TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVB SUBSTANCES

RESULTS OF THE EVALUATION OF THE PBT/VPVB PROPERTIES OF:

Substance name: Terpenes and Terpenoids, turpentine-oil, 3-carene fraction

EC number: 294-866-9

CAS number: 91770-80-8

Molecular formula: not applicable

Structural formula: not applicable

Summary of the evaluation:

It is concluded that terpenes and terpenoids, turpentine-oil, 3-carene fraction is not considered as a PBT substance based on the properties of its constituents. The substance may contain, depending on the producer, impurities, which are potential PBT/vPvB-substances based on QSAR-estimates.

Terpenes and terpenoids, turpentine-oil, 3-carene fraction does not fulfil the PBT criteria based on mainly screening data on monoterpenes, which are expected to be main constituents in the substance. One of the monoterpenes (camphene) may meet the P/vP criteria according to screening data. Other monoterpenes included do not meet the P/vP criteria on the basis of screening data. The monoterpenes do not meet the B criterion based on screening data. An experimental BCF for camphene confirms the conclusion. Terpene derivatives, which are expected to be present as impurities, do not fulfil the P/vP and B criteria based on screening data.

β-pinene (one of the main constituents) is concluded to not fulfil the T criterion and this conclusion is applicable also for α-pinene (one of the main constituents) due to a structural similarity. For other substances the ecotoxicity assessment was not completed.

The substance may contain as impurity sesquiterpenes, which may fulfil the P/vP, B/vB and T criteria based on QSAR-estimates of the most common sesquiterpene, β-caryophyllane.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name: Terpenes and Terpenoids, turpentine-oil, 3-carene fraction
EC Number: 294-866-9
CAS Number: 91770-80-8
IUPAC Name:
Molecular Formula: not applicable
Structural Formula: not applicable
Molecular Weight: not applicable
Synonyms: Dipentene, Oulu 405, Oulu 405T; turpentine, 3-carene fraction

1.1 Purity/impurities/additives

Terpenes and Terpenoids, turpentine-oil, 3-carene fraction ("δ-carene fraction") belongs to the group of UVCBs.

Composition of turpentine ("raw turpentine", "turpentine oil"), the starting material for δ-carene fraction, is presented in **Table 1.1a**. Distillation of turpentine oil in reduced pressure produces δ-carene fraction among other fractions. The composition of δ-carene fraction, as reported by industry, has been described in **Table 1.1b**. Compounds most often reported in industrial turpentine products (e.g. in turpentine) are listed in **Table 1.1c**. Structural formula of these compounds are included in the Annex. These compounds are also the constituents covered by the PBT-assessment because they can be expected due to the production technique to be present in the substance at least in trace levels depending on the producer.

Table 1.1a Composition of turpentine according to Gullichen and Fogelholm (1999)

Consituent/impuritiy	Concentration (% w/w)
α-pinene, CAS 80-56-8 and 7785-70-8	60-83
β-pinene, CAS 127-91-3	2-7
δ-carene, CAS 13466-78-9	11-28
Others : camphene (CAS 79-92-5), dipentene monoterpenes	2-6
Higher boiling terpenes, terpenalcohols, sesquiterpenes	5-10

Table 1.1b Constituents in δ-carene fraction according to suppliers (Suomen kemianteollisuus 1998; Arizona Chemicals, 2002)

Consituent/impuritiy	Concentration (% w/w)
δ –carene, CAS 13466-78-9	60
Other monoterpenes : Dipentene, CAS 138-86-3 Camphene, CAS 79-92-5 etc.	40

Table 1.1c Substances (as pure substances) included in the assessment

CAS	Common substance name (used in this report)	Name in EINECS
	C10H16 –terpenes (monoterpenes)	
80-56-8(1)	α-pinene	Pin-2(3)-ene
127-91-3(2)	β-pinene	Pin-2(10)-ene
13466-78-9(2)	δ-carene	3,7,7-trimethylbicyclo[4.1.0] hept-3-ene
79-92-5(1)	Camphene	Camphene
5989-27-5(1)	Limonene/dipentene	(R)-p-metha-1,8-diene
	Terpene- derivatives	
104-46-1(2)	Anethole	Anethole
104-67-6(2)	Methylchavicol	Undecan-4-olide
	C15H24 –terpenes (sesquiterpenes)	
87-44-5(2)	β -caryophyllane	Caryophyllene

1) The substance is also produced/imported under this CAS-nr. at HPV –level. The marketed substance may contain also other constituents.
2) The substance is also produced/imported under this CAS-nr. at LPV –level. The marketed substance may contain also other constituents.

1.2 Physico-chemical properties

Table 1.2 Summary of physico-chemical properties. For details and references, see European Commission (2000a)

REACH ref Annex, §	Property	Value	Comments
V, 5.1	Physical state at 20 C and 101.3 Kpa	liquid	
V, 5.2	Melting / freezing point	-	
V, 5.3	Boiling point	162-174°C at 1013 hPa	Forchem Oy (data not evaluated)
V, 5.5	Vapour pressure	2 hPa at 20°C	Forchem Oy; for δ-carene (data not evaluated)
V, 5.7	Water solubility	"insoluble"	Forchem Oy (data not evaluated)
V, 5.8	Partition coefficient n-octanol/water (log value)	4.5-5.5 (at 35°C) at pH 2	OECD 117; Forchem Oy (data not evaluated)
VII, 5.19	Dissociation constant	-	

Water solubility and logKow of the possible constituents and impurities are presented in **Table 4.2** in Section 4.3.1.

2 MANUFACTURE AND USES

Two companies have notified the substance under Regulation 93/793/EEC. The raw material of the substance is turpentine ("turpentine oil", "raw turpentine"), which is captured from process vapours of steaming and cooking phases in pulp mills. According to Gullichen and Fogelholm (1999), the purity of turpentine varies depending on at which phase of the pulping process it is obtained. Steaming phase produces the purest fraction. Variation of the contents can be also expected to be caused by the quality variation in the raw material (softwood).

Turpentine is further distilled to gain monoterpene fractions like α-pinene-fraction, β-pinene-fraction, δ-carene fraction and gum turpentine. Distillate residues contain higher boiling terpenes, terpenalcohols and sesquiterpenes (Gullichen and Fogelholm, 1999).

3 CLASSIFICATION AND LABELLING

The substance is not classified under Directive 67/548/EEC.

4 ENVIRONMENTAL FATE PROPERTIES

4.1 Degradation (P)

4.1.1 Abiotic degradation

These terpene and terpenoid compounds are not expected to be susceptible to hydrolysis in surface water. In the atmosphere, these compounds react with free radicals and ozone formed in the atmosphere from ions, such as nitrate, chloride, and ammonium, in the presence of sunlight (Corchnoy and Atkinson, 1990). Calculated T½ in the air for α-pinene is less than 3 hours (AOPWIN v 1.92). This abiotic degradation evaluation relies on secondary sources and no experimental abiotic degradation study reports were evaluated or located under this assessment.

4.1.2 Biotic degradation

The available data on biodegradation of the expected constituents and impurities are presented in **Table 4.1**.

Table 4.1 Persistency of possible constituents and impurities in δ-carene fraction

	BIOWIN 2 v4.02	BIOWIN 3 v4.02	BIOWIN 6 v4.02	Experimental data	Screening (v)P criteria fulfilled? (see also Section 4.1.4)
C10H16 – terpenes (monoterpenes)					
α-pinene	0.34	2.69	0.33	Readily biodegradable. 62% mineralization in 28 days, 70% in 42 days; OECD 301B, closed bottles used (Astra Zeneca, 2004a)	No
β-pinene	0.34	2.69	0.39	No data on pure substance. In a test with gum terpentine (50.8% α-pinene, 36.8% β-pinene), 52% mineralization in 28 days was observed; OECD 301B-test, closed bottles used (Astra Zeneca, 2001). When comparing to the test result with pure α-pinene it can be concluded that β-pinene did not slow down the biodegradation significantly. Hence β-pinene is considered biodegradable.	No (at limit)
δ-carene	0.34	2.69	0.33	Not readily biodegradable. 53% mineralization in 28 days, 74% in 42 days; OECD 301B, closed bottles used (Astra Zeneca, 2004b). Degradation curve did not reach plateau at day 42. δ-carene can be considered as biodegradable.	No (at limit)
camphene	0.34	2.69	0.39	Not readily biodegradable. 1-4% in 28 days in an OECD 301C -test (MITI 1992). Other test –results cited in European Commission (2000b) support the result (data not evaluated)	Yes

	BIOWIN 2 v4.02	BIOWIN 3 v4.02	BIOWIN 6 v4.02	Experimental data	Screening (v)P criteria fulfilled? (see also Section 4.1.4)
limonene/dipentene	0.75	2.90	0.33	Readily biodegradable. > 70% degradation in 28 days in an OECD 301C -test (MITI 1992).	No
Terpene-derivatives				-	
anethole	0.96	2.81	0.54	-	No
methylchavicol (C11H20O2)	0.998	3.23	0.93	-	No
C15H24–terpenes (sesquiterpenes)				-	
β -caryophyllane	0.17	2.54	0.13	-	Yes

4.1.3 Other information [1]

No data available.

4.1.4 Summary and discussion of persistence

Standard ready biodegradability test results are available for the monoterpenes included in this assessment. Of these substances only camphene seems to be not biodegradable. It is not possible to judge whether this difference is caused by an arbitrary test error or by a true difference in the degradation rate. It must be noted that camphene has very similar BIOWIN –estimates as the other monoterpenes. On the other hand, applicability of BIOWIN for monoterpenes and β-caryophyllane is questionable, because the program does not calculate any fragment corrections for specific substructure entities and uses instead a molecular weight correction factor. The quaternary carbons are identified as "carbon with 4 single bonds and no hydrogens" without distinguishing the cyclic structure they are connected with. For the two terpene derivatives anethole and methylchavicol BIOWIN predicts ready biodegradability. For these two substances BIOWIN domain is considered more reliable.

In the absence of experimental data for the sesquiterpene β-caryophyllane, an overall conclusion is drawn that the substance is potentially persistent.

4.2 Environmental distribution

Data not reviewed for this report.

[1] For example, half life from field studies or monitoring data

4.2.1 Adsorption

4.2.2 Volatilisation

4.2.3 Long-range environmental transport

4.3 Bioaccumulation (B)

4.3.1 Screening data

The available data on water solubility, logKow and bioaccumulation for expected constituents and impurities of δ-carene fraction are presented in **Table 4.2**.

Table 4.2 Water solubility, logKow and BCF of possible constituents and impurities

	Water solubility (mg l^{-1} at 25ºC)	LogKow	BCF	B/vB criterion fulfilled? (see also Section 4.3.4)
$C_{10}H_{16}$ – terpenes (monoterpenes)				
α-pinene	4.07 (WSKOW v1.41) 2.49 (Li and Perdue, 1995 in WSKOW exper. database)	4.27 (KOWWIN v1.67) 4.83 (Li and Perdue, 1995 in KOWWIN exper. database)	1,045 (BCFWIN v2.15 using logKow of 4.83)	No (screening data)
β-pinene	7.06 (WSKOW v1.41)	4.35 (KOWWIN v1.67) 4.16 (Griffin et al., 1999, in KOWWIN exper. database)	446 (BCFWIN v2.15 using logKow of 4.35)	No (screening data)
δ-carene	4.58 (WSKOW v1.41) 2.91 (WSKOW v1.41)	4.61 (KOWWIN v1.67) 4.38 (Griffin et al., 1999, in KOWWIN exper. database)	708 (BCFWIN v2.15 using logKow of 4.61)	No (at the limit; screening data)
camphene	6.27 (WSKOW v1.41) 4.6 (Chem Inspect Test Inst WSKOW exper. database) 4.2 (at 20 ºC; Hoechst AG, 1991 in European Commission,2000b; data not evaluated)	4.35 (KOWWIN v1.67) 4.22 (Griffin et al., 1999, in KOWWIN exper. database)	446 (BCFWIN v2.15 using logKow of 4.35) 606-1,290 (MITI, 1992; OECD 305 with *Cyprinus carpio*, test conc. 1.5 mg l^{-1})	No
limonene/ dipentene	4.58 (WSKOW v1.41) 13.8 (Massaldi and King, 1979, WSKOW exper. database)	4.83 (KOWWIN v1.67) 4.57 (Li and Perdue, 1995 in KOWWIN exper. database) 4.38 (Griffin et al., 1999, in KOWWIN exper. database)	1,045 (BCFWIN v2.15 using logKow of 4.83)	No (screening data)
Terpene-derivatives				

	Water solubility (mg l-1 at 25ºC)	LogKow	BCF	B/vB criterion fulfilled? (see also Section 4.3.4)
anethole	98.68 (WSKOW v1.41) 111 (Yalkowsky and Dannefels, 1992, WSKOW exper. database)	3.39 (KOWWIN v1.67)	81 (BCFWIN v2.15 using logKow of 3.39)	No (screening data)
methylchavicol	128.3 (WSKOW v1.41)	3.06 (KOWWIN v1.67)	128.3 (BCFWIN v2.15 using logKow of 3.06)	No (screening data)
C15H24–terpenes (sesquiterpenes)				
β -caryophyllane	0.05 (WSKOW v1.41)	6.3 (KOWWIN v1.67)	14,200 (BCFWIN v2.15 using logKow of 6.3)	Yes (screening data)

4.3.2 Measured bioaccumulation data

An experimentally derived BCF is available only for camphene (see **Table 4.2**).

4.3.3 Other supporting information[2]

No data available.

4.3.4 Summary and discussion of bioaccumulation

Experimental data on bioaccumulation are available only for camphene. Testing would be hence necessary to determine the actual bioaccumulation potential for the remaining compounds. Testing of the substance as a whole is not appropriate for this assessment due to the multitude and probably large concentration range of the anticipated constituents and impurities. The most important candidate for testing would be β-caryophyllane, which is predicted to have a very high bioaccumulation potential.

Other compounds included are expected to have a moderate to high bioaccumulation potential based on BCFWIN–estimates. Part of the logKow –values available for α-pinene, δ-carene and limonene are slightly higher than the screening criterion of 4.5. However, it is considered that BCFWIN estimates for these monoterpenes are in line with the BCFWIN-estimate and the measured BCF for camphene. Therefore BCFWIN estimates of monoterpenes are considered reliable enough to conclude that these substances are not likely to exceed the B criterion. The two terpene derivatives anethole and methylchavicol do not meet the B criterion based on their logKow-values. Hence, further bioaccumulation testing of monoterpenes and terpene derivatives is not needed in the frame of this assessment.

5 HUMAN HEALTH HAZARD ASSESSMENT

Data not reviewed for this report.

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[2]For example, measured concentrations in biota

6 ENVIRONMENTAL HAZARD ASSESSMENT

Table 6.1 presents the available ecotoxicity data on the substances included. The available data, where δ-carene fraction has been used as a test substance, have not been included here as they do not reflect the possible ecotoxicity of minor constituents and impurities. Long-term ecotoxicity data are available only for β-pinene. Due to the similarity of α-pinene and β-pinene, the result is applicable also for α-pinene. Chronic testing of the other constituents and impurities would be necessary to determine the actual level of ecotoxicity.

Table 6.1 Ecotoxicity of expected constituents and impurities of δ-carene fraction. The results have been cited in European Commission (2000a and 2000b), and partly in confidential IUCLIDs

	Ecotoxicity
C10H16 – terpenes (monoterpenes)	
α-pinene	Only short-term data are available. With pure substance: 96-hour LC_{50} = 0.28 mg l^{-1} 96-hour LC_{50} = 1 mg l^{-1} *Chaetogammarus marinus* (NOEC 0.18 mg l^{-1}) 48-hour EC_{50} = 41 mg l^{-1} Daphnia Several test results with gum terpentine containing α-pinene available.
β-pinene	48-hour EC_{50} = 1.25 mg l^{-1} Daphnia 48-hour EC_{50} = 1.44 mg l^{-1} Green algae 60-day LOEC = 320 µg l^{-1} (growth rainbow trout fry) (Passino-Reader et al., 1995)
δ-carene	No data on pure substance available.
camphene	48-hour LC_{50} = 2 mg l^{-1} fish (MITI, 1992) 48-hour LC_{50} <1.8 mg l^{-1} 72-hour LC_{50} < 2 mg l^{-1} 96-hour LC_{50} < 0.19 mg l^{-1}
limonene/dipentene	-
Terpene-derivatives	-
anethole	-
methylchavicol	LC/EC_{50} 17-1,500 mg l^{-1}
C15H24–terpenes (sesquiterpenes)	
β -caryophyllane	ECOSAR v0.99 (logKow of 6.3 used): 96-hour LC_{50} = 0.014 mg l^{-1} (fish) 48-hour EC_{50} = 0.020 mg l^{-1} (daphnia) 96-hour EC_{50} = 0.012 mg l^{-1} (green algae) 30-day EC_{50} = 0.004 mg l^{-1} (fish)

6.1 Aquatic compartment (including sediment)

See **Table 6.1**.

6.1.1 Toxicity test results

6.1.1.1 Fish

Acute toxicity

Long-term toxicity

6.1.1.2 Aquatic invertebrates

Acute toxicity

Long-term toxicity

6.1.1.3 Algae and aquatic plants

6.1.2 Sediment organisms

No data available.

6.1.3 Other aquatic organisms

Data not evaluated for this report.

6.2 Terrestrial compartment

No data available.

6.3 Atmospheric compartment

No data available.

7 PBT AND vPvB

7.1 PBT, vPvB assessment

Terpenes and Terpenoids, turpentine-oil, 3-carene fraction ("δ-carene fraction") is expected to contain a variety of constituents and impurities due to its production method. Data on the substance itself does not provide appropriate information on the PBT-properties of its minor constituents and impurities. Eight substances have been selected for this assessment based on information from industry on the contents of δ-carene fraction and according to other information on substances in turpentine products. An overview and conclusion of the PBT-properties is presented in **Table 7.1**. The available data have been presented and discussed in **Section 4.1**, **4.3** and **6**.

Table 7.1 Overview of the PBT-properties of possible constituents and impurities of δ-carene fraction

	P/vP criteria fulfilled?	B/vB criteria fulfilled?	T criteria fulfilled?	Overall conclusion
$C_{10}H_{16}$ – terpenes (monoterpenes)				
α-pinene	No (screening data, measured)	No (screening data, estimated BCF)	Long term data not available (acute data > 0.1 mg l^{-1}; not T based on read-across from β-pinene)	Not PBT (based on screening data)
β-pinene	No (at limit; screening data, measured)	No (screening data, estimated BCF)	No (long-term data available)	Not PBT (based on screening data)
δ-carene	No (at limit; screening data, measured)	No (at limit; screening data, estimated BCF)	Experimental data not available (potentially not T based on similarity with α-pinene	Not PBT (based on screening data)
camphene	Yes (screening data, measured)	No (measured BCF available)	Long-term data not available	Not PBT
limonene/dipentene	No (screening data, measured)	No (screening data, estimated BCF)	Experimental data not available	Not PBT (based on screening data)
Terpene-derivatives				
anethole	No (screening data, estimated)	No (screening data, estimated BCF)	Experimental data not available	Not PBT (based on screening data)
methylchavicol ($C_{11}H_{20}O_2$)	No (screening data, estimated)	No (screening data, estimated BCF)	Long term data not available (acute data > 0.1 mg l^{-1}; potentially not T)	Not PBT (based on screening data)
$C_{15}H_{24}$–terpenes (sesquiterpenes)				
β -caryophyllane (as a representative of the group)	Yes (screening data, estimated)	Yes (screening data, estimated BCF > 5,000)	Experimental data not available, T criterion fulfilled based on QSARs	PBT/vPvB (based on screening data)

Summary: Terpenes and Terpenoids, turpentine-oil, 3-carene fraction does not fulfil the PBT criteria based on mainly screening data on monoterpenes, which are expected to be main constituents in the substance. One of the monoterpenes (camphene) may meet the P/vP criteria according to screening data. Other monoterpenes included do not meet the P/vP criteria on the basis of screening data. The monoterpenes do not meet the B criterion based on screening data. An experimental BCF for camphene confirms the conclusion.

β-pinene (one of the main constituents) is concluded to not fulfil the T criterion and this conclusion is applicable also for α-pinene (one of the main constituents) due to a structural similarity. For other constituents the ecotoxicity assessment was not completed.

Terpene derivatives, which are expected to be present as impurities, do not fulfil the P/vP and B criteria based on screening data. The substance is expected to contain as impurity also sesquiterpenes, which may fulfil the P/vP, B/vB and T criteria based on QSAR-estimates of the most common sesquiterpene, β –caryophyllane.

It is concluded that terpenes and terpenoids, turpentine-oil, 3-carene fraction is not considered as a PBT substance based on the properties of its constituents. The substance may contain, depending on the producer, impurities, which are potential PBT/vPvB-substances based on QSAR-estimates.

INFORMATION ON USE AND EXPOSURE

Not relevant as the substance is not identified as a PBT.

OTHER INFORMATION

The information and references used in this report were taken from the following sources:

Arizona Chemicals (2002) Personal communication received by the Rapporteur per email in 2002.

Astra Zeneca (2004a) Alpha-pinene: Determination of Ready Biodegradability (CO_2 evolution). Report nr. BLS3163/B provided with Arizona Chemicals communication on 16.4.2004.

Astra Zeneca (2004b) Delta-3-carene: Determination of Ready Biodegradability (CO_2 evolution). Draft report nr. BLS3164/B. Arizona Chemicals communication on 16.4.2004.

Astra Zeneca (2001) Ready Biodegradability of Gum Turpentine. Report nr. BL7034/B/2001.

Corchnoy SB and Atkinson R (1990) Kinetics of gas-phase reactions of OH and NO3 radicals with 2-carene, 1,8-cineole, p-cymene, and terpinolene. Environ Sci Technol 24: 1497±1502

European Commission (2000a) IUCLID Dataset, Terpenes and Terpenoids, turpentine-oil, 3-carene, CAS 91770-80-8, 19.2.2000.

European Commission (2000b) IUCLID Dataset, Camphene, CAS 79-92-5, 19.2.2000.

Gullichen J and Fogelholm C-J (1999) Chemical Pulping, in scientific series of Papermaking Science and Technology, publication 6b, Helsinki 1999

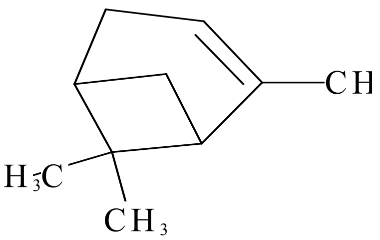
MITI (1992) Biodegradation and Bioaccumulation data of Existing Chemicals based on CSCL Japan, Compiled under the Supervision of Chemical Products Safety Division, Basic Industries Bureau MITI, ed. by CITI, 1992. Published by Japan Chemical Industry Ecology-Toxicology & Information Center.

Passino-Reader DR, Berlin WH and Hickey JP (1995) Chronic Bioassays of Rainbow Trout Fry with Compounds Representative of Contaminants in Great Lakes Fish. J. Great Lakes Res., 21(3), 373-383.

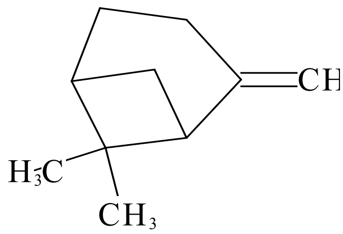
Suomen kemianteollisuus (1998) Editors: Riistama, K., Laitinen, J., Vuori, M. Publisher: Chemas Oy, Finland.

ANNEX

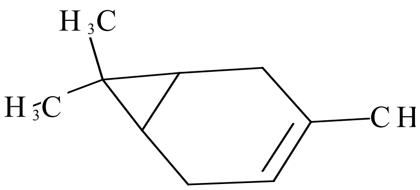
Structural formulas of the substances covered by this assessment. The CAS numbers refer here to the pure substances, not to any terpene fraction on the market



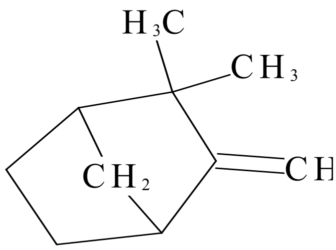
α-pinene (CAS 80-56-8 and 7785-70-8)



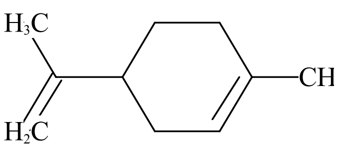
β-pinene (CAS 127-91-3)



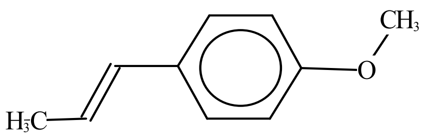
δ-carene (CAS 13466-78-9)



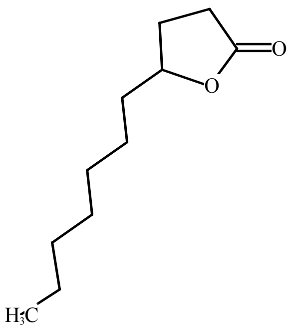
Camphene (CAS 79-92-5)



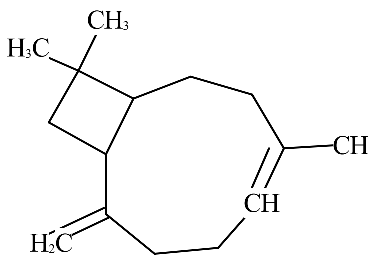
Limonene (CAS 5989-27-5)



Anethole (CAS 104-46-1)



Methylchavicol (CAS 104-67-6)



β -caryophyllane (CAS 87-44-5)