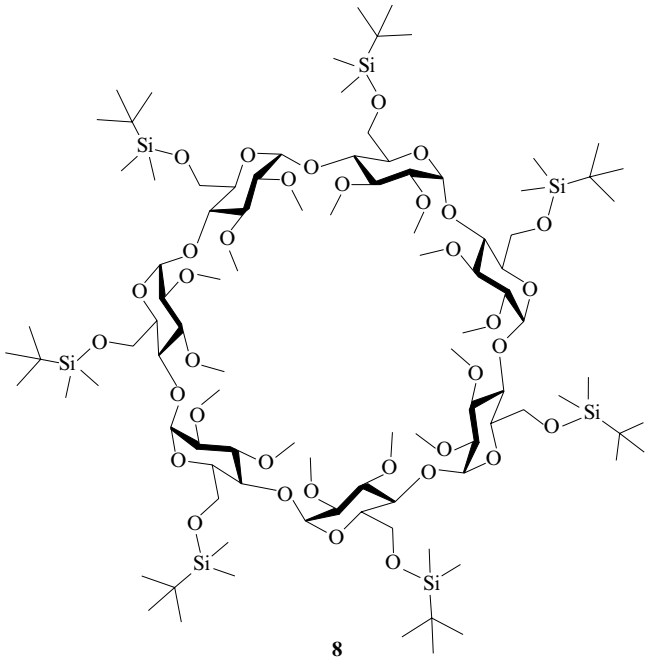
Cyclodextrins and their simple derivatives have high melting points. Since cyclodextrins used as stationary phases in GLC should exist in the liquid (non-crystalline) state, the analysis should be performed at high temperatures. However, the enantioselectivity of chiral stationary phases, as a rule, sharply decreases with temperature. Hence, cyclodextrins and their simple derivatives are of little use in chiral capillary GLC because these compounds cannot serve as efficient chiral selectors at temperatures at which they are converted into the liquid state.

One way of solving this problem is to dilute high-melting-point cyclodextrin derivatives with polysiloxanes, with the result that the enantioselectivity of resolution is achieved at temperatures lower than the melting points of pure cyclodextrins,[53] the nature of polysiloxane having an effect on both the efficiency of the column and its enantioselectivity.[54 – 56] However, the use of low-melting-point cyclodextrin derivatives is presently the approach of choice. This field of investigation originated in 1988 in the research by König and co-workers,[57 – 60] who synthesised liquid or wax-like (at room temperature) cyclodextrin derivatives, which had high thermal stability, were well soluble in low-polarity organic solvents and polysiloxanes and exhibited high enantioselectivity in the separation of a wide range of low-molecular-weight compounds. More recently, numerous such derivatives have been synthesised and many of these compounds proved to be very efficient in the enantioselective analysis of volatile plant substances.[29, 61 – 66]

Of all available cyclodextrin derivatives, heptakis(2,6-di-*O*-methyl-3-*O*-n-pentyl)- (**7**) and heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyl-dimethylsilyl)-β-cyclodextrins (**8**) are the most popular chiral selectors, which were employed in most of successful experiments on the separations of terpene compounds and essential oil components.



7



8

Cyclodextrin derivatives containing the *tert*-butyldimethylsilyl group are of particular interest because these compounds are more easily mixed with various polysiloxanes (the latter are used as diluting agents and have gained wide acceptance in capillary gas chromatography), which facilitates the

¶ Due to the ability of cyclodextrins to distinguish positional isomers, functional groups, homologues and enantiomers, these compounds are widely used for the separation of various compounds by different physicochemical methods. In particular, the review [45] presented data on new applications of cyclodextrins in gel electrophoresis, isotachophoresis, isoelectric focusing, preparative scale electrophoretic techniques, thin-layer chromatography, electrochemically modulated liquid chromatography, microdialysis, the separation on hollow fiber, liquid and composite membranes, foam floatation enrichment, solid- and liquid-phase extraction and counter-current chromatography.

preparation of chiral stationary phases. Although the polysiloxane component in these phases is called a diluting agent, it is not absolutely inert in chromatographic experiments. Thus, stationary phases prepared based on the same chiral selector but with the use of various polysiloxane diluting agents show somewhat different enantioselectivity (see, for example, the studies [55, 56, 67–69]). The temperature of the analysis can be lowered and, as a consequence, the enantioselectivity of separation can be increased with the use of non-polar and low-polarity polysiloxanes as diluting agents for cyclodextrin derivatives.[70] The enantioselectivity of columns packed with chiral stationary phases depends also on the ratio of the cyclodextrin selector to the diluting agent. For example, for the phases containing 20%, 40% or 60% of octakis(2,6-di-*O*-n-pentyl-3-*O*-butanoyl)-γ-cyclodextrin, the maximum selectivity factor (R_α, α)† for different enantiomers is achieved with the use of mixtures containing either 60% or 40% of the selector.[71]

The enantioselectivity of cyclodextrin phases depends on both the cyclodextrin cavity size and the nature and number of substituents at positions 2, 3 and 6 of α-D-glucopyranosyl residues in the cyclodextrin molecule.[31, 33] The elution order of enantiomers can change depending on the size of the cyclodextrin molecule.[38] For example, the relative retention times of oxygen-containing essential oil components on α-cyclodextrin-based phases are shorter than those on chiral stationary phases based on β-cyclodextrin derivatives.[72] An investigation of 22 compounds showed that the retention times of analytes measured relative to n-undecane depend on their structures. This fact can be used in the preliminary analysis of unknown compounds to assign them to a particular structural group.

The type and position of substituents in cyclodextrin derivatives are apparently of equal importance.[73, 74] Even small changes in the molecular structure of cyclodextrin derivatives can substantially influence the enantioselectivity of the phase. Consequently, all steps of the synthesis must be carefully controlled to obtain unambiguous results, because the substitution reactions, which are not brought to completion, often produce mixtures of cyclodextrin derivatives.[75] In addition, to achieve the reproducibility of the results of the subsequent enantioselective analysis, it is necessary to characterise the resulting products in detail.[76]

In spite of the fact that capillary columns for chiral GLC are available in catalogues of many manufacturers and suppliers of gas-chromatographic systems, researchers prepare stationary phases and columns by themselves primarily with the aim of obtaining new, more selective and efficient, columns. Examples of the synthesis of cyclodextrin chiral selectors for chiral GLC are given below.

Mono-2-*O*-alkyl-substituted cyclodextrin derivatives can be synthesised by the treatment of cyclodextrins with dimethyl sulfate, diethyl sulfate or allyl bromide in a 0.37 M aqueous solution of sodium hydroxide.[77] The products are purified by fractional crystallisation from a water–toluene system followed by column chromatography. In the last step, the products are crystallised from water. 2-*O*-Propylcyclodextrins can be prepared by reduction of the corresponding allyl derivatives.[77] *O*-Pentyl derivatives of cyclodextrins have gained the widest acceptance.

It should be noted that the influence of the chain length of the alkyl substituent on the enantioselectivity of stationary phases is still debated. For example, the size of the alkyl substituent in 2,3-di-*O*-alkyl-6-*O*-*tert*-butyldimethylsilyl derivatives of cyclodextrins was found to have a substantial effect on the chromatographic characteristics of chiral phases. According to the data published in the study,[70] heptakis(2,3-di-*O*-ethyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin and octakis(2,3-di-*O*-ethyl-6-*O*-*tert*-butyldimethylsilyl)-γ-cyclodextrin are equally efficient in the separation of racemic mixtures of volatile compounds, whereas columns with the corresponding 2,3-di-*O*-methyl derivatives are less suitable for these purposes. The synthesis of cyclodextrin long-chain derivatives has been documented.[78]

† The selectivity factor is defined as the ratio of the retention times of enantiomers (as a rule, in isothermal conditions).

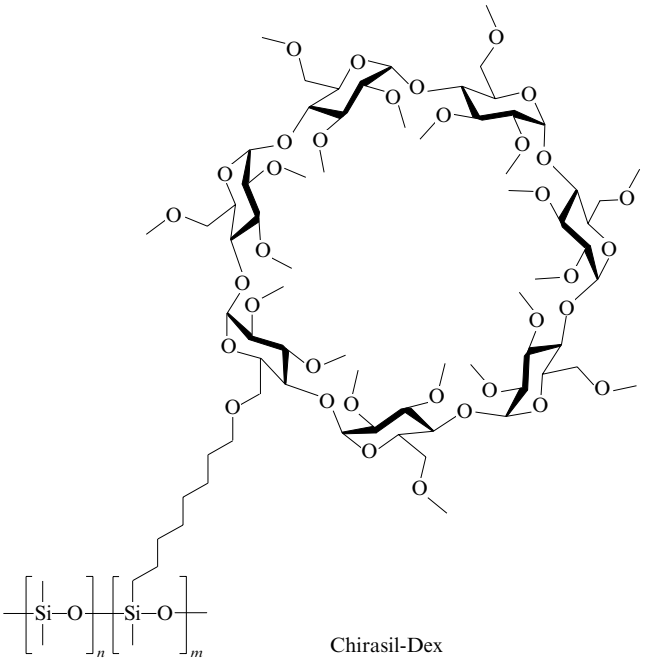
c. Optimisation of the selectivity of cyclodextrin chiral selectors

When analysing complex mixtures consisting of chiral compounds of different polarity with different functional groups, it is necessary to use simultaneously several chiral stationary phases with different enantioselectivity to separate all enantiomeric pairs. Several procedures for the preparation of mixed chiral stationary phases have been developed in recent years.[73, 79–81] The simplest approach is based on the use of a mixture of cyclodextrin derivatives having mutually complementing enantioselectivities. This approach was used with advantage for the simultaneous (in one analysis) enantiomeric resolution of different classes of compounds (monoterpene hydrocarbons, alcohols, ketones and lactones).[80]

Another procedure for optimisation of the properties of chiral cyclodextrin selectors is based on the selective replacement of some functional groups in D-glucopyranose rings. For example, the resolving properties of two cyclodextrins, *viz*., compound **8** and its 2,3-di-*O*-acetyl analog, were combined in one compound by replacing the 3-*O*-methyl group with the acetyl group in one of the glucopyranosyl groups in compound **8**. The resulting β-cyclodextrin has the resolving properties of individual 2,3-di-*O*-methyl and 2,3-di-*O*-acetyl derivatives.[73] Analogously, the useful properties of octakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)- and octakis(2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl)-γ-cyclodextrins were combined in octakis(3-*O*-acetyl-2-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)- and octakis(2-*O*-acetyl-3-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-γ-cyclodextrins.[79]

The enantioselectivity can be increased and more universal columns can be prepared also by mixing two chiral selectors of different nature. The addition of the chiral non-polymeric selector Lipodex E [octakis(3-*O*-butanoyl-2,6-di-*O*-n-pentyl)-γ-cyclodextrin] to an L-valine-based polymer was demonstrated[82] to give a mixed stationary phase showing good enantioselectivity for a wider range of enantiomeric pairs compared to phases containing these individual chiral selectors, the selectivity factors for all the compounds under study in the enantiomeric resolution on the mixed phase having values averaged over these two phases. For examples, enantiomers of linalool cannot be resolved on a column with an L-valine-base stationary phase ($\alpha = 1.00$), but they can be resolved on a column with the Lipodex E phase ($\alpha = 1.05$). Enantiomers of linalool can also be resolved on the mixed stationary phase. In the latter case, the selectivity factor ($\alpha = 1.02$) is smaller than that on Lipodex E but is larger than that on the L-valine-based phase.

To improve cyclodextrin phases, they are chemically grafted to the polysiloxane backbone, which is, in turn, chemically attached to the inner surface of the column.[83] Due to strong retention of the chiral stationary phase, such columns are more durable and are characterised by high stability. In addition, these columns can easily be regenerated by washing with solvents.[29] The Chirasil-Dex phase consisting of a cyclodextrin-type selector based on mono-6-*O*-octamethylenepermethyl-β-cyclodextrin, which is chemically grafted to polymethylpolysiloxane, is an example of such stationary phases.[84] This convenient and rather stable phase is widely used for the enantioselective analysis of various compounds.



Chirasil-Dex

The Chirasil-γ-Dex phase is constructed analogously and consists of octakis(2,6-di-*O*-n-pentyl-3-*O*-butanoyl)-γ-cyclodextrin grafted to polymethylpolysiloxane through the octamethylene spacer.[71]

In recent years, efforts have been made to design universal phases for chiral GLC. In particular, combined (hybrid) phases (for example, the Chirasil-Calixval-Dex phase) belong to such phases. The Chirasil-Calixval-Dex phase consists of two chiral selectors, *viz*., calixarene with pendant L-valine-based diamide groups and polymethylated β-cyclodextrin, chemically grafted to poly(hydromethyl)dimethylpolysiloxane. This combined phase retains the enantioselectivity of each chiral selector and combines their resolving properties. The selectand is bound to this phase both through hydrogen bonds with the calixarene fragments and due to the inclusion into the cyclodextrin cavity. These combined phases provide the separation of both nonpolar compounds (hydrocarbons) and polar amino acid derivatives.[81]

2. Chromatography conditions

a. Temperature of the analysis

Modern commercially available capillary columns with chiral stationary phases based on substituted cyclodextrins allow operations in the temperature range from 10 to 250 °C, which is sufficient for the analysis of volatile aliphatic, alicyclic and aromatic compounds, mono- and sesquiterpenoids, diterpenes and some most volatile aldehydes, alcohols, ethers and esters of the diterpene series. Thermally labile compounds, for example, furan derivatives, can be separated on cyclodextrin phases by supercritical fluid chromatography at 45 °C and at a carbon dioxide pressure of 200 kg cm^{-2}.[85]

As shown by numerous examples, the enantioselectivity of cyclodextrin selectors generally increases with decreasing temperature used for the gas chromatographic separation. Hence, to achieve better results, shorter chromatographic columns should be used. In this case, not only the temperature of the analysis can be lowered, thus improving the enantioselectivity of separation, but also the time of the analysis can be reduced.[68] Examples of the super-fast enantiomeric resolution were documented. For instance, less than 10 s were required to resolve enantiomers of bromochlorofluoromethane on a 50-cm column at ambient temperature (26 °C).[86]

The enantiomeric resolution of the sesquiterpene erythrodiene can be offered as an example of the temperature dependence of enantioselectivity. At 120 °C, the resolution was not achieved, whereas the α factor at 100 °C was 1.027.[87]

b. Detection

Both conventional detection methods developed for achiral chromatography (for example, flame ionisation or chemiluminescence detectors for the determination of small amounts of sulfur-containing compounds[88]) and specific methods based on special properties of optical isomers are used in the gas chromatographic resolution of enantiomeric mixtures. In spite of the fact that the measurement of the angle of rotation of the plane of polarised light is the simplest way of recognising enantiomers, polarimetric detectors have found no use in chiral gas chromatography. This is because the widely accepted separation on capillary columns requires high-sensitivity detectors, while polarimetric detectors are not sufficiently sensitive.

The olfactometric detection is used in studies of fragrance components. After the separation on a column with a chiral

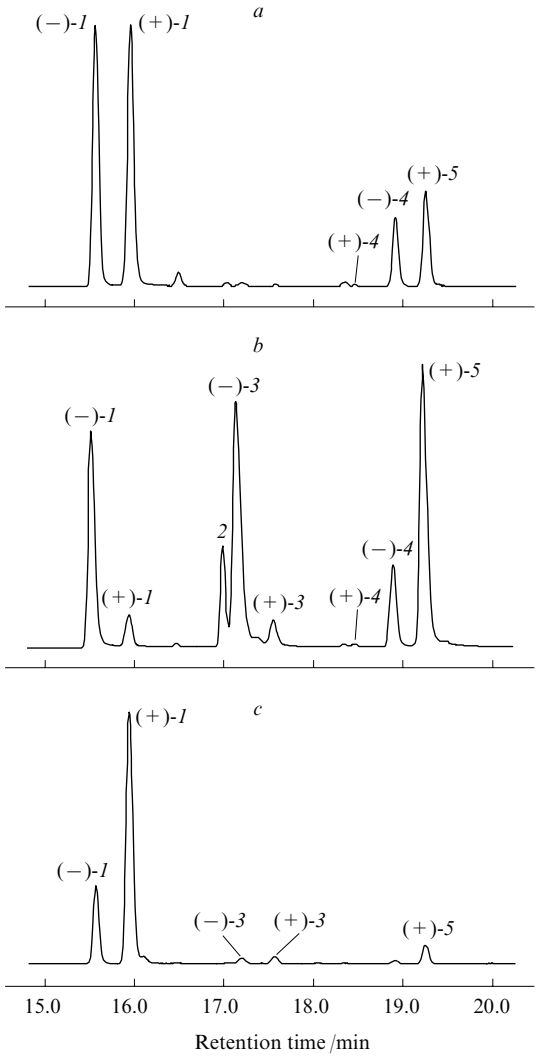


Figure 1. Chromatograms of monoterpene hydrocarbons from oleoresin of the Siberian stone pine (*Pinus sibirica* Du Tour.) (*a*), the Siberian spruce (*Picea obovata* Ledeb.) (*b*) and the Scots pine (*Pinus sylvestris* L.) (*c*) obtained by chiral gas chromatography/mass spectrometry on a 30 m × 0.25 mm CycloSil-B column (0.25 μm) at temperatures from 50 to 180 °C (the heating rate was 2 deg min^{-1}).
The peaks of compounds are identified by Arabic numerals: (*1*) α-pinene, (*2*) β-myrcene, (*3*) camphene, (*4*) β-pinene, (*5*) 3-carene.

stationary phase, the eluate is divided into two portions. One portion is delivered to a 'usual' (flame ionisation, mass selective, *etc*.) detector, and the odour of another portion of the eluate is evaluated by a human nose *via* a sniffing port.[19] Studies of flavours characteristic of branched carboxylic acids that are present in Parmesan cheese and lamb meat can be referred to as examples.[18, 19]

The olfactometric detection plays an important role in studies of flavour components of foodstuff because components present in large amounts not nearly always make a decisive contribution to a particular flavour. The analysis of the flavour of freshly squeezed orange juice showed that components that are hardly possible to identify reliably by conventional analysis because of their small amounts, play a great role in the flavour formation, and their true role can be revealed only by the olfactometric detection.[89]

The enantioselective analysis of individual components in mixtures of compounds without their preliminary preparative separation can be performed with the use of mass-spectrometric detectors. However, due to some characteristic features of mass-spectrometric detectors and the related substantial differences in the detector sensitivity to different groups of compounds, the quantitative analysis by gas chromatography/mass spectrometry presents difficulties. At the same time, the quantitative analysis of the enantiomeric composition of mixtures is very easy to perform by chiral gas chromatography/mass spectrometry, *i.e*., by the direct method without the use of correction or the sensitivity factors, because enantiomers behave identically in mass spectrometric detectors. The chromatographic peak area ratio of enantiomers is equal to the enantiomeric ratio in the analyte.

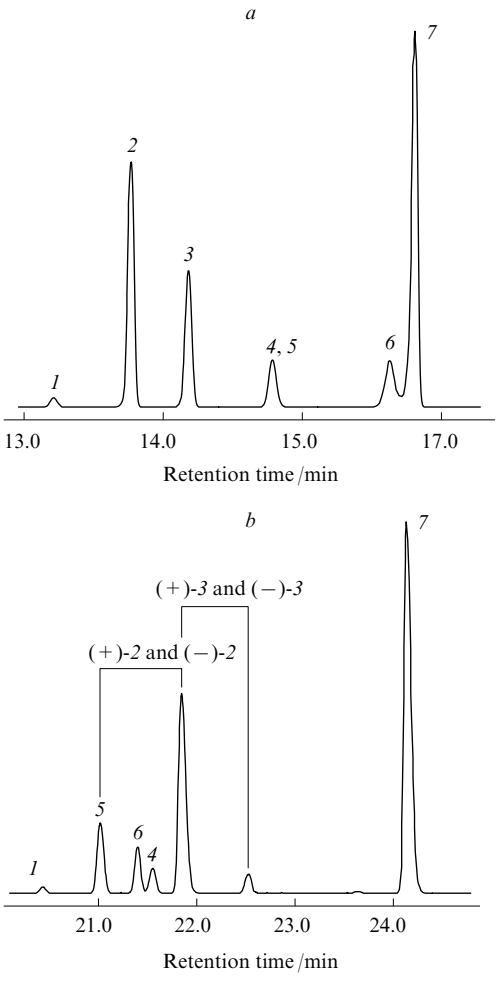


Figure 2. Fragments of chromatograms for the fractions of monoterpene hydrocarbons of essential oil from aerial parts of the *Seseli buchtormense* (Fischer ex Sprengel) W.Koch obtained on DB-1701 (*a*) and CycloSil-B (*b*) columns.
(*a*) 30 m × 0.25 mm DB-1701 column (0.25 μm), temperature 50 – 220 °C (the heating rate was 2 deg min^{-1}); (*b*) 30 m × 0.25 mm CycloSil-B column (0.25 μm), temperature 50 – 180 °C (the heating rate was 2 deg min^{-1}). The peaks of compounds are identified by Arabic numerals: (*1*) α-terpinene, (*2*) limonene, (*3*) β-phellandrene, (*4*) *p*-cymol, (*5*) *cis*-β-ocimene, (*6*) *trans*-β-ocimene, (*7*) γ-terpinene.

Figure 1 shows chromatograms for the separation of mixtures of monoterpene hydrocarbons. It can be seen that pairs of overlapping peaks are absent in the chromatograms, *i.e*., the separation was successful. The results of the more complex enantiomeric resolution by chromatography in the analysis of multicomponent mixtures containing limonene and β-phellandrene are presented in Fig. 2. These monoterpene hydrocarbons, which are present in many plants, are often found simultaneously and exist as pairs of compounds, which cause complications, because the peaks of these components are unseparable on many columns with widely used nonpolar polysiloxane phases. This pair of monoterpene hydrocarbons was successfully separated on the DB-1701 phase (Fig. 2 *a*). However, researchers run into difficulty when attempting to resolve each compound into individual enantiomers on CycloSil-B columns (Fig. 2 *b*) because the peak of (−)-limonene coincided with that of (+)-β-phellandrene.

In some cases, when the target components cannot be detected directly (for example in the analysis of labile compounds), their derivatives are synthesised. For instance, to detect (*R*)-3-mercapto-2-methylpropanol in red grape wines, compounds, which are present in the low-temperature vacuum distillation fraction, are subjected to acetylation, and the target compounds are determined as *O*,*S*-diacetyl derivatives.[17] Enantiomers of some terpene alcohols are resolved as *O*-trifluoroacetyl derivatives.[62]

III. Two-dimensional gas-liquid chromatography

In the analysis of plant volatiles and food extracts, researchers have, as a rule, to deal with very complex mixtures, which are impossible to separate on modern columns. Considerable progress in studies of such mixtures has been made only with the use of two-dimensional GLC.[90] This method is based on the successive separation of samples on two different columns. The analyte is delivered to column 1 (the so-called precolumn), where the preliminary separation of components is performed. Then the required fraction of the eluate is taken and divided into two portions. One portion is delivered to detector 1, and another portion is passed to column 2 (the so-called main column), in which the second separation is performed followed by the detection with detector 2. The precolumn is a usual 10 – 30 m capillary column with a low-polarity polysiloxane phase. This column is used to perform the rough separation of the starting complex mixture and isolate the required (narrow) fraction for the subsequent precision analysis on the main column. The main column is filled with a stationary phase containing a chiral selector, which offers considerable scope for the direct enantioselective analysis of components of complex mixtures of natural compounds.[87]

The direct enantioselective analysis cannot be applied to most of mixtures of sesquiterpene compounds, unlike mixtures of monoterpenoids, because of a high 'density' of components in chromatograms and a large number of overlapping peaks. Only the use of the two-dimensional chromatographic techniques allows the direct analysis of such mixtures. Figure 3 presents the results of analysis of a mixture of sesquiterpene hydrocarbons isolated from oleoresin of the *Abies nephrolepis*

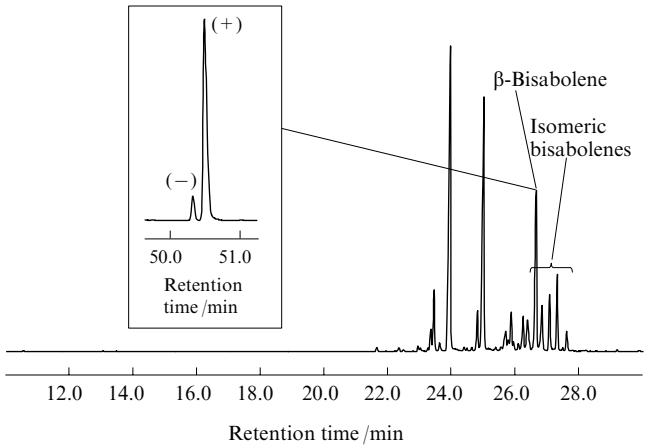
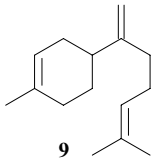


Figure 3. Determination of the optical purity of β-bisabolene in a mixture of sesquiterpene hydrocarbons from oleoresin of the *Abies nephrolepis* Maxim. by two-dimensional GLC.
Column 1: CPSil-5, 25 m × 0.25 mm (0.25 μm), temperature 50 – 200 °C (the heating rate was 4 deg min^{-1}); column 2: 30% heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin in OV-1701 (in the inset), 25 m × 0.25 mm (0.125 μm), temperature 50 – 180 °C (the heating rate was 2 deg min^{-1}).

followed by the determination of the optical purity of β-bisabolene (**9**) in a complex isomeric mixture.



9

The first chromatographic separation of a mixture of sesquiterpene hydrocarbons was performed on a column with a polysiloxane phase to isolate a fraction containing β-bisabolene (the retention time varies from 26.60 to 26.70 min). The resolution of this fraction into individual enantiomers was carried out on a column with a β-cyclodextrin-based phase. It should be noted that the direct analysis (using the one-dimensional technique) of the fraction of sesquiterpene hydrocarbons is of no use because the mixture contains, along with β-bisabolene, all other isomeric (*Z*)-α-, (*E*)-α-, (*Z*)-γ- and (*E*)-γ-bisabolenes, which hinder the analysis of enantiomers of β-bisabolene.

There are two radically different arrangements of the precolumn and the main column in two-dimensional chiral GLC (in one or two different thermostats). Manufacturers of gas-chromatographic systems suggest simple solutions for two-dimensional chromatography as instruments in which both columns are placed in a single thermostat. However, this instrumental simplicity, despite a price benefit, offers less possibilities for tuning. In the overwhelming majority of cases, to achieve the most efficient resolution by two-dimensional chiral GLC, the precolumn and the main column with a chiral stationary phase should operate under different temperature conditions, which cannot be provided in instruments, in which both columns are placed in a single thermostat.

A quick technique was developed for the analysis of the enantiomeric composition of mixtures by two-dimensional chiral GLC with the use of a short (1 m) column packed with a cyclodextrin phase. The satisfactory enantiomeric resolution of limonene according to this procedure took only 8 s (!), and the enantiomeric composition of all monoterpene compounds isolated from bergamot oil was determined within 8 – 9 min.[91]

A combination of liquid and gas chromatography (LC-GC) is another efficient combined method for the determination of the enantiomeric composition of mixtures. However, only a few examples of the successful application of this method were documented.[40]

IV. Preparative enantiomeric resolution

The preparative enantiomeric resolution of volatile natural compounds by chiral GLC with the use of cyclodextrin stationary phases is performed on packed columns filled with a solid support coated with modified cyclodextrin as the stationary phase. This method allows the isolation of milligram amounts of individual enantiomers.[92]

The characteristic feature of preparative chiral GLC is that the best enantiomeric resolution is, as a rule, achieved at the minimum temperatures of the analysis because a lowering of the temperature leads to an increase in the retention times of the components. To decrease the temperature of the analysis, rather short columns and a packing material with a small (compared to usual preparative columns) amount of a stationary phase are used. In addition, the separation is performed at carrier gas flow rates 3 – 4 times higher than the optimal rates. An increase in the carrier gas flow rate leads to a slight decrease in the efficiency of the column. However, this drawback is compensated, on the whole, by the gain in enantioselectivity of resolution due to lowering of the temperature.

Preparative chiral GLC is generally carried out on a 1.8 – 2.0-m steel column with a diameter of 4 – 5 mm filled with a solid support (for example, with the Chromosorb W/HP sorbent with a grain size of 100 – 120 mesh) coated with a 20% – 50% solution of modified cyclodextrin [heptakis(2,6-di-*O*-methyl-3-*O*-n-pentyl)-β-cyclodextrin,[93] heptakis(2,3-di-*O*-methyl-6-*O*-n-hexyl)-β-cyclodextrin,[94] octakis(2,3-di-*O*-n-pentyl-6-*O*-methyl)-γ-cyclodextrin,[95] octakis(2,6-di-*O*-methyl-3-*O*-n-pentyl)-γ-cyclodextrin[96] or heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin[96]] in polysiloxane [OV-1701,[97] PS-086[95] or SE-52 (Ref. 96)] as the stationary phase (2% – 6%). The carrier gas flow rate is 200 – 400 ml min^{-1}; the temperature is chosen depending on the nature of the compounds and is varied from 35 – 45 °C (for monoterpene hydrocarbons) to 100 – 120 °C (for sesquiterpenes). The temperature of the chromatographic analysis should be chosen so as to achieve the selectivity factor of $\geqslant$1.1. In this case, enantiomers of an optical purity of no less than 90% can be obtained.

Under these conditions, 1 – 2 mg of racemic compounds can be separated in a single chromatographic run. Milligram amounts of pure enantiomers (up to 97% *ee*) can be obtained by repeated chromatographic steps, these amounts being sufficient for the determination of the sign of optical rotation and, consequently, for the determination of the elution order of enantiomers, as well as for biological assays and pharmacokinetic studies.[92]

The preparative enantiomeric resolution with the use of capillary columns with a large inner diameter (0.53 mm) and a larger layer thickness of the stationary phase was documented.[98,99] Such columns provide better resolution compared to packed columns. However, this approach has found little application apparently because of rather complex technical equipment and labour-consuming experiments associated with a low capacity of capillary columns compared to packed columns.

Some plant volatiles exist in the gaseous state. However, no examples of the enantioselective analysis of gaseous plant metabolites have yet been reported, although a procedure for the preparative resolution of chiral gaseous compounds on

cyclodextrin phases at room temperature was elaborated for bromochlorofluoromethane.[100]

V. Identification of enantiomers

The reliable assignment of peaks of optical isomers plays a decisive role in chiral chromatography. Since the mechanism of enantiodifferentiation based on interactions of a chiral selector with an enantiomeric pair remains to be elucidated, it is impossible to predict the elution order of enantiomers. Taking into account the fact that the selectivity of columns depends, among other factors, on the chromatographic conditions, it can be concluded that the identification of enantiomers is a complex problem. Generally, at least two model samples are required for the reliable assignment of peaks. One sample should contain both enantiomers (the presence of a racemic mixture is preferable). This sample is used for choosing the optimal chromatographic conditions. Another sample should be enriched in a particular enantiomer with the aim that the elution order of optical isomers can be determined under the optimised conditions.

Many of the most widespread monoterpene compounds are commercially available both as racemic mixtures and individual enantiomers. The situation is more difficult with less widespread compounds. Researchers often have to synthesise such compounds or isolate them from natural mixtures. This is particularly true for sesquiterpene compounds because only a few of them are present in catalogues of manufacturers of chemicals. Moreover, natural sources, from which the target compound can easily be isolated in required amounts, are unknown for many sesquiterpenoids. In this connection, studies aimed at preparing individual sesquiterpenoids or their mixtures of known composition for the use as reference samples in chiral GLC deserve particular notice. For example, the easily available natural sesquiterpene hydrocarbon germacrene D was transformed [101] into mixtures of sesquiterpenoids of known composition containing selinane-, cadalene-, eudesmane- and oppositane-type sesquiterpenoids and other related compounds belonging to the biogenetic tree of germacrane by acid-catalysed, photoinduced or thermally induced rearrangements. However, far not all important sesquiterpenes required as reference compounds can be synthesised from known precursors by rearrangements. Extracts of some lower plants and fungi can be mentioned as sources of 'unusual' enantiomers of plant sesquiterpenoids.[95]

Extensive experimental data on the enantiomeric resolution of plant volatiles, fragrance and flavour compounds by chiral GLC on capillary columns with stationary phases based on chiral selectors are available. Data on the separation factors of enantiomers of various compounds, including plant compounds, were published. In particular, enantiomers were analysed on capillary columns with phases based on octakis(6-*O*-methyl-2,3-di-*O*-n-pentyl)-γ-cyclodextrin,[102] heptakis(2,6-di-*O*-methyl-3-*O*-n-pentyl)-β-cyclodextrin (Ref. 103) and octakis(3-*O*-butyryl-2,6-di-*O*-n-pentyl)-γ-cyclo-dextrin.[104] The enantiomeric separation of octane-1,3-diol, (5*Z*)-octene-1,3-diol, ethyl 3-hydroxyoctanoate and ethyl (5*Z*)-3-hydroxyoctenoate on a column with heptakis(2,3-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin was documented.[15, 105] However, the published data summaries are not always useful in practice because they contain no information on the elution order of enantiomers. Data on the resolution of 260 enantiomeric pairs of cyclopropane derivatives were presented in the review,[106] where the selectivity factors were reported without mentioning the conditions of resolution. The successful enantiomeric resolution of γ- and δ-thiolactones of the fatty acid series (C_6, C_8, C_{10}, C_{12}),[107] optical isomers of various natural and synthetic compounds,[108] trifluoroacetates of terpene and nonterpene alcohols [62] and β- and γ-lactones of the fatty acid series was documented.[62] However, the elution orders of these enantiomers were also not reported, although the selectivity factors were published.

The aim of the present review was to provide the most detailed information on the chirospecific analysis of plant volatiles. Tables 1–4 summarise data on the enantiomeric resolution of natural plant compounds and selected important

Table 1. Enantiomeric resolution of mono- and sesquiterpenoids and related compounds by chiral GLC on stationary phases containing cyclodextrin derivatives as chiral selectors.

Selectand	Chiral selector [a]	Column temperature (°C) or the temperature conditions (see comments in the text)	α	First-eluted enantiomer	Ref.
Borneol	β-(2,3-Ac-6-TBS)	80°	1.032		108
Borneol [b]	γ-(2,6-Pe-3-But)	90°		(+)	62
Isoborneol	β			(−)	109
	β-(2,3-Ac-6-TBS)	90°	1.038		108
Isoborneol [b]	γ-(2,6-Pe-3-But)	90°		(−)	62
Verbenone	γ-(2,6-Pe-3-But)	60°(2) – 200°(4°)		(+)	110
Vitispirane I	β-(2,6-Me-3-Pe)	60°(25) – 240°(1.5°)		(2*R*,5*R*)	111
Vitispirane II	β-(2,6-Me-3-Pe)	60°(25) – 240°(1.5°)		(2*R*,5*S*)	111
Dill ether	γ-(2,3-But-6-TBS)	60° – 200°(2.5°)	1.014	(3*R*,3a*R*,7a*S*)	112
Dill ether (*cis* isomer)	γ-(2,3-But-6-TBS)	60° – 200°(2.5°)	1.018	(3*S*,3a*R*,7a*S*)	112
Camphene	β-(2,3-Pe-6-Me)	35°	1.074	(−)	113
	β-(2,3-Pe-6-Me)	70° – 220°(6°)	1.04	(−)	10
	β-(2,6-Pe-3-Me)	60°		(−)	114
	γ-(2,3-Pe-6-Me)	35°	1.000 [c]		113
	γ-(2,3-Pe-6-Me)	45°	1.000 [c]		113
	α (see [d])	70°	2.31	(−)	49
α-Campholenal	β-(2,3,6-Me)	110°		(*R*)	21
Camphor	γ-(2,6-Pe-3-But)	100° – 160°(2°)		(+)	62
	β-(2,3-Ac-6-TBS)	100°	1.054	(*S*)	108
	γ-(2,6-Pe-3-But)			(+)	114
	γ-(2,6-Pe-3-But)	50°(2) – 100°(1°)		(1*R*)-(+)	8
	β-(2,3-Ac-6-TBS)	60°(18) – 120°(1°) – 200°(10°)		(1*S*)	115
	β-(2,3-Et-6-TBS)	60°(10) – 120°(3°)		(−)	9

Table 1 (continued).

Selectand	Chiral selector [a]	Column temperature (°C) or the temperature conditions (see comments in the text)	α	First-eluted enantiomer	Ref.
trans-Carveol	γ-(2,3-Pe-6-Me)	50°(1.5) – 110°(2°)(8) – 200°(20°)(6)	1.014	(+)	116
cis-Carveol	γ-(2,3-Pe-6-Me)	50°(1.5) – 110°(2°)(8) – 200°(20°)(6)	1.022	(−)	116
Carvone	α (see [d])	70°	1.11	(+)	49
	β-(2,3-Ac-6-TBS)	110°	1.05	(*R*)-(−)	108
	α-(2,3,6-Pe)	100°		(−)	114
	β-(2,3-Me-6-TBS)	100°	1.018	(+)	73
	β-(2,3-Ac-6-TBS)	100°	1.065	(−)	73
	γ-(2,3-Pe-6-Me)	50°(1.5) – 110°(2°)(8) – 200°(20°)(6)	1.015	(+)	116
3-Carene	β-(2,3-Pe-6-Me)	35°	1.040	(+)	113
	β-(2,3-Pe-6-Me)	70° – 220°(6°)	1.03	(+)	10
	γ-(2,3-Pe-6-Me)	35°	1.000 [c]		113
	γ-(2,3-Pe-6-Me)	45°	1.388	(+)	113
	β-(2,6-Pe-3-AcF)			(−)	37
Lavandulol	β-(2,3-Ac-6-TBS)	60°(18) – 120°(1°) – 200°(10°)		(*R*)	115
	β-(2,3-Ac-6-TBS)	80°	1.022	(*R*)	108
Limonene	β-(2,3-Pe-6-Me)	35°	1.026	(−)	113
	β-(2,3-Pe-6-Me)	70° – 220°(6°)	1.01	(−)	10
	β-(2,6-Pe-3-Me)	60°		(−)	114
	β-(2,3-Et-6-TBS)	45°(6) – 180°(2°)		(−)	117
	γ-(2,3-Pe-6-Me)	35°	1.261	(+)	113
	γ-(2,3-Pe-6-Me)	45°	1.180	(+)	113
	γ-(2,3-Pe-6-Me)	55°		(+)	118
	β (see [e])	40°(8) – 200°(2°)		(−)	119
	β-(2,3,6-Me)			(−)	37
	γ-(2,3,6-Me)	50°	1.03	(+)	120
	α (see [d])	70°	1.11	(+)	49
	γ-(2,3-Pe-6-Me)	50°(1.5) – 110°(2°)(8) – 200°(20°)(6)	1.044	(+)	116
trans-Limonene 1,2-epoxide	γ-(2,3,6-Me)	50°	1.01	(+)	120
cis-Limonene 1,2-epoxide	γ-(2,3,6-Me)	50°	1.04	(−)	120
Linalyl acetate	β-(2,3-Ac-6-TBS)	60°(18) – 120°(1°) – 200°(10°)		(*R*)	115
	β-(2,3-Ac-6-TBS)	80°	1.021	(*R*)	108
Linalool	β-(2,3-Ac-6-TBS)	60°(18) – 120°(1°) – 200°(10°)		(*R*)	115
	β-(2,3-Ac-6-TBS)	80°	1.08	(*R*)-(−)	108
	β-(2,3-Ac-6-TBS)	60°(20) – 120°(1.3°)		(*R*)-(−)	11
	β-(2,3-Et-6-TBS)	45°(6) – 180°(2°)		(−)	117
	β-(2,3,6-Pe)	80°		(−)	114
	α (see [d])	70°	1.000 [c]		49
	β-(2,3,6-Me)			(−)	37
(*E*)-3,7-Dimethylocta-1,5-diene-3,7-diol	β-(2,3-Me-6-TBS)	60°(25) – 200°(2°)		(3*R*)	121
	β-(2,3-Ac-6-TBS)	60°(30) – 200°(2°)	1.000 [c]		121
3,7-Dimethylocta-1,7-diene-3,6-diol (I)	β-(2,3-Me-6-TBS)	60°(25) – 200°(2°)		(3*R*,6*S*)	121
	β-(2,3-Ac-6-TBS)	60°(30) – 200°(2°)		(3*R*,6*S*)	121
3,7-Dimethylocta-1,7-diene-3,6-diol (II)	β-(2,3-Me-6-TBS)	60°(25) – 200°(2°)		(3*R*,6*R*)	121
	β-(2,3-Ac-6-TBS)	60°(30) – 200°(2°)		(3*S*,6*S*)	121
(*E*)-3,7-Dimethylocta-1,6-diene-3,8-diol	β-(2,3-Me-6-TBS)	60°(25) – 200°(2°)	1.000 [c]		121
	β-(2,3-Ac-6-TBS)	60°(30) – 200°(2°)		(6*S*)	121
(*Z*)-3,7-Dimethylocta-2,7-diene-1,6-diol	β-(2,3-Me-6-TBS)	60°(25) – 200°(2°)		(3*R*)	121
	β-(2,3-Ac-6-TBS)	60°(30) – 200°(2°)	1.000 [c]		121
(*E*)-3,7-Dimethylocta-2,7-diene-1,6-diol	β-(2,3-Me-6-TBS)	60°(25) – 200°(2°)		(3*R*)	121
	β-(2,3-Ac-6-TBS)	60°(30) – 200°(2°)	1.000 [c]		121
trans-Linalool oxide (pyranoid)	β-(2,3,6-Me)			(2*S*)	41
	β-(2,3,6-Et)			(2*S*)	41
	β-(2,3-Ac-6-TBS)			(2*R*)	41
	β-(2,3-Me-6-TBS)			(2*S*)	41
cis-Linalool oxide (pyranoid)	β-(2,3,6-Me)			(2*S*)	41
	β-(2,3,6-Et)			(2*S*)	41
	β-(2,3-Ac-6-TBS)			(2*S*)	41
	β-(2,3-Me-6-TBS)			(2*S*)	41

Table 1 (continued).

Selectand	Chiral selector [a]	Column temperature (°C) or the temperature conditions (see comments in the text)	α	First-eluted enantiomer	Ref.
trans-Linalool oxide (furanoid)	β-(2,3,6-Me)			(2*R*)	41
	β-(2,3,6-Et)			(2*R*)	41
	β-(2,3-Pe-6-Me)			(2*R*)	41
	β-(2,3-Ac-6-TBS)			(2*S*)	41
	β-(2,3-Me-6-TBS)			(2*R*)	41
cis-Linalool oxide (furanoid)	β-(2,3,6-Me)			(2*R*)	41
	β-(2,3,6-Et)			(2*R*)	41
	β-(2,3-Pe-6-Me)			(2*R*)	41
	β-(2,3-Ac-6-TBS)			(2*R*)	41
	β-(2,3-Me-6-TBS)			(2*R*)	41
p-Menth-1-ene-8-thiol	β-(2,3-Me-6-TBS)			(*S*)	38
trans-8-Mercapto-*p*-menth-3-one	β-(2,3,6-Me)	110°		(1*R*,4*R*)	122
trans-8-Mercapto-*p*-menth-3-one	γ-(2,3-Ac-6-TBS)	80° – 125°(1.5°)(40) – 190°(3°)		(1*R*,4*R*)	123
cis-8-Mercapto-*p*-menth-3-one	β-(2,3,6-Me)	110°		(1*R*,4*S*)	122
cis-8-Mercapto-*p*-menth-3-one	γ-(2,3-Ac-6-TBS)	80° – 125°(1.5°)(40) – 190°(3°)		(1*S*,4*R*)	123
trans-8-Acetylmercapto-*p*-menth-3-one	γ-(2,3-Ac-6-TBS)	80° – 125°(1.5°)(40) – 190°(3°)		(1*R*,4*R*)	123
cis-8-Acetylmercapto-*p*-menth-3-one	γ-(2,3-Ac-6-TBS)	80° – 125°(1.5°)(40) – 190°(3°)		(1*S*,4*R*)	123
Menthyl acetate	γ-(2,3-Pe-6-Me)	85°		(−)	118
	β-(2,3-Ac-6-TBS)	90°	1.035		108
	β-(2,3,6-Me)			(−)	37
	β-(2,3-Me-6-TBS)	47°(19) – 70°(20°)(15) – 210°(1.5°)		(−)	124
Menthol	γ-(2,3-Pe-6-Me)	75°(15) – 150°(2°)		(+)	118
	β-(2,3-Ac-6-TBS)	90°	1.048		108
	α (see [d])	70°	1.000 [c]		49
	β-(2,3-Me-6-TBS)	47°(19) – 70°(20°)(15) – 210°(1.5°)		(+)	124
Isomenthol	β-(2,3-Ac-6-TBS)	100°	1.043		108
Neomenthol	β-(2,3-Me-6-TBS)	47°(19) – 70°(20°)(15) – 210°(1.5°)		(+)	124
	β-(2,3-Ac-6-TBS)	100°	1.039		108
	α (see [d])	70°	1.000 [c]		49
Neoisomenthol	β-(2,3-Me-6-TBS)	47°(19) – 70°(20°)(15) – 210°(1.5°)		(−)	124
Menthone	γ-(2,3-Pe-6-Me)	75°(15) – 150°(2°)		(+)	118
	β-(2,3-Ac-6-TBS)	75°	1.073		108
	α (see [d])	70°	1.10	(+)	49
	β-(2,3-Me-6-TBS)	47°(19) – 70°(20°)(15) – 210°(1.5°)		(−)	124
	γ-(2,6-Pe-3-But)[f]	80°	1.088 – 1.164	(2*R*,5*S*)-(+)	71
	γ-(2,6-Pe-3-But)	100° – 160°(2°)		(+)	62
	γ-(2,6-Pe-3-AcF)			(+)	37
	β-(2,3,6-Me)		1.000 [c]		37
Isomenthone	γ-(2,3-Pe-6-Me)	75°(15) – 150°(2°)		(+)	118
	β-(2,3-Ac-6-TBS)	75°	1.059		108
	α (see [d])	70°	1.21	(−)	49
	γ-(2,6-Pe-3-But)			(+)	31
	γ-(2,6-Pe-3-But)	100° – 160°(2°)		(+)	62
	γ-(2,6-Pe-3-AcF)		1.000 [c]		37
	β-(2,3,6-Me)			(+)	37
	β-(2,3-Me-6-TBS)	47°(19) – 70°(20°)(15) – 210°(1.5°)		(+)	124
Menthofuran	β-(2,3,6-Me)			(*R*)	37
Methyl citronellate	β-(2,3-Ac-6-TBS)	60°(13) – 85°(0.4°)		(*R*)-(+)	11
Mintlactone	β-(2,6-Pe-3-AcF)			(6*R*,7a*R*)-(−)	37
Mintlactone, dehydromyrtenal	β-(2,6-Pe-3-AcF)			(*S*)-(−)	37
	γ-(2,6-Pe-3-But)	120°		(+)	114
Myrtenol [b]	β-(2,6-Pe-3-Me)	100°		(−)	114
Nerol oxide	γ-(2,3-But-6-TBS)			(*R*)-(+)	41
cis-Pinane	β (see [e])	40°(8) – 200°(2°)		(−)	119
trans-Pinane	γ-(2,6-Pe-3-But)[f]	26°	1.018 – 1.044	(1*R*)-(+)	71
α-Pinene	β-(2,3-Pe-6-Me)	35°	1.054	(−)	113
	γ-(2,6-Pe-3-But)[f]	26°	1.032 – 1.068	(1*R*)-(+)	71
	β-(2,3-Pe-6-Me)	70° – 220°(6°)	1.04	(−)	10
	γ-(2,3-Pe-6-Me)	35°	1.053	(+)	113
	γ-(2,3-Pe-6-Me)	45°	1.000 [c]		113
	β (see [e])	40°(8) – 200°(2°)		(−)	119
	γ-(2,3-Pe-6-Me)	55°		(+)	118

Table 1 (continued).

Selectand	Chiral selector [a]	Column temperature (°C) or the temperature conditions (see comments in the text)	α	First-eluted enantiomer	Ref.
α-Pinene	α (see [d])	70°	2.22	(−)	49
	γ-(2,6-Pe-3-But)[f]	26°	1.03 – 1.07	(+)	71
	β-(2,3,6-Me)			(−)	37
	β-(2,6-Pe-3-Me)	60°		(−)	114
β-Pinene	β-(2,3-Pe-6-Me)	35°	1.034	(−)	113
	β-(2,3-Pe-6-Me)	70° – 220°(6°)	1.008	(−)	10
	β-(2,3-Et-6-TBS)	45°(6) – 180°(2°)		(+)	117
	γ-(2,3-Pe-6-Me)	35°	1.060	(+)	113
	γ-(2,3-Pe-6-Me)	45°	1.043	(+)	113
	γ-(2,3-Pe-6-Me)	55°		(+)	118
	α (see [d])	70°	1.86	(−)	49
	β-(2,3,6-Me)			(+)	37
α-Pinene epoxide	β-(2,3,6-Me)	100°		(−)	21
Isopinocampheol	α (see [d])	70°	1.15	(−)	49
trans-Pinocarveol [b]	β-(2,6-Pe-3-Me)	100°		(−)	114
Piperitone	γ-(2,3-Pe-6-Me)	75°(15) – 150°(2°)		(−)	118
	β-(2,3-Ac-6-TBS)	90°	1.037		108
	γ-(2,6-Pe-3-But)	100° – 160°(2°)		(−)	114
Pulegone	α (see [d])	70°	1.000 [c]		49
	β-(2,3,6-Me)	130°		(*R*)	122
trans-Rose oxide	γ-(2,6-Me-3-Pe)			(2*S*)	41
	β-(2,3-Ac-6-TBS)	70°	1.040	(2*R*,4*R*)	108
	γ-(2,6-Pe-3-AcF)			(2*S*)	41
	γ-(2,6-Pe-3-AcF)			(+)	37
	β-(2,3-Ac-6-TBS)			(2*R*)	41
	β-(2,3-Ac-6-TBS)	60°(20) – 120°(1.3°)		(2*R*,4*R*)-(−)	11
	γ-(2,3-Ac-6-TBS)			(2*R*)	41
	α-(2,3,6-Me)		1.000 [c]		37
	γ-(2,3,6-Me)		1.000 [c]		37
	γ-(2,6-Pe-3-But)			(+)	37
cis-Rose oxide	γ-(2,6-Me-3-Pe)			(2*S*)	41
	β-(2,3-Ac-6-TBS)	70°	1.039	(2*R*,4*S*)	108
	γ-(2,6-Pe-3-AcF)			(2*S*)	41
	β-(2,3-Ac-6-TBS)			(2*R*)	41
	β-(2,3-Ac-6-TBS)	60°(20) – 120°(1.3°)		(2*R*,4*S*)-(+)	11
	γ-(2,3-Ac-6-TBS)			(2*R*)	35
	α-(2,3,6-Me)			(−)	37
	γ-(2,3,6-Me)			(−)	37
	γ-(2,6-Pe-3-But)		1.000 [c]		37
	γ-(2,6-Pe-3-AcF)			(−)	37
trans-Rose oxide ketone	β-(2,3-Ac-6-TBS)			(2*S*)	41
cis-Rose oxide ketone	β-(2,3-Ac-6-TBS)			(2*R*)	41
Sabinene	β-(2,3-Pe-6-Me)	35°	1.063	(+)	113
	β-(2,3-Pe-6-Me)	70° – 220°(6°)	1.02	(+)	10
	γ-(2,3-Pe-6-Me)	35°	1.124	(−)	113
	γ-(2,3-Pe-6-Me)	45°	1.093	(−)	113
	β-(2,3-Et-6-TBS)	45°(6) – 180°(2°)		(+)	117
Terpinen-4-ol	β-(2,3-Ac-6-TBS)	60°(18) – 120°(1°) – 200°(10°)		(*R*)	115
	β-(2,3-Ac-6-TBS)	110°	1.042	(*R*)	108
	β-(2,3-Et-6-TBS)	45°(6) – 180°(2°)		(+)	117
	α (see [d])	70°	1.000 [c]		49
	β-(2,3,6-Me)			(+)	37
α-Terpineol	α (see [d])	70°	1.000 [c]		49
	β-(2,3-Ac-6-TBS)	80°	1.059		108
	β-(2,3,6-Me)			(−)	37
	β-(2,3-Et-6-TBS)	45°(6) – 180°(2°)		(−)	117
α-Tujene	β-(2,3-Pe-6-Me)	35°	1.045	(+)	113
	γ-(2,3-Pe-6-Me)	35°	1.040	(−)	113
	γ-(2,3-Pe-6-Me)	45°	1.000 [c]		113
Fencholenal	β-(2,3,6-Me)	115°		(*R*)	21

Table 1 (continued).

Selectand	Chiral selector [a]	Column temperature (°C) or the temperature conditions (see comments in the text)	α	First-eluted enantiomer	Ref.
Fenchone	α (see [d])	70°	2.01	(−)	49
	γ-(2,6-Pe-3-But)	100° – 160°(2°)		(−)	62
	γ-(2,6-Pe-3-But)[f]	70°	1.083 – 1.131	(1*R*)-(−)	71
α-Phellandrene	β-(2,3-Pe-6-Me)	35°	1.020	(−)	113
	γ-(2,3-Pe-6-Me)	35°	1.248	(+)	113
	γ-(2,3-Pe-6-Me)	45°	1.202	(+)	113
	γ-(2,3,6-Pe)	80°		(+)	114
	α (see [d])	70°	1.24	(−)	49
β-Phellandrene	β-(2,3-Pe-6-Me)	35°	1.030	(−)	113
	β-(2,3-Pe-6-Me)	70° – 220°(6°)	1.000 [c]		10
	γ-(2,3-Pe-6-Me)	35°	1.000 [c]		113
	γ-(2,3-Pe-6-Me)	45°	1.000 [c]		113
Ho-trienol	β-(2,3-Me-6-TBS)	60°(25) – 200°(2°)		(3*R*)	121
	β-(2,3-Ac-6-TBS)	60°(30) – 200°(2°)		(3*R*)	121
Citronellal	β-(2,3-Ac-6-TBS)	60°(20) – 120°(1.3°)		(*S*)-(−)	11
	β-(2,3-Ac-6-TBS)	90°	1.036		108
	β-(2,6-Pe-3-Ac)			(−)	37
	α (see [d])	70°	1.000 [c]		49
Citron	α (see [d])	70°	1.000 [c]		49
Citronellol	β-(2,3-Ac-6-TBS)	60°(20) – 120°(1.3°)		(*S*)-(−)	11
	β-(2,3-Ac-6-TBS)	80°	1.022	(*S*)-(−)	108
Citronellol [b]	γ-(2,6-Pe-3-But)	110°		(+)	62
α-Ionone	β-(2,3,6-Me)	120°		(−)	23
	β-(2,3-Ac-6-TBS)	135°	1.029		108
	γ-(2,6-Pe-3-AcF)	120°		(−)	23
	γ-(2,6-Pe-3-But)	75°		(−)	23
	β-(2,3-Me-6-TBS)	60 – 200°		(*S*)	16
	β-(2,3,6-Me)			(−)	37
α-Irone (I)	β-(2,3-Ac-6-TBS)	125°	1.049		108
α-Irone (II)	β-(2,3-Ac-6-TBS)	125°	1.238		108
2,3-Dehydro-α-ionol I [(2,6,6-trimethyl-cyclohexa-2,4-dienyl)but-3-ene-2-ol]	β-(2,6-Me-3-Pe)	100°(60) – 200°(2°)	1.003	(2*R*,1′*S*)	125
3,4-Dehydro-γ-ionol I	β-(2,6-Me-3-Pe)	100°(60) – 200°(2°)	1.004	(2*S*,1′*S*)	125
3,4-Dehydro-γ-ionol I	β-(2,6-Me-3-Pe)	100°(95) – 200°(1°)	1.003	(2*R*,1′*R*)	125
3,4-Dehydro-γ-ionol II	β-(2,6-Me-3-Pe)	100°(60) – 200°(2°)	1.002	(2*S*,1′*R*)	125
Riesling acetal	β-(2,3,6-Me)	60°(15) – 220°(2°)		(5*R*,6*S*,9*S*)	126
Theaspirane A	β-(2,3,6-Me)			(2*R*,5*R*)-(−)	37
	β-(2,3,6-Me)	80°(20) – 220°(2°)	1.016	(2*R*,5*R*)	127
Theaspirane B	β-(2,3,6-Me)			(2*S*,5*R*)-(+)	37
	β-(2,3,6-Me)	80°(20) – 220°(2°)	1.010	(2*S*,5*R*)	127
Theaspirone A	β-(2,3,6-Me)	80°(20) – 220°(2°)	1.007	(2*R*,5*R*)	127
	β-(2,3,6-Me)			(2*R*,5*R*)-(+)	37
	β-(2,6-Me-3-Pe)	60°(25) – 240°(1.5°)		(2*R*,5*R*)	111
Theaspirone B	β-(2,3,6-Me)	80°(20) – 220°(2°)	1.006	(2*S*,5*R*)	127
	β-(2,3,6-Me)			(2*S*,5*R*)-(+)	37
	β-(2,6-Me-3-Pe)	60°(25) – 240°(1.5°)		(2*S*,5*R*)	111
trans-Edulan I	β-(2,6-Me-3-Pe)	60°(20) – 200°(2°)		(2*S*,8a*R*)	128
cis-Edulan II	β-(2,6-Me-3-Pe)	60°(20) – 200°(2°)		(2*R*,8a*R*)	128
trans-3,4-Dihydro-3-oxoedulan	β-(2,6-Me-3-Pe)	60°(20) – 200°(2°)	1.003	(2*S*,8a*R*)	129
cis-3,4-Dihydro-3-oxoedulan	β-(2,6-Me-3-Pe)	60°(20) – 200°(2°)	1.016	(2*S*,8a*S*)	129
(*E*)-2,3-Dihydrofarnesal	β-(2,3-Ac-6-TBS)	110°(40) – 160°(1°)		(3*S*)	130
(*Z*)-2,3-Dihydrofarnesal	β-(2,3-Ac-6-TBS)	110°(40) – 160°(1°)		(3*S*)	130
(*E*)-2,3-Dihydrofarnesoic acid	β-(2,3-Me-6-TBS)	130°(5) – 155°(1.5°)(5) – 162°(0.5°) – 200°(2°)(20)	1.000 [c]		130
(*Z*)-2,3-Dihydrofarnesoic acid	β-(2,3-Me-6-TBS)	130°(5) – 155°(1.5°)(5) – 162°(0.5°) – 200°(2°)(20)		(3*S*)	130

[a] The following abbreviations are used: AcF is trifluoroacetyl, Bu is n-butyl, But is butyryl (butanoyl), Pe is n-pentyl and TBS is *tert*-butyldimethylsilyl; [b] determined as trifluoroacetate; [c] enantiomers are not resolved; [d] A 0.162 M solution of α-cyclodextrin in glycerol; [e] 10% β-cyclodextrin in polysiloxane SPB-35; [f] Chirasil-γ-Dex phase: the chiral selector γ-(2,6-Pe-3-But) is grafted to polymethylpolysiloxane through the octamethylene spacer.

Table 2. Enantiomeric resolution of sesquiterpene hydrocarbons by chiral GLC under isothermal conditions on stationary phases containing cyclodextrin derivatives as chiral selectors.

Selectand	Column 1 [a]			Column 2 [b]			Ref.
	α	column temperature /°C	first-eluted enantiomer	α	column temperature /°C	first-eluted enantiomer	
α-Amorphene	1.385	120	(−)	1.193	120	(−)	87
γ-Amorphene	1.895	115	(+)	1.218	115	(+)	87
δ-Amorphene	1.394	120	(+)				131
ε-Amorphene				1.093	115	(+)	87
Aristolene	1.078	90 [c]	(−)				87
Aristolochene	1.120	110	(+)				132
Aromadendrene	1.170	120	(−)	1.437	120	(−)	87
Alloaromadendrene	1.233	110	(−)	1.379	110	(−)	87
α-Barbatene	1.025	90	(−)				97
β-Barbatene	1.057	90	(−)				97
cis-α-Bergamotene	1.070	100	(−)				132
trans-α-Bisabolene	1.036	85 [c]	(−)				93
β-Bisabolene	1.018	85 [c]	(−)	1.050	115	(−)	93
Bicyclogermacrene	1.000 [d]			1.078	100	(+)	93
Bicycloelemene	1.100	80 [c]	(+)	1.143	110		87
α-Bourbonene				1.152	105	(+)	87
β-Bourbonene	1.068	105 [c]	(+)	1.081	105	(−)	87
Valencene	1.120	110 [c]	(−)	1.075	125	(−)	87
Geijerene				1.071	115		87
Germacrene D	1.11	110 [c]	(+)	1.074	115	(+)	133
α-Gurjunene	1.000 [d]			1.344	110	(−)	87
γ-Gurjunene	1.000 [d]			1.150	100	(+)	134
Zonarene				1.170	120	(−)	87
Epizonarene				1.437	120	(−)	87
Isobarbatene	1.032	90 [c]	(+)				97
Isobicyclogermacrene	1.037	105 [c]	(+)				87
Isolongifolene	1.120	85 [c]	(+)				87
Isosativene	1.049	105 [c]	(+)				87
α-Ylangene	1.220	90	(+)				87
β-Ylangene	1.088	120	(+)	1.064	115	(−)	87
Cadina-l,4-diene	1.038	115	(−)	1.249	120	(+)	87
α-Cadinene				1.140	120	(−)	87
β-Cadinene				1.145	120	(−)	87
γ-Cadinene	1.257	115	(−)	1.249	115	(−)	87
δ-Cadinene	1.680	115 [c]	(−)	1.260	115	(−)	93
ε-Cadinene	1.230	120	(+)				87
α-Calocorene	1.084	120 [c]	(+)				13
trans-Calamenene				1.257	120	(−)	93
cis-Calamenene				1.272	120	(−)	93
Calarene	1.045	90 [c]	(+)	1.026	100	(+)	135
Caryophyllene	1.131	95 [c]	(+)	1.065	100	(+)	95
Clovene	1.039	80 [c]	(−)				87
α-Copaene	1.084	90 [c]	(+)	1.015	90 [c]		93
β-Copaene				1.052	115	(−)	87
α-Cubebene	1.173	90 [c]	(+)	1.030	100	(+)	135
β-Cubebene	1.000 [d]			1.028	90 [c]	(−)	135
Cuparene	1.027	105 [c]	(−)	1.048	120	(−)	135
α-Cuprenene	1.029	95 [c]	(−)				87
Iso-*ar*-curcumene	1.031	110		1.041	110		87
ar-Curcumene	1.030	85	(+)	1.030	115	(+)	93
Ledene	1.05	105 [c]	(−)				135
Longifolene	1.048	80 [c]	(−)				87
α-Longipinene	1.030	80 [c]	(+)	1.028	105	(−)	87
α-Microbiotene	1.020	110	(−)				136
β-Microbiotene	1.022	110	(+)				136
cis-Muurol-4-ene		110 [c]	(1R)				137
cis-Muurol-4-ene		110 [c]	(1R)				137
α-Muurolene	1.206	105 [c]	(−)	1.056	125	(−)	87

Table 2 (continued).

Selectand	Column 1 [a]			Column 2 [b]			Ref.
	α	column temperature /°C	first-eluted enantiomer	α	column temperature /°C	first-eluted enantiomer	
γ-Muurolene	1.146	115 [c]	(−)	1.163	115	(+)	87
ε-Muurolene				1.124	115	(−)	87
α-Neocallitropsene	1.066	110	(−)				87
α-Selinene	1.110	110 [c]	(−)				87
α-7-*epi*-Selinene	1.060	105	(+)	1.085	105	(−)	132
δ-Selinene	1.148	110 [c]	(+)	1.136	115	(+)	135
δ-Selinene	1.133	120	(+)	1.073	120	(+)	138
Thujopsene	1.048	110	(+)				135
α-Cedrene	1.079	110 [c]	(+)	1.076	110	(+)	135
β-Elemene	1.000 [d]			1.024	90	(+)	95
γ-Elemene	1.023	110	(+)				135
δ-Elemene	1.026	80 [c]		1.063	90 [c]		93
Eremophyllene	1.063	100 [c]	(−)	1.024	100 [c]	(−)	87
Erythrodiene	1.027	100					87

[a] 50% β-(2,6-Me-3-Pe) in polysiloxane OV-1701; [b] 50% β-(2,3-Me-6-TBS) in polysiloxane OV-1701; [c] the corresponding cyclodextrin was taken in an amount of 20%; [d] enantiomers are not resolved.

Table 3. Enantiomeric resolution of diterpenoids by chiral GLC under isothermal conditions on stationary phases containing cyclodextrin derivatives as chiral selectors.

Selectand	Chiral selector	Column temperature /°C	α	First-eluted enantiomer	Ref.
Abieta-7,13-diene	β-(2,3-Me-6-TNS)	150	1.02	(+)	139
15-Beyerene	β-(2,6-Me-3-Pe)	145	1.03	(+)	139
Dolabradiene	γ-(2,6-Me-3-Pe)	120		(−)	140
15-Kaurene	β-(2,6-Me-3-Pe)	145	1.04	(−)	139
16-Kaurene	β-(2,6-Me-3-Pe)	145	1.08	(−)	139
Isopimara-8,15-diene	β-(2,3-Me-6-TBS)	150		(−)	141
13-*epi*-Manoyl oxide	β-(2,3-Me-6-TBS)	140		(+)	140
Pimara-8,15-diene	β-(2,3-Me-6-TBS)	150		(+)	141
Pimara-8(14),15-diene	γ-(2,6-Me-3-Pe)	120		(+)	140
Rosa-5,15-diene	γ-(2,6-Me-3-Pe)	120		(+)	140
Sclarene	γ-(2,6-Me-3-Pe)	150		(−)	140
Sclareol	β-(2,3-Me-6-TBS)	175		(−)	140

Table 4. Enantiomeric resolution of non-terpene flavour and fragrance compounds by chiral GLC on stationary phases containing cyclodextrin derivatives as chiral selectors.

Selectand	Chiral selector	Column temperature (°C) or the temperature conditions	α	First-eluted enantiomer	Ref.
2-Methylbutanal	β-(2,3-Ac-6-TBS)	40°(5) – 220°(1.5°)		(*R*)	142
Filbertone	β-(2,3-Ac-6-TBS)	80°	1.108		108
Alk-1-en-3-ols (C_5-C_9)	γ-(2,3-Bu-6-TBS)	40°(5) – 220°(1°)		(*R*)	142
Alkan-3-ols (C_6-C_8)	γ-(2,3-Bu-6-TBS)	40°(5) – 220°(1°)		(*R*)	142
Alkan-2-ols (C_5-C_{10})	γ-(2,3-Bu-6-TBS)	40°(5) – 220°(1°)		(*S*)	142
Oct-1-en-3-ol	β-(2,3-Ac-6-TBS)	80°	1.044	(*S*)	108
	β-(2,3-Ac-6-TBS)	60°(18) – 120°(1°) – 200°(10°)		(*S*)	115
	β-(2,3-Ac-6-TBS)	60°(20) – 120°(1.3°)		(*S*)-(+)	11
Octan-3-ol	β-(2,3-Ac-6-TBS)	60°(18) – 120°(1°) – 200°(10°)		(*R*)	115
	β-(2,3-Ac-6-TBS)	60°(20) – 120°(1.3°)		(*R*)-(−)	11
	β-(2,3-Ac-6-TBS)	80°	1.013	(*R*)	108
Octane-1,3-diol	β-(2,3-Ac-6-TBS)				105
1,3-Dioxanes	β-(2,3-Ac-6-TBS)				143
2-Methylbutan-1-ol	β-(2,3-Me-6-TBS)	70°(5) – 200°(1.5°)		(*R*)	38
	β-(2,3-Ac-6-TBS)	50°	1.064	(*R*)	108
2-Methylpentan-1-ol	β-(2,3-Ac-6-TBS)	70°	1.065	(*R*)	108
2-Methylhexan-1-ol	β-(2,3-Ac-6-TBS)	70°	1.071	(*R*)	108
2-Ethylhexan-1-ol	β-(2,3-Ac-6-TBS)	70°	1.075	(*R*)	108
2-Methylbutyl acetate	β-(2,3-Me-6-TBS)	70°(5) – 200°(1.5°)		(*S*)	32
3-Butyl-4-vinylcyclopentene	CP-Cyclodex 236 M	30°(4) – 215°(1°)	1.009	(3*S*,4*S*)-(+)	144

Table 4 (continued).

Selectand	Chiral selector	Column temperature (°C) or the temperature conditions	α	First-eluted enantiomer	Ref.
Ethyl 2-methylbutanoate	β-(2,3-Me-6-TBS)	70°(5) – 200°(1.5°)		(*R*)	38
	β-(2,3,6-Me)			(*R*)-(−)	37
Propyl 2-methylbutanoate	β-(2,3-Ac-6-TBS)	55°	1.033	(*S*)	108
Methyl 2-methylbutanoate	β-(2,3-Me-6-TBS)	60°(13) – 108°(1.5°) – 200°(2.5°)		(*R*)	16
Methyl jasmonate	β-(2,3,6-Me)			(1*R*,2*R*)-(−)	31
	β-(2,6-Me-3-Pe)	120°		(−)	92
Methyl *epi*-jasmonate	β-(2,6-Pe-3-AcF)			(1*R*,2*S*)-(+)	37
Methyl 2-hydroxypropanoate (methyl lactate)	γ-(2,6-Pe-3-But)[a]	80°	1.198 – 1.236	(*S*)-(−)	71
Ethyl 2-hydroxypropanoate (ethyl lactate)	β-(2,3-Me-6-TBS)	80°(7) – 200°(2°)		(*R*)	14
Ethyl 4-hydroxy-5-oxohexanoate	β-(2,6-Me-3-Pe)	100°(20) – 200°(2°)		(*R*)	145
Methyl lipoate	β-(2,6-Pe-3-Ac)	180°		(*R*)	118
α-Hydroxy acid methyl esters ($C_{10}-C_{22}$)	β-(2,3-Me-6-TBS)	110° – 175°(1.5°) – 190°(0.5°)		(*R*)	123
Methyl 2-methylcarboxylates (C_4-C_7)	β-(2,3-Me-6-TBS)	40° – 230°(1.5°)		(*R*)	123
Methyl 2-ethylhexanoate	β-(2,3-Me-6-TBS)	40° – 230°(1.5°)		(*R*)	123
Methyl 4-methylcarboxylates (C_6-C_9)	β-(2,3-Me-6-TBS)	40° – 230°(1.5°)		(*S*)	123
2-Methylbutyric acid	β-(2,3-Me-6-TBS)	70°(5) – 200°(1.5°)		(*S*)	38
	β-(2,3,6-Me)			(*S*)-(+)	37
2-Methylcarboxylic acids (C_4-C_7)	β-(2,3-Me-6-TBS)	90°(5) – 230°(1.5°)		(*S*)	123
	γ-(2,3-Me-6-TBS)	80°(5) – 230°(1.5°)		(*S*)	123
2-Methylbutanoic acid	β-(2,3-Me-6-TBS)	40°(5) – 85°(5°) – 140°(1.5°) – 230°(4°)		(2*S*)	18
2-Methylpentanoic acid	γ-(2,3-Me-6-TBS)	40°(5) – 100°(10°) – 130°(1°) – 235°(3°)		(2*S*)	19
	β-(2,3-Me-6-TBS)	40°(5) – 85°(5°) – 140°(1.5°) – 230°(4°)		(2*S*)	18
2-Methylhexanoic acid	γ-(2,3-Me-6-TBS)	40°(5) – 100°(10°) – 130°(1°) – 235°(3°)		(2*S*)	19
	β-(2,3-Me-6-TBS)	40°(5) – 85°(5°) – 140°(1.5°) – 230°(4°)		(2*S*)	18
2-Methylheptanoic acid	γ-(2,3-Me-6-TBS)	40°(5) – 100°(10°) – 130°(1°) – 235°(3°)		(2*S*)	19
	β-(2,3-Me-6-TBS)	40°(5) – 85°(5°) – 140°(1.5°) – 230°(4°)		(2*S*)	18
2-Methyloctanoic acid	γ-(2,3-Me-6-TBS)	40°(5) – 100°(10°) – 130°(1°) – 235°(3°)		(2*R*)	19
2-Ethylhexanoic acid	β-(2,3-Me-6-TBS)	90°(5) – 230°(1.5°)		(*S*)	123
	γ-(2,3-Me-6-TBS)	40°(5) – 100°(10°) – 130°(1°) – 235°(3°)		(2*S*)	19
	γ-(2,3-Me-6-TBS)	80°(5) – 230°(1.5°)		(*S*)	123
3-Methylcarboxylic acids (C_5-C_7)	β-(2,3-Me-6-TBS)	90°(5) – 230°(1.5°)		(*S*)	123
3-Methylcarboxylic acids (C_5, C_8-C_{10})	γ-(2,3-Me-6-TBS)	80°(5) – 230°(1.5°)	1.000[d]		123
3-Methylenanthic acid	γ-(2,3-Me-6-TBS)	80°(5) – 230°(1.5°)		(*S*)	123
4-Methylcarboxylic acids (C_6-C_9)	β-(2,3-Me-6-TBS)	90°(5) – 230°(1.5°)		(*R*)	123
4-Methylhexanoic acid	γ-(2,3-Me-6-TBS)	80°(5) – 230°(1.5°)	1.000[d]		123
	β-(2,3-Me-6-TBS)	90°(5) – 190°(1.5°)(20)		(4*R*)	130
4-Methylcarboxylic acids (C_8, C_9)	γ-(2,3-Me-6-TBS)	80°(5) – 230°(1.5°)		(*R*)	123
4-Ethyloctanoic acid	β-(2,3-Me-6-TBS)	90°(5) – 230°(1.5°)		(4*R*)	18, 19
	γ-(2,3-Me-6-TBS)	40°(5) – 100°(10°) – 130°(1°) – 235°(3°)		(4*R*)	19
4-Pentanolide	β-(2,3-Ac-6-TBS)	140°	1.422		108
4-Hexanolide	β-(2,3-Ac-6-TBS)	140°	1.221	(*R*)	108
4-Heptanolide	β-(2,3-Ac-6-TBS)	140°	1.061	(*R*)	108
4-Octanolide	β-(2,3-Ac-6-TBS)	155°	1.056	(*R*)	108
	β-(2,3-Me-6-TBS)	60°(13) – 108°(1.5°) – 200°(2.5°)		(*R*)	16
4-Nonanolide	β-(2,3-Ac-6-TBS)	160°	1.047	(*R*)	108
4-Decanolide	β-(2,3-Me-6-TBS)	60°(13) – 108°(1.5°) – 200°(2.5°)		(*R*)	16
	β-(2,3-Ac-6-TBS)	165°	1.043	(*R*)	108
4-Undecanolide	β-(2,3-Ac-6-TBS)	170°	1.042	(*R*)	108
4-Dodecanolide	β-(2,3-Ac-6-TBS)	175°	1.038	(*R*)	108
	β-(2,3-Me-6-TBS)	60°(13) – 108°(1.5°) – 200°(2.5°)		(*R*)	16
γ-Lactones (C_7-C_{12})	β-(2,6-Pe-3-Ac)			(*R*)-(+)	37
5-Hexanolide	β-(2,3-Ac-6-TBS)	140°	1.121	(*R*)	108
5-Octanolide	β-(2,3-Ac-6-TBS)	145°	1.070	(*S*)	108
5-Nonanolide	β-(2,3-Ac-6-TBS)	140°	1.039	(*S*)	108
5-Decanolide	β-(2,3-Ac-6-TBS)	155°	1.030	(*S*)	108
5-Undecanolide	β-(2,3-Ac-6-TBS)	170°	1.023	(*S*)	108
5-Dodecanolide	β-(2,3-Ac-6-TBS)	175°	1.022	(*S*)	108
δ-Lactones (C_8-C_{12})	β-(2,3-Ac-6-TBS)	45°(2) – 120°(20°)(15) – 125°(3°) – 175°(1.5°)		(*S*)	146
δ-Lactones (C_8-C_{14})	γ-(2,6-Pe-3-AcF)			(*S*)-(−)	37
δ-Lactones ($C_{13}-C_{18}$)	β-(2,3-Ac-6-TBS)	45°(2) – 120°(20°)(35) – 160°(2°) – 200°(1°)		(*S*)	146
	β-(2,3-Ac-6-TBS)	120°(15) – 220°(1.5°)		(*S*)	123

Table 4 (continued).

Selectand	Chiral selector	Column temperature (°C) or the temperature conditions	α	First-eluted enantiomer	Ref.
Dec-2-en-5-olide (massoilactone)	α-(2,6-Pe-3-Ac)	80° – 160°(1°)		(*S*)-(+)	147
4-Methyl-5-decanolide	β-(2,3-Me-6-TBS)	60°(13) – 108°(1.5°) – 200°(2.5°)		(*R*)	148
γ-Jasmine lactone	β-(2,6-Pe-3-Ac)			(+)	37
δ-Jasmine lactone	β-(2,6-Pe-3-Ac)			(*R*)-(−)	37
Sherry lactone	γ-(2,6-Pe-3-Bu)				149
Furaneol	β-(2,3-Me-6-TBS)	35°(2) – 80°(20°)(5) – 230°(1°)		(−)	150
2-Methyl-4-pentyl-1,3-dioxane	β-(2,3-Ac-6-TBS)	50°(30) – 220°(1°)		(2*S*,4*R*)	143
3-Mercapto-2-methylpropan-1-ol diacetate	β-(2,3-Me-6-TBS)	50° – 210°(1°)		(−)	17
trans-2-Methyl-4-propyl-1,3-oxathiane	β-(2,3,6-Me)			(2*R*,4*R*)-(+)	37
	β-(2,3-Ac-6-TBS)	100°	1.100	(2*R*,4*S*)	108
	γ-(2,3-But-6-TBS)	40°(5) – 105°(5°)(22) – 150°(1.5°) – 220°(1.5°)(30)		(2*R*,4*R*)	151
cis-2-Methyl-4-propyl-1,3-oxathiane	β-(2,3,6-Me)			(2*R*,4*S*)-(−)	37
	β-(2,3-Ac-6-TBS)	100°	1.227	(2*R*,4*R*)	108
	γ-(2,3-But-6-TBS)	40°(5) – 105°(5°)(22) – 150°(1.5°) – 220°(1.5°)(30)		(2*R*,4*S*)	151
2,2-Dimethyl-4-propyl-1,3-oxathiane	γ-(2,3-But-6-TBS)	40°(5) – 105°(5°)(22) – 150°(1.5°) – 220°(1.5°)(30)		(4*S*)	151
	β-(2,3-Ac-6-TBS)	80°	1.043		108
3-(Methylthio)hexan-1-ol	β-(2,3,6-Me)			(*R*)-(−)	37
	β-(2,3-Ac-6-TBS)	95°	1.035	(*S*)	108
2-Mercapto-3-pentanone	β-(2,3,6-Me)			(+)	37
3-(Methylthio)butanal	γ-(2,3-But-6-TBS)	50°(5) – 220°(1.5°)(30)		(*S*)	6
3-(Methylthio)butan-1-ol	γ-(2,3-But-6-TBS)	50°(5) – 220°(1.5°)(30)		(*S*)	6
3-Mercaptobutan-1-ol	γ-(2,3-But-6-TBS)	50°(5) – 220°(1.5°)(30)		(*S*)	6
3-Mercaptohexan-1-ol	β-(2,3-Ac-6-TBS)	95°	1.164	(*S*)	108
3-Mercaptohexyl acetate	γ-(2,3-But-6-TBS)	40°(5) – 105°(5°)(22) – 150°(1.5°) – 220°(1.5°)(30)		(*R*)	151
3-Mercaptohexyl propanoate	γ-(2,3-But-6-TBS)	40°(5) – 105°(5°)(22) – 150°(1.5°) – 220°(1.5°)(30)		(*R*)	151
3-Mercaptohexyl butanoate	γ-(2,3-But-6-TBS)	40°(5) – 105°(5°)(22) – 150°(1.5°) – 220°(1.5°)(30)		(*R*)	151
3-Butylhexahydrophthalide I	β-(2,3-Ac-6-TBS)	110°(120) – 120°(1.5°)(5) – 180°(1°)	1.037	(3*S*,3a*S*,7a*R*)	152
	β-(2,3-Ac-6-TBS)	40°(5) – 140°(60°)(25) – 180°(1.5°)	1.032	(3*S*,3a*S*,7a*R*)	152
3-Butylhexahydrophthalide II	β-(2,3-Ac-6-TBS)	110°(120) – 120°(1.5°)(5) – 180°(1°)	1.014	(3*S*,3a*R*,7a*S*)	152
	β-(2,3-Ac-6-TBS)	40°(5) – 120°(60°)(70) – 180°(1°)	1.018	(3*S*,3a*R*,7a*S*)	152
3-Butylhexahydrophthalide III	β-(2,3-Ac-6-TBS)	110°(120) – 120°(1.5°)(5) – 180°(1°)	1.010	(3*S*,3a*R*,7a*R*)	152
	β-(2,3-Ac-6-TBS)	40°(5) – 105°(60°)(120) – 125°(1.5°)(30)	1.009	(3*S*,3a*R*,7a*S*)	152
3-Butylhexahydrophthalide IV	β-(2,3-Ac-6-TBS)	110°(120) – 120°(1.5°)(5) – 180°(1°)	1.023	(3*S*,3a*S*,7a*S*)	152
	β-(2,3-Ac-6-TBS)	40°(5) – 140°(60°)(25) – 180°(1.5°)	1.031	(3*S*,3a*S*,7a*S*)	152
3-Butylphthalide	γ-(2,3-TBS)	140°(5) – 180°(2°)		(3*S*)	153
	β-(2,3-Ac-6-TBS)	95°(25) – 109°(2.5°)°(160) – 150°(1.2°)(30)		(3*S*)	154
3a,7a-*trans*-3-Butylhexahydrophthalide	β-(2,3-Ac-6-TBS)	95°(25) – 109°(2.5°)(160) – 150°(1.2°)(30)		(3*S*,3a*R*,7a*R*)	154
				(3*S*,3a*S*,7a*S*)	154
3a,7a-*cis*-3-Butylhexahydrophthalide	β-TBS [b]	140°(1) – 160°(1°)(1) – 200°(20°)(10)			155
	β-(2,3-Ac-6-TBS)	95°(25) – 109°(2.5°)(160) – 150°(1.2°)(30)		(3*S*,3a*S*,7a*R*)	154
3-Methylalkane-1-thiols	β-(2,3-Me-6-TBS)				6
Pentane-2-thiol	β-(2,3-Et-6-TBS)	40°	1.04	(*S*)	88
Solerole I	β-(2,3-Ac-6-TBS)	100°(20) – 200°(2°)		(4*S*,5*S*)	156
	γ-(2,6-Me-3-Pe)	110°(30) – 200°(1°)		(4*S*,5*S*)	156
Solerole II	β-(2,6-Me-3-Pe)	100°(20) – 200°(2°)		(4*R*,5*S*)	156
	γ-(2,6-Me-3-Pe)	110°(30) – 200°(1°)		(4*S*,5*R*)	156
Solerone	β-(2,3-Ac-6-TBS)	100°(20) – 200°(3°)		(*R*)	145
Lilial aldehyde	β-(2,3-Ac-6-TBS)	40°(5) – 110°(60°)(35) – 140°(1.5°)		(*S*)	20
2-Phenylpropanal	β-(2,3-Ac-6-TBS)	40°(5) – 100°(60°)(30)		(*R*)	157
2-Phenylpropanol	β-(2,3-Ac-6-TBS)	40°(5) – 100°(60°)(30)		(*R*)	157
2-Phenylpropanal dimethylacetal	β-(2,3-Ac-6-TBS)	40°(4) – 100°(60°)(10) – 140°(1.5°)		(*R*)	157
Arabinitol [c]	α-(2,3,6-Pe)	110°		(*D*)	118
Geosmin	β-(2,3-Me-6-TBS)	60°(35) – 200°(1.5°)		(+)	2

[a] The Chirasil-γ-Dex phase: the chiral selector γ-(2,6-Pe-3-But) is grafted to polymethylpolysiloxane through the octamethylene spacer; [b] 6-*tert*-butyldimethylsilyl-β-cyclodextrin in polysiloxane; [c] as pentakis(trifluoroacetyl) derivatives; [d] enantiomers are not resolved.

flavour compounds, such as mono- and sesquiterpenoids and related compounds (Table 1), sesquiterpene hydrocarbons (Table 2), diterpenoids (Table 3) and various aliphatic and alicyclic compounds (Table 4). These data include the types of chiral selectors (modified cyclodextrin), the temperature conditions of chromatography, the selectivity factors and the elution orders of enantiomers.

The following abbreviations are used in the tables to denote chiral cyclodextrin selectors involved in stationary phases: the nature of the starting cyclodextrin (α, β or γ) followed

(in parentheses) by the position and the nature of substituents in modified cyclodextrin molecules. For example, the notation β-(2,6-Me-3-Pe) means that the stationary phase for chiral GLC was prepared based on heptakis(2,6-di-*O*-methyl-3-*O*-n-pentyl)-β-cyclodextrin. For the temperature conditions, the following abbreviations are used: 60°(18) – 120°(1°)(10) – 200°(10°)(5). This means that heating is performed for 18 min at 60 °C followed by the rise of the temperature to 120 °C at a rate of 1 deg min^{-1}, storage at 120 °C for 10 min, the rise of the temperature to 200 °C at a rate of 10 deg min^{-1} and storage at 200 °C for 5 min. For many enantiomeric pairs, the selectivity factors (α) and first-eluted enantiomer are given.

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References

1. H G Haring, F Rijkens, H Boelens, A Van der Gen *J. Agric. Food Chem.* **20** 1018 (1972)
2. P Darriet, S Lamy, S La Guerche, M Pons, D Dubourdieu, D Blancard, P Steliopoulos, A Mosandl *Eur. Food Res. Technol.* **213** 122 (2001)
3. H Guth *Helv. Chim. Acta* **76** 1559 (1996)
4. E Brenna, C Fuganti, S Serra *Tetrahedron: Asymmetry* **14** 1 (2003)
5. R Zawirska-Wojtasiak *Food Chem.* **86** 113 (2004)
6. B Weber, A Mosandl *Z. Lebensm.-Unters.-Forsch. A* **204** 194 (1997)
7. B Faber, K Bangert, A Mosandl *Flavour Fragr. J.* **12** 305 (1997)
8. U Ravid, E Putievsky, I Katzir *Flavour Fragr. J.* **8** 225 (1993)
9. F Tateo, M Bononi, E D Dominicis, V Fumagalli *Anal. Commun.* **36** 149 (1999)
10. Y Holm, P Vuorela, R Hiltunen *Flavour Fragr. J.* **12** 397 (1997)
11. P Kreis, A Mosandl *Flavour Fragr. J.* **9** 249 (1994)
12. U Hener, S Faulhaber, P Kreis, A Mosandl *Pharmazie* **50** 60 (1995)
13. I H Hardt, A Reick, C Fricke, W A Königt *Flavour Fragr. J.* **10** 165 (1995)
14. A Kaunzinger, M Wüst, H Grobmiller, S Burow, U Hemmrich, A Dietrich, T Beck, U Hener, A Mosandl, A Rapp *Z. Lebensm.-Unters.-Forsch. A* **203** 499 (1996)
15. T Beuerle, P Schreier, P Brunerie, C Bicchi, W Schwab *Phytochemistry* **43** 145 (1996)
16. M Kreck, A Scharrer, S Bilke, A Mosandl *Eur. Food Res. Technol.* **213** 389 (2001)
17. P Bouchilloux, P Darriet, D Dubourdieu, R Henry, S Reichert, A Mosandl *Eur. Food Res. Technol.* **210** 349 (2001)
18. V Karl, A Kauzinger, J Gutser, P Steuer, J Angles-Angel, A Mosandl *Chirality* **6** 420 (1994)
19. V Karl, J Gutser, A Dietrich, B Maas, A Mosandl *Chirality* **6** 427 (1994)
20. D Bartschat, S Börner, A Mosandl, J W Bats *Z. Lebensm.-Unters.-Forsch. A* **205** 76 (1997)
21. R Reinhardt, A Steinborn, W Engewald, K Anhalt, K Schulze *J. Chromatogr., A* **697** 475 (1995)
22. A Steinborn, R Reinhardt, W Engewald, K Wyssuwa, K Schulze *J. Chromatogr., A* **697** 485 (1995)
23. F Quattrini, G Biressi, M Juza, M Mazzotti, C Fuganti, M Morbidelli *J. Chromatogr., A* **865** 201 (1999)
24. T J Ward *Anal. Chem.* **74** 2863 (2002)
25. N R Srinivas, W C Shyu, R H Barbhaiya *Biomed. Chromatogr.* **9** 1 (1995)
26. G Sàndor *Fresenius' J. Anal. Chem.* **362** 4 (1998)
27. K-R Kim, J Lee, D Ha, J H Kim *J. Chromatogr., A* **891** 257 (2000)
28. W A König *TrAC — Trends Anal. Chem.* **12** 130 (1993)
29. V Schurig *TrAC — Trends Anal. Chem.* **21** 647 (2002)
30. L A Kartsova *Molekulyarnoe Raspoznavanie v Khromatografii: Ispol'zovanie Makrotsiklov v Sostave Khromatograficheskikh Faz* (Molecular Recognition in Chromatography: The Use of Macrocycles in Chromatographic Phases) (St Petersburg: St Petersburg State University, 2004)
31. Z Juvancz, P Petersson *J. Microcolumn Sep.* **8** 99 (1996)
32. B Feibush *Chirality* **10** 382 (1998)
33. V Schurig *J. Chromatogr., A* **906** 275 (2001)
34. V Schurig *J. Chromatogr., A* **965** 315 (2002)
35. W A König *Gas Chromatographic Enantiomer Separation with Modified Cyclodextrins* (Heidelberg: Hüthig, 1992)
36. A Mosandl *J. Chromatogr., A* **624** 267 (1992)
37. P Werkhoff, S Brennecke, W Bretschneider, M Güntert, R Hopp, H Surburg *Z. Lebensm.-Unters.-Forsch. A* **196** 307 (1993)
38. A Mosandl *Food Rev. Int.* **11** 597 (1995)
39. C Bicchi, V Manzin, A D'Amato, P Rubiolo *Flavour Fragr. J.* **10** 127 (1995)
40. C Bicchi, A D'Amato, P Rubiolo *J. Chromatogr., A* **843** 99 (1999)
41. M Wmst, A Mosandl *Eur. Food Res. Technol.* **209** 3 (1999)
42. R G Mariaca, M I Imhof, J O Bosset *Eur. Food Res. Technol.* **212** 253 (2001)
43. L He, T E Beesley *J. Liq. Chromatogr. Relat. Technol.* **28** 1075 (2005)
44. M V Rekharsky, Y Inoue *Chem. Rev.* **98** 1875 (1998)
45. E Schneiderman, A M Stalcup *J. Chromatogr., B* **745** 83 (2000)
46. J Szejtli *Chem. Rev.* **98** 1743 (1998)
47. W A König, R Krebber, G Wenz *J. High Resolut. Chromatogr.* **12** 641 (1989)
48. Yu A Zhdanov, Yu E Alekseev, E V Kompantseva, E N Vergeichik *Usp. Khim.* **61** 1025 (1992) [*Russ. Chem. Rev.* **61** 563 (1992)]
49. M Asztemborska, D Sybilska, R Nowakowski, G Perez *J. Chromatogr., A* **1010** 233 (2003)
50. R Reinhardt, W Engewald, U Himmelreich, B Christian, B Koppenhoefer *J. Chromatogr. Sci.* **33** 236 (1995)
51. W A König, C Fricke, Y Saritas, B Momeni, G Hohenfeld *J. High Resolut. Chromatogr.* **20** 55 (1997)
52. W A König *Chirality* **10** 499 (1998)
53. V Schurig, H-P Nowotny *J. Chromatogr., A* **441** 155 (1988)
54. H-G Schmarr, A Mosandl, A Kaunzinger *J. Microcolumn Sep.* **3** 395 (1991)
55. A Dietrich, B Maas, G Brand, V Karl, A Kaunzinger, A Mosandl *J. High Resolut. Chromatogr.* **15** 769 (1992)
56. A Dietrich, B Maas, A Mosandl *J. Microcolumn Sep.* **6** 33 (1994)
57. W A König, S Lutz, P Mischnick-Lübbecke, B Brassat, G Wenz *J. Chromatogr.* **447** 193 (1988)
58. W A König, S Lutz, G Wenz *Angew. Chem., Int. Ed. Engl.* **27** 979 (1988)
59. W A König, S Lutz, G Wenz, E von der Bey *J. High Resolut. Chromatogr.* **11** 506 (1988)
60. W A König, S Lutz, C Colberg, N Schmidt, G Wenz, E von der Bey, A Mosandl, C Günther, A Kustermann *J. High Resolut. Chromatogr.* **11** 621 (1988)
61. W A König, S Lutz, M Hagen, R Krebber, G Wenz, K Baldenius, J Ehlers, H T Dieck *J. High Resolut. Chromatogr.* **12** 35 (1989)
62. W A König, R Krebber, P Mischnick *J. High Resolut. Chromatogr.* **12** 732 (1989)
63. W A König, R Krebber, G Wenz *J. High Resolut. Chromatogr.* **12** 641 (1989)
64. W A König, D Icheln, T Runge, I Pforr, A Krebs *J. High Resolut. Chromatogr.* **13** 702 (1990)
65. G Wenz, P Mischnick, R Krebber, M Richters, W A König *J. High Resolut. Chromatogr.* **13** 724 (1990)
66. W A König, B Gehrcke, D Icheln, P Evers, J Dönnecke, W Wang *J. High Resolut. Chromatogr.* **15** 367 (1992)
67. C Bicchi, G Artuffo, A D'Amato, V Manzin, A Galli, M Galli *J. High Resolut. Chromatogr.* **16** 209 (1993)
68. I H Hardt, W A König *J. Microcolumn Sep.* **5** 35 (1993)
69. C Bicchi, A D'Amato, V Manzin, A Galli, M Galli *J. Microcolumn Sep.* **7** 327 (1995)

70. C Bicchi, A D'Amato, V Manzin, A Galli, M Galli *J. Chromatogr., A* **742** 161 (1996)
71. H Grosenick, V Schurig *J. Chromatogr., A* **761** 181 (1997)
72. T J Betts *J. Chromatogr., A* **724** 403 (1996)
73. M Junge, W A König *J. Sep. Sci.* **26** 1607 (2003)
74. G Chen, X Shi *Anal. Chim. Acta* **498** 39 (2003)
75. H Cousin, O Trapp, V Peulon-Agasse, X Pannecoucke, L Banspach, G Trapp, Z Jiang, J C Combret, V Schurig *Eur. J. Org. Chem.* 3273 (2003)
76. A Jaus, M Oehme *J. Chromatogr., A* **905** 59 (2001)
77. J Jindrich, J Pitha, B Lindberg, P Seffers, K Harata *Carbohydr. Res.* **266** 75 (1995)
78. M-Y Nie, L-M Zhou, X-L Liu, Q-H Wang, D-Q Zhu *Anal. Chim. Acta* **408** 279 (2000)
79. C Bicchi, G Brunelli, G Cravotto, P Rubiolo, M Galli *J. Sep. Sci.* **25** 125 (2002)
80. S Tamogami, K-i Awano, M Amaike, Y Takagi, T Kitahara *Flavour Fragr. J.* **16** 349 (2001)
81. A Ruderisch, J Pfeiffer, V Schurig *J. Chromatogr., A* **994** 127 (2003)
82. P A Levkin, A Levkina, H Czesla, S Nazzi, V Schurig *J. Sep. Sci.* **30** 98 (2007)
83. J Dönnecke, W A König, O Gyllenhaal, J Vessman, C Schulze *J. High Resolut. Chromatogr.* **17** 779 (1994)
84. V Schurig, M Jung, S Mayer, M Fluck, H Negura, H Jakubetz *J. Chromatogr., A* **694** 119 (1995)
85. H F Kasai, M Tsubuki, K Takahashi, M Shirao, Y Matsumoto, T Honda, Y Seyama *J. Chromatogr., A* **977** 125 (2002)
86. H Grosenick, V Schurig, J Costante, A Collet *Tetrahedron: Asymmetry* **6** 87 (1995)
87. W A König, N Bülow, Y Saritas *Flavour Fragr. J.* **14** 367 (1999)
88. T König, C Ruff, M Kleinschnitz, P Schreier, N Fischer, W Neugebauer *J. High Resolut. Chromatogr.* **21** 371 (1998)
89. A Hinterholzer, P Schieberle *Flavour Fragr. J.* **13** 49 (1998)
90. J Beens, U A T Brinkman *Analyst (Cambridge, UK)* **130** 123 (2005)
91. R Shellie, P J Marriott *Anal. Chem.* **74** 5426 (2002)
92. I Hardt, W A König *J. Chromatogr., A* **666** 611 (1994)
93. W A König, A Reick, I Hardt, B Gehrcke, K-H Kubeczka, H Muhle *J. High Resolut. Chromatogr.* **17** 315 (1994)
94. M M Sonwa, W A König, K-H Kubeczka, O Motl *Phytochemistry* **45** 1435 (1997)
95. C Fricke, A Reick, I H Hardt, W A König, H Muhle *Phytochemistry* **39** 1119 (1995)
96. A M Adio, C Paul, P Kloth, W A König *Phytochemistry* **65** 199 (2004)
97. W A König, A Reick, Y Saritas, I H Hardt, K-H Kubeczka *Phytochemistry* **42** 461 (1996)
98. C Bicchi, A D'Amato, V Manzin, A Galli, M Galli *J. High Resolut. Chromatogr.* **20** 493 (1997)
99. C Bicchi, C Balbo, A D'Amato, V Manzin, P Schreier, A Rozenblum, P Brunerie *J. High Resolut. Chromatogr.* **21** 103 (1998)
100. M Juza, E Braun, V Schurig *J. Chromatogr., A* **769** 119 (1997)
101. N Bülow, W A König *Phytochemistry* **55** 141 (2000)
102. *J. High Resolut. Chromatogr.* **16** 312 (1993)
103. W A König *J. High Resolut. Chromatogr.* **16** 338 (1993)
104. W A König *J. High Resolut. Chromatogr.* **16** 569 (1993)
105. T Beuerle, W Schwab *Z. Lebensm.-Unters.-Forsch. A* **205** 215 (1997)
106. B Koppenhoefer, U Epperlein *J. Chromatogr. Sci.* **33** 244 (1995)
107. I Roling, H-G Schmarr, W Eisenreich, K-H Engel *J. Agric. Food Chem.* **46** 668 (1998)
108. B Maas, A Dietrich, A Mosandl *J. High Resolut. Chromatogr.* **17** 169 (1994)
109. P Kreis, A Dietrich, A Mosandl *Pharmazie* **49** 761 (1994)
110. U Ravid, E Putievsky, I Katzir, E Lewinsohn, N Dudai *Flavour Fragr. J.* **12** 109 (1997)
111. P Herion, G Full, P Winterhalter, P Schreier, C Bicchi *Phytochem. Anal.* **4** 235 (1993)
112. S Reichert, M Wüst, T Beck, A Mosandl *J. High Resolut. Chromatogr.* **21** 185 (1998)
113. W A König, A Krüger, D Icheln, T Runge *J. High Resolut. Chromatogr.* **15** 184 (1992)
114. W A König, R Krebber, P Evers, G Bruhn *J. High Resolut. Chromatogr.* **13** 328 (1990)
115. P Kreis, A Mosandl *Flavour Fragr. J.* **7** 187 (1992)
116. H J Bouwmeester, J A R Davies, H Toxopeus *J. Agric. Food Chem.* **43** 3057 (1995)
117. L Mondello, M Catalfamo, C Dugo, P Dugo *J. Microcolumn Sep.* **10** 203 (1998)
118. W A König *Drug Stereochemistry. Analytical Methods and Pharmacology* (Ed. I W Wainer) (New York: Marcel Dekker, 1993) p. 107
119. N Yassaa, B Y Meklati, A Cecinato *Atmos. Environ.* **34** 2809 (2000)
120. G P Blanch, G J Nicholson *J. Chromatogr. Sci.* **36** 37 (1998)
121. F Luan, D Hampel, A Mosandl, M Wüst *J. Agric. Food Chem.* **52** 2036 (2004)
122. T Köpke, A Mosandl *Z. Lebensm.-Unters.-Forsch. A* **194** 372 (1992)
123. B Maas, A Dietrich, V Karl, A Kaunzinger, D Lehmann, T Köpke, A Mosandl *J. Microcolumn Sep.* **5** 421 (1993)
124. B Faber, A Dietrich, A Mosandl *J. Chromatogr., A* **666** 161 (1994)
125. W Neugebauer, P Schreier *J. Agric. Food Chem.* **43** 1647 (1995)
126. B Dollman, G Full, P Schreier, P Winterhalter, M Güntert, H Sommer *Phytochem. Anal.* **6** 106 (1995)
127. G Full, P Winterhalter, G Schmidt, P Herion, P Schreier *J. High Resolut. Chromatogr.* **16** 642 (1993)
128. G Schmidt, G Full, P Winterhalter, P Schreier *J. Agric. Food Chem.* **43** 185 (1995)
129. G Schmidt, W Neugebauer, P Winterhalter, P Schreier *J. Agric. Food Chem.* **43** 1898 (1995)
130. D Bartschat, C Kuntzsch, M Heil, A Schittrigkeit, K Schumacher, M Mang, A Mosandl, R Kaiser *Phytochem. Anal.* **8** 159 (1997)
131. S Melching, N Bülow, K Wihstutz, S Jung, W A König *Phytochemistry* **44** 1291 (1997)
132. Y Saritas, N Bülow, C Fricke, W A König, H Muhle *Phytochemistry* **48** 1019 (1998)
133. C O Schmidt, H J Bouwmeester, J-W de Kraker, W A König *Angew. Chem., Int. Ed.* **37** 1400 (1998)
134. M M Sonwa, W A König *Phytochemistry* **58** 799 (2001)
135. W A König, A Reick, C Fricke, S Melching, Y Saritas, I H Hardt *Proceedings of the 13th International Congress of Flavours, Fragrances and Essential Oils* (Ed. K-H C Baser) (Istanbul: AREP Publ., 1995) p. 169
136. S Melching, A Blume, W A König, H Muhle *Phytochemistry* **48** 661 (1998)
137. Y Saritas, M M Sonwa, H Iznaguen, W A König, H Muhle, R Mues *Phytochemistry* **57** 443 (2001)
138. W A König, N Bülow, C Fricke, S Melching, A Reick, H Muhle *Phytochemistry* **43** 629 (1996)
139. M Pietsch, W A König *J. High Resolut. Chromatogr.* **20** 257 (1997)
140. M Pietsch, W A König *Phytochem. Anal.* **11** 99 (2000)
141. H Oikawa, H Toshima, S Ohashi, W A König, H Kenmoku, T Sassa *Tetrahedron Lett.* **42** 2329 (2001)
142. B Maas, A Dietrich, D Bartschat, A Mosandl *J. Chromatogr. Sci.* **33** 223 (1995)
143. C Dietrich, T Beuerle, B Withopf, P Schreier, P Brunerie, C Bicchi, W Schwab *J. Agric. Food Chem.* **45** 3178 (1997)
144. T Kajiwara, Y Akakabe, K Matsui, K Kodama, H Koga, T Nagakura *Phytochemistry* **45** 529 (1997)
145. D Häring, T König, B Withopf, M Herderich, P Schreier *J. High Resolut. Chromatogr.* **20** 351 (1997)
146. D Lehmann, B Maas, A Mosandl *Z. Lebensm.-Unters. -Forsch. A* **201** 55 (1995)
147. A Bernreuther, V Lander, M Huffer, P Schreier *Flavour Fragr. J.* **5** 71 (1990)
148. D Bartschat, D Lehmann, A Dietrich, A Mosandl, R Kaiser *Phytochem. Anal.* **6** 130 (1995)
149. R Näf, A Jaquier, A F Boschung, M Lindström *Flavour Fragr. J.* **10** 243 (1995)

150. G Bruche, A Dietrich, A Mosandl *Z. Lebensm.-Unters.-Forsch. A* **201** 249 (1995)
151. B Weber, B Maas, A Mosandl *J. Agric. Food Chem.* **43** 2438 (1995)
152. D Bartschat, M Wüst, A Mosandl, H Hanssum *J. High Resolut. Chromatogr.* **20** 251 (1997)
153. D Bartschat, B Maas, S Smietana, A Mosandl *Phytochem. Anal.* **7** 131 (1996)
154. D Bartschat, T Beck, A Mosandl *J. Agric. Food Chem.* **45** 4554 (1997)
155. G G G Manzardo, S Kürsteiner-Laube, D Perrin *Z. Lebensm.-Unters.-Forsch. A* **203** 501 (1996)
156. D Krajewski, W Neugebauer, I K Amajoyi, P Schreier, C Bicchi *Z. Lebensm.-Unters.-Forsch. A* **201** 378 (1995)
157. D Bartschat, A Mosandl *Z. Lebensm.-Unters.-Forsch. A* **202** 266 (1996)