

Note

Separation of some monoterpenic constituents of essential oils by gas-liquid chromatography

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The application of gas-liquid chromatography (GLC) using liquid stationary phases of various polarity and solid carriers having low catalytic activity for the analysis of menthane-related hydrocarbons¹⁻³ proved useful for synthetic studies of rare *o*-menthane derivatives that do not comply with the isoprene rule⁴⁻⁷. Many of these substances are plant growth stimulants⁸ and GLC can be used to study the dependence of the physiological action of these compounds on their chemical structure.

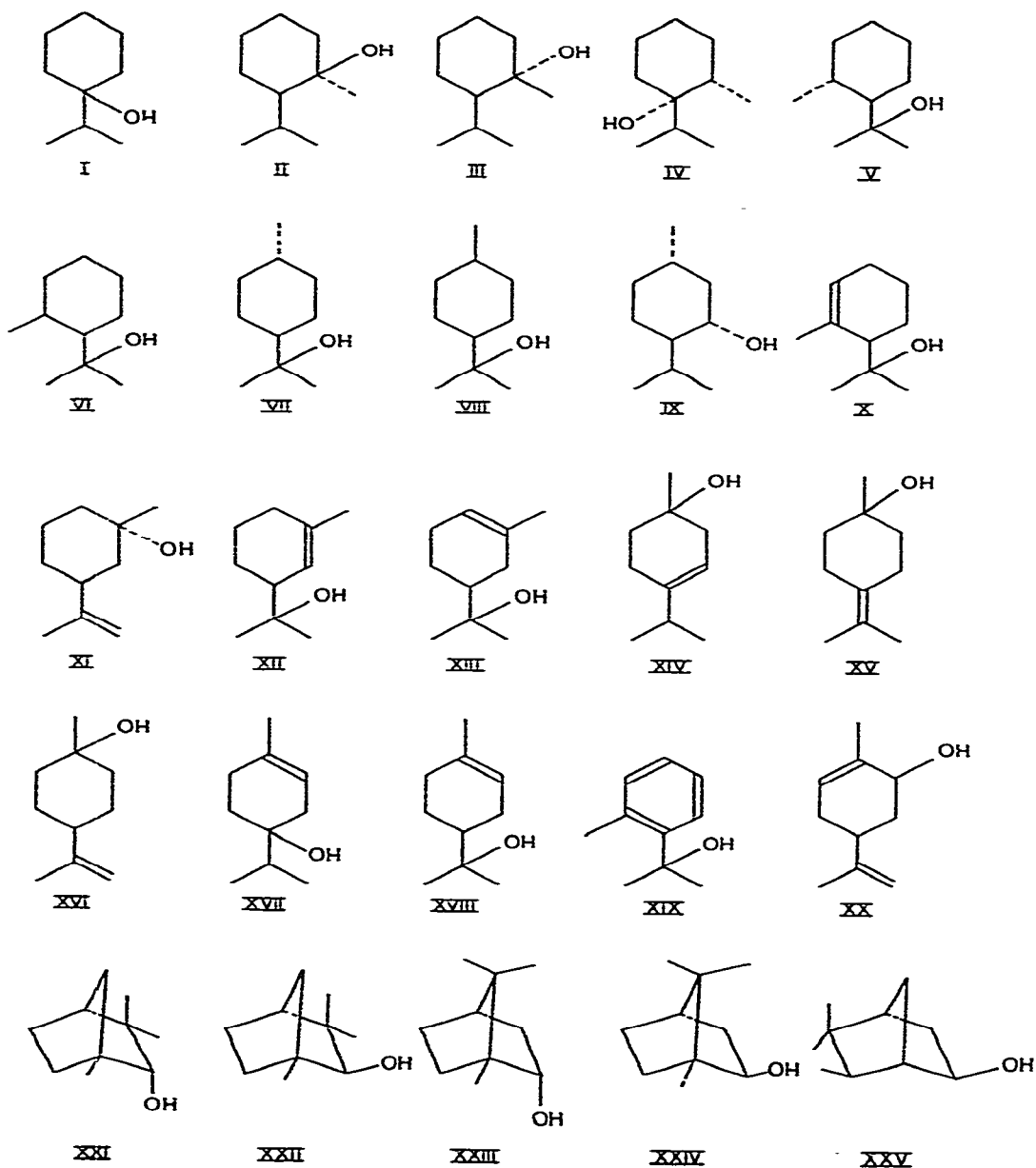
Earlier, when studying mixtures of monoterpene alcohols by GLC, the composition of the stereoisomers of *o*-menthan-3-ols¹¹, carvomenthols and α -1-oxycarvomenthols¹², components from pine oil flotation¹³, were studied. There is a need for further studies of mixtures of monoterpene alcohols and related compounds as many of them are used in manufacturing perfumes and drugs¹⁴, they also serve as standard flotation agents in enriching non-ferrous metal ores¹⁵ and plant growth stimulants¹⁶.

In this work, three liquid stationary phases, Apiezon M, silicone XE-60 and Carbowax 6000, were compared, for separating 1-isopropylcyclohexanol (I), *trans*- (II) and *cis*-*o*-menthan-1-ol (III), *trans*-*o*-menthan-2-ol (IV), *trans*- (V) and *cis*-*o*-menthan-8-ol (VI), *trans*- (VII) and *cis*-*p*-menthan-8-ol (VIII), 1-menthol (IX), *o*-menth-6-en-8-ol (X), *cis*-*m*-menth-8-en-1-ol (XI), *m*-menth-1-en-8-ol (XII), *m*-menth-6-en-8-ol (XIII), *p*-menth-3-en-1-ol (XIV), *p*-menth-4(8)-en-1-ol (XV), *p*-menth-8-en-1-ol (XVI), *p*-menth-1-en-4-ol (XVII), *p*-menth-1-en-8-ol (XVIII), *o*-cymenol-8 (XIX), carveol (XX), fenchol (XXI), isofenchol (XXII), borneol (XXIII), isoborneol (XXIV) and isocamphanol (XXV).

The analyses were carried out using an LChM-7A chromatograph (U.S.S.R.) fitted with stainless-steel columns (6 m \times 4 mm I.D.). Helium was used as the carrier gas. The stationary phases (15% Apiezon M, 5% XE-60, 15%, w/w Carbowax 6000) were deposited on Chromaton N AW DMCS (Lachema, Brno, Czechoslovakia). The column temperatures were 150°C (helium flow-rate 216 and 110 ml/min for Apiezon M and XE-60, respectively) and 165°C (112 ml/min for Carbowax 6000).

Retention times of these compounds relative to *p*-menth-1-en-8-ol (α -terpineol) chromatographed on the three stationary phases are given in Table I.

None of the stationary phases separated all of the components, and combination is necessary. For example, vapours of *cis*- and *trans*-*o*-menthan-1-ols, *p*-menth-3-en-1-ol and fenchol, *p*-menth-1-en-4-ol and *m*-menth-6-en-8-ol, and *trans*-*p*-



menthan-8-ol and *o*-menth-6-en-8-ol, which are inseparable on Apiezon M, are separated on silicone XE-60 and Carbowax 6000. On XE-60 1-menthol and fenchol are not separated, they can be identified using Apiezon M, and 1-menthol and *cis-p*-menthan-8-ol, which are inseparable on Carbowax 6000, are satisfactorily resolved on XE-60.

In contrast to monoterpene hydrocarbons and related compounds, no dependence of the retention times of alcohols on their boiling points is observed for any of

TABLE I

RETENTION TIMES OF MONOTERPENES AND SIMILAR COMPOUNDS RELATIVE TO α -TERPINEOL

Alcohol	Stationary phase		
	Apiezon M	XE-60	Carbowax 6000
1-Isopropylcyclohexanol	—	—	0.49
<i>trans</i> - <i>o</i> -Menthan-1-ol	0.67	0.60	0.49
<i>cis</i> - <i>o</i> -Menthan-1-ol	0.67	0.69	0.68
<i>trans</i> - <i>o</i> -Menthan-2-ol	0.93	0.55	0.55
<i>trans</i> - <i>o</i> -Menthan-8-ol	0.87	0.63	0.66
<i>cis</i> - <i>o</i> -Menthan-8-ol	0.97	0.72	0.77
<i>trans</i> - <i>p</i> -Menthan-8-ol	0.82	0.66	0.62
<i>cis</i> - <i>p</i> -Menthan-8-ol	—	0.92	0.73
1-Menthol	0.83	0.83	0.74
<i>o</i> -Menth-6-en-8-ol	0.82	0.94	0.82
<i>cis</i> - <i>m</i> -Menth-8-en-1-ol	0.67	0.93	0.78
<i>m</i> -Menth-1-en-8-ol	0.69	0.95	0.77
<i>m</i> -Menth-6-en-8-ol	0.94	1.10	1.04
<i>p</i> -Menth-3-en-1-ol	0.83	0.67	0.60
<i>p</i> -Menth-4(8)-en-1-ol	0.73	0.96	0.85
<i>p</i> -Menth-8-en-1-ol	0.70	0.79	0.78
<i>p</i> -Menth-1-en-4-ol	0.97	0.77	0.69
<i>p</i> -Menth-1-en-8-ol (α -terpineol)	1.00	1.00	1.00
<i>o</i> -Cymenol-8	1.05	1.63	2.39
Isofenchol	0.59	0.81	0.65
Fenchol	0.63	0.83	0.63
Isoborneol	0.85	1.04	0.90
Borneol	0.90	1.19	1.05
Isocamphanol	1.10	1.31	1.31
Carveol	1.32	1.42	—

the stationary phases studied. For example, on Apiezon M *p*-menth-1-en-4-ol, boiling point 200–212°C¹⁷, is retained longer than 1-menthol, boiling point 216°C¹⁸; on XE-60, 1-menthol and fenchol, both with boiling point 201–202°C, have similar retention times; on Carbowax 6000 1-menthol is eluted earlier than *p*-menth-8-en-1-ol (α -terpineol), which has a boiling point of 209–210°C (all boiling points at 760 mmHg).

Apparently the retention of monoterpene alcohols and related compounds is influenced by the structure and the availability of hydrogen bonds. On Carbowax 6000, where hydrogen bonding represents the major attractive forces¹⁹, *trans*-*p*-menthan-8-ol, owing to the formation of a hydrogen bond between the hydroxy group and the ether oxygen atom of the stationary phase, is retained longer than its stereoisomeric analogue *trans*-*o*-menthan-8-ol, whose hydroxy groups are shielded owing to the 1,2-substituents. For the same reason in *p*-menth-1-en-4-ol the hydroxy group on C₄ is sterically less accessible than in *p*-menth-3-en-1-ol, where it is screened by a methyl group.

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