

## STUDIES ON TERPENES

## I. A SYSTEMATIC ANALYSIS OF MONOTERPENE HYDROCARBONS BY GAS-LIQUID CHROMATOGRAPHY\*

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(Received June 22nd, 1961)

## INTRODUCTION AND REVIEW OF THE LITERATURE

The analysis and elucidation of the structure of terpenes is hampered by special difficulties. On the one hand these substances usually occur in mixtures of closely related compounds, on the other hand when treated with even mild reagents they are liable to various kinds of isomerization and to rearrangement of the carbon skeleton. It is obvious that the advent of gas-liquid chromatography, which is an extremely powerful and non-aggressive method of separation, has opened up new possibilities for studying the terpenes. The recent literature shows many examples.

BERNHARD<sup>1</sup>, for instance, succeeded in separating five of the terpenes occurring in lemon oil, using polyethylene glycol as the column liquid. LIBERTI AND CARTONI<sup>2,3</sup> used columns of different polarities. BAYER *et al.*<sup>4</sup> showed that addition of sodium caproate to silicone vacuum grease results in a considerable reduction of the asymmetry of the elution peaks. STAHL AND TRENNHEUSER<sup>5</sup> obtained good separations of terpenes on a polypropylene glycol column. MATSUURA *et al.*<sup>6</sup> measured retention data on squalane and tricresyl phosphate as liquid phases. Apiezon-L was used, among others, by EGLINTON<sup>7</sup> for the separation of  $\alpha$ - and  $\beta$ -pinene, and by WESTAWAY AND WILLIAMS<sup>8</sup> for a study of dipentene fractions. VON RUDLOFF<sup>9</sup> employed no less than four different stationary liquids and related certain physical properties of the terpenes to the separations obtained. ZUBYK AND CONNER<sup>10</sup> measured relative retention values of a number of synthetic terpenes on didecyl phthalate and Carbowax at various temperatures. The mixtures of terpenes obtained by dehydration of linalool with acetic anhydride was analysed by ASCOLI AND CRESCENZI<sup>11</sup> on a tricresyl phosphate column. They showed that under the condition applied three olefinic isomers were obtained. A study of the dehydration of  $\alpha$ -terpineol with several acidic reagents was carried out by VON RUDLOFF<sup>12</sup>. The complex mixture of terpenes obtained with aqueous oxalic acid was almost completely separated when using rape seed oil as a liquid phase. A bibliographic review of chromatographic methods used in the analysis of essential oils and their constituents has been given by CALVARANO<sup>13,14</sup>.

\* Part of a thesis by M. H. KLOUWEN, Groningen, 1961.

Gas chromatography has also been applied to the analysis of terpenes in essential oils. Lemon oil, for instance, was investigated by BERNHARD<sup>15</sup>, CLARK AND BERNHARD<sup>16</sup> and more recently by BERNHARD<sup>17</sup> on Craig polyesters as stationary phases. TEISSEIRE<sup>18</sup> studied in some detail the composition of the oil of clary sage on a polyethylene glycol column. Essential oils of the family Pinaceae were analysed by CVRKAL AND JANAK<sup>19</sup> and also by BANNISTER *et al.*<sup>20</sup>, tangerine oil<sup>21</sup> and Italian orange oil<sup>22</sup> by CALVARANO and sage oil by BRIESKORN AND WENGER<sup>23</sup>.

Most of the studies just mentioned are of a special nature and it was felt that there might be a need for a more systematic gas chromatographic study of the terpene hydrocarbons. The present publication is the first of a proposed series on this subject. It deals with the identification of a number of terpene hydrocarbons by means of their retention values on stationary phases of widely divergent polarities. It includes a discussion on the relation of structure and retention data, with the aid of which structural formulas for hitherto unidentified terpenes are proposed.

## EXPERIMENTAL AND RESULTS

### *Apparatus and methods*

Details of the columns, liquid phases and operating conditions are summarized in Table I. From this table it can be seen that EMBACEL was used as the support. It should be noted that use of the acid-washed grade is essential, since with this support in contrast to for instance firebrick, double bond isomerization of the terpenes, with a few exceptions is almost negligible. It is also important that the support be properly impregnated. If not, even EMBACEL will show residual adsorption towards a number of the terpene hydrocarbons, resulting in tailing of the elution peaks. Good results were obtained with the following procedure:

TABLE I

### OPERATING CONDITIONS

The following conditions apply to all experiments.

Apparatus: Gas chromatograph with thermal conductivity detection, manufactured by Consolidated Electro-dynamics Corp.

Column: 3 m length 1/6 in. i.d., copper coiled.

Solid support: Diatomaceous earth, acid washed EMBACEL (May & Baker) 60/100 mesh.

Sample size: The sample size is kept below 5  $\mu$ l.

Column liquid	Apiezon-L	Silicone oil*	Reoplex 100	Carbowax 4000	$\beta,\beta'$ -Oxydipropionitrile
Supplier	A. E. I. (Metropolitan Vickers)	May & Baker Ltd.	Geigy Ltd.	Chemische Werke Hüls	American Cyanamid Co.
Ratio liquid : support (w/w)	20:100	20:100	20:100	20:100	15:100
Column temperature ( $^{\circ}$ C)	120	100	110	100	70
Hydrogen flow rate (ml/min)	75	75	75	75	60
Gas inlet pressure (mm Hg)	1520	1710	1330	1820	1330

\* With this column sabinene always decomposes and occasionally also  $\beta$ -pinene (see *e.g.*<sup>26</sup>).

To the liquid phase, dissolved in a volume of methylene chloride equal to the volume of support to be used, EMBACEL was added, after which the solvent was evaporated at 40° under continuous stirring. The dry packing was then sieved and a 60/100 mesh fraction was used for filling the column. This is done in the conventional manner by knocking the (straight) column on a wooden floor under gentle vibration.

#### *Sources and properties of terpene hydrocarbons*

Terpene hydrocarbons of acceptable purity are with one or two exceptions not commercially available although it is known that there are products that consist for the major part of one or two isomers of known structure. The 22 terpenes mentioned in this study together with the material in which they are present or from which they have been obtained are summarized in Table II.

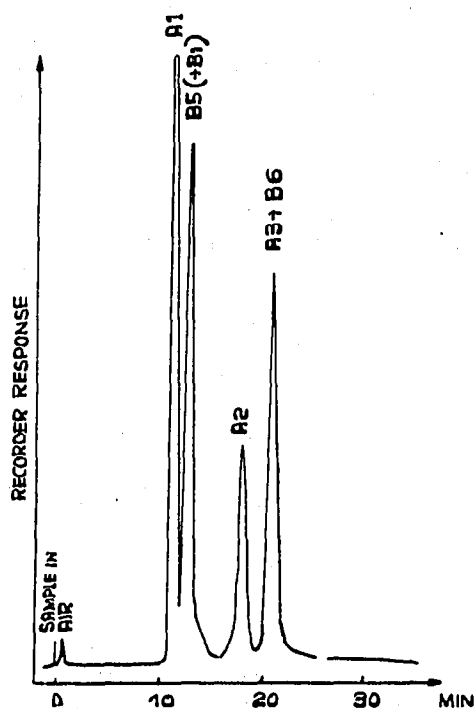


Fig. 1. Chromatogram of a crude mixture of terpene hydrocarbons obtained from linalool by dehydration with potassium bisulphate. Stationary phase:  $\beta, \beta'$ -oxydipropionitrile. Operating conditions: see Table I. Code: see Table III.

The retention volumes of these terpenes were measured relative to a standard substance. For this purpose limonene was selected, as this component is fairly stable, occurs in many essential oils, and has a central position on the chromatogram. The relative retention volumes are listed in Table III. It is noted that the value for sabinene on silicone oil is missing as this terpene was decomposed under the conditions applied. The list further mentions ocimene X and ocimene Y, two acyclic terpenes, the structural formulas of which still form a point of discussion.

Figs. 1 and 2 show that the ocimenes occur in rather large quantities in the dehydration product of linalool as will be shown in more detail in a forthcoming paper.

TABLE II  
SOURCES OF TERPENE HYDROCARBONS

Hydrocarbon	Source
Myrcene	The Glidden Co., Jacksonville, Florida, U.S.A.
Ocimene X and Y	obtained by dehydration of linalool with potassium bisulphate <sup>37</sup>
<i>cis</i> - and <i>trans</i> -Allo-ocimene	The Glidden Co.
$\alpha$ -Terpinene	obtained by dehydration of $\alpha$ -terpineol with oxalic acid <sup>38</sup>
$\alpha$ -Phellandrene	Fluka A.G., Buchs S.G., Switzerland
$\gamma$ -Terpinene	from ajowane oil
$\beta$ -Phellandrene	from angelica seed oil
Limonene	from orange oil
Terpinolene	obtained by dehydration of linalool
<i>p</i> -Cymene	from ajowane oil
$\alpha$ -Pinene	from turpentine oil
$\beta$ -Pinene	from nutmeg oil
$\alpha$ -Thujene	from cubeb oil
Sabinene	from savin oil
$\Delta^3$ -Carene	provided by Dr. Y. R. NAVES
Camphene	The Glidden Co.
$\alpha$ - and $\beta$ -Fenchene	obtained by dehydration of $\alpha$ -fenchyl alcohol with potassium bisulphate <sup>39</sup>
Santene	provided by Prof. Dr. N. J. TOIVONEN
Tricyclene	from camphene

TABLE III  
RETENTION VOLUMES OF TERPENE HYDROCARBONS RELATIVE TO THAT OF LIMONENE ( $\times 10^3$ )

Compound	Code	Stationary phase				
		Apiezon-L	Silicone oil	Reoplex 100	Carbowax 4000	$\beta, \beta'$ -Oxydipropionitrile
Myrcene	A 1	604	758	<u>725</u> *	767	868
Ocimene X	A 2	870	1000	1080	<u>1158</u>	1422
Ocimene Y	A 3	948	1080	1200	1292	1670
<i>trans</i> -4,5- <i>cis</i> -6,7-Allo-ocimene	A 4	<u>1740</u>	1820	2400	2620	3740
<i>trans</i> -4,5- <i>trans</i> -6,7-Allo-ocimene	A 5	<u>1920</u>	1950	2670	2960	4320
$\alpha$ -Terpinene	B 1	880	930	900	<u>900</u>	1000
$\alpha$ -Phellandrene	B 2	855	860	<u>845</u>	830	830
$\gamma$ -Terpinene	B 3	<u>1190</u>	<u>1170</u>	1240	1286	1350
$\beta$ -Phellandrene	B 4	1040	1050	1078	1070	<u>1170</u>
Limonene (Dipentene)	B 5	1000	1000	1000	<u>1000</u>	1000
Terpinolene	B 6	<u>1425</u>	<u>1418</u>	<u>1485</u>	1600	1630
<i>p</i> -Cymene	B 7	930	945	1308	1480	2400
$\alpha$ -Pinene	C 1	508	565	410	368	<u>276</u>
$\beta$ -Pinene	C 2	<u>718</u>	735	640	622	<u>560</u>
$\alpha$ -Thujene	C 3	<u>432</u>	528	402	363	<u>318</u>
Sabinene	C 4	610	—	660	650	<u>735</u>
$\Delta^3$ -Carene	C 5	850	910	772	770	<u>668</u>
Camphene	C 6	610	620	521	488	<u>450</u>
$\beta$ -Fenchene	C 7	541	589	468	<u>434</u>	<u>378</u>
$\alpha$ -Fenchene	C 8	594	633	530	487	<u>435</u>
Santene	C 9	<u>320</u>	<u>420</u>	<u>292</u>	308	242
Tricyclene	C 10	484	532	389	343	<u>267</u>

\* The underlined values give an indication of the stationary phase with which they are best distinguished from other terpenes.

There is good evidence that these terpenes are the *cis* and *trans* isomers of  $\beta$ -ocimene\*. The mechanism of the dehydration of linalool is indicated in Fig. 3 (see also VAN OS AND ELEMA<sup>24</sup>).

Table III has already proved to be of great value in our work on the development of new methods of analysis of essential oils. Figs. 4 and 5 for instance show chromatograms of monoterpene hydrocarbons present in angelica seed oil and in savin oil on a  $\beta, \beta'$ -oxydipropionitrile column.

Table IV is a collection of some important physical constants of the terpenes. The literature data for these constants are far from consistent, probably because they were obtained with samples of insufficient purity. The values that appeared to be most reliable were selected.

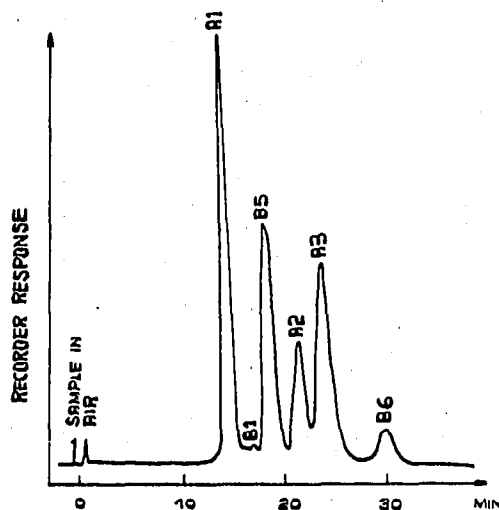


Fig. 2. Chromatogram of a crude mixture of terpene hydrocarbons from linalool by dehydration with potassium bisulphate. Stationary phase: Carbowax 4000, Operating conditions: see Table I. Code: see Table III.

Some authors<sup>25</sup> studied the correlation of structure in the terpene series with exaltations of the molecular refraction. We did not find any linear relationship between the exaltations and gas chromatographic data.

### Selectivity

The monoterpene hydrocarbons have only (if any) "permanent" small dipoles, although they may show large differences in polarizability. It is to be expected that the order of elution on "non-polar" column liquids such as Apiezon-L or silicone oil will be that of the boiling points of these hydrocarbons. This has been confirmed as can be seen from Fig. 6, where the logarithms of the relative retention volumes on silicone oil are plotted against the boiling points. Plots of this nature are of value for

\* While this manuscript was being corrected a study on the structure of ocimene was published by H. FARNOW AND F. PORSCH (*Dragocoberichte*, 8 (1961) 75). They established that the dehydration product of linalool contains *cis*- and *trans*- $\beta$ -ocimene, the latter having the longer retention time on a polypropylene glycol column. Consequently our assumption about the structures of ocimene X and Y appears to be correct.

estimating the boiling point of an unknown terpene hydrocarbon from its relative retention volume.

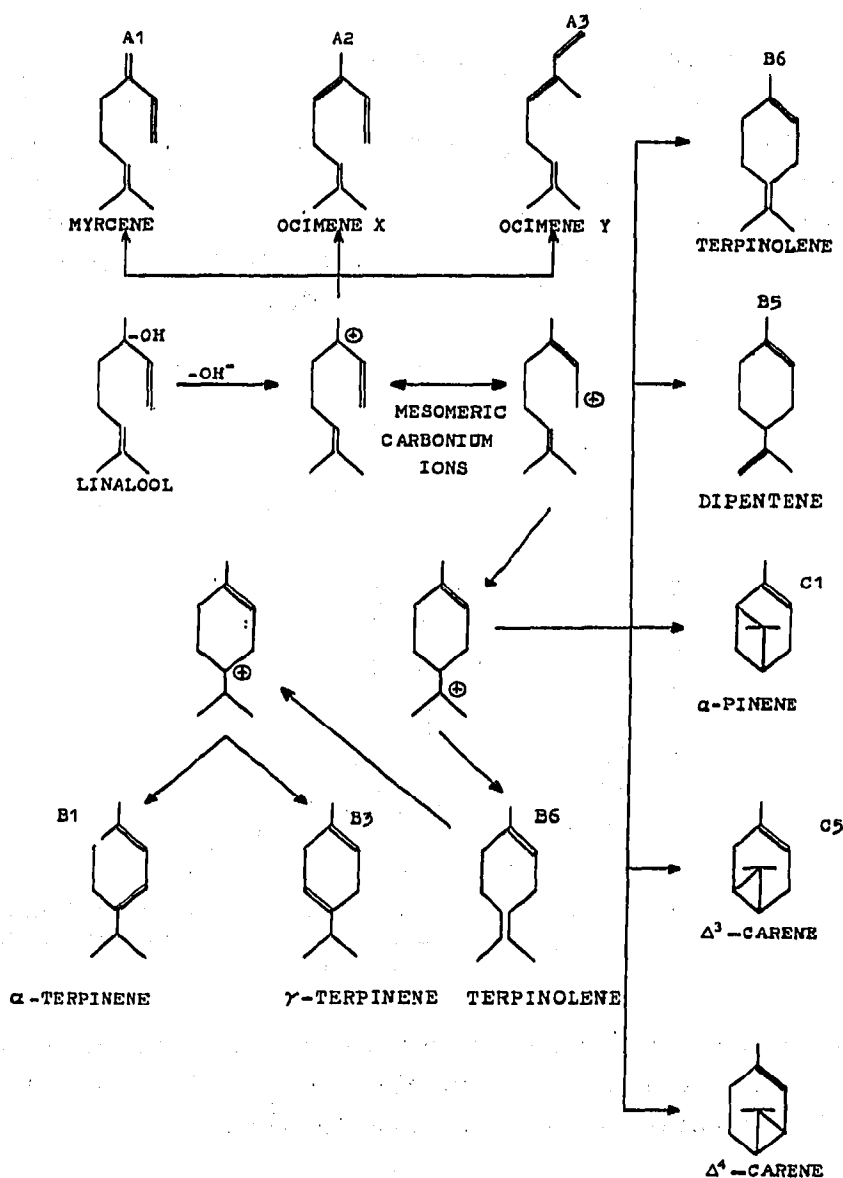


Fig. 3. Reaction mechanism of the dehydration of linalool by means of proton-active catalysts.

If for a certain group or class of substances and for a certain stationary liquid the plot of log retention volume against boiling point yields a straight line (or approximately a straight line) the stationary liquid is said to be a non-selective solvent for this group or class of substances.

According to this definition Apiezon-L and silicone oil can for all practical purposes be considered as non-selective towards the monoterpene hydrocarbons. When considering this class of compounds the other column liquids are selective solvents and it is said that the solvent  $\beta,\beta'$ -oxydipropionitrile has a higher selectivity or is more selective than for instance Reoplex 100.

For the identification and for the elucidation of structure of unknown terpenes use can be made of other forms of graphical presentation. A method first suggested by JAMES and coworkers<sup>26</sup> consists in plotting the logarithm of the retention volumes

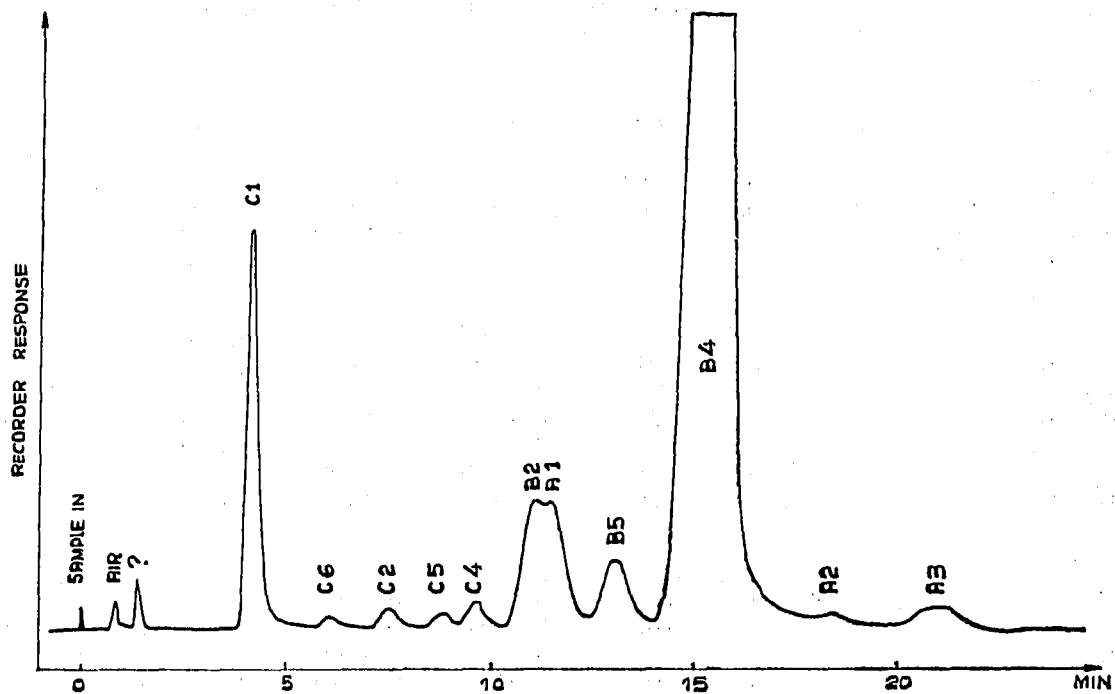


Fig. 4. Separation of the monoterpene hydrocarbons of a sample of Dutch angelica seed oil on  $\beta,\beta'$ -oxydipropionitrile. Operating conditions: see Table I. Code: see Table III.

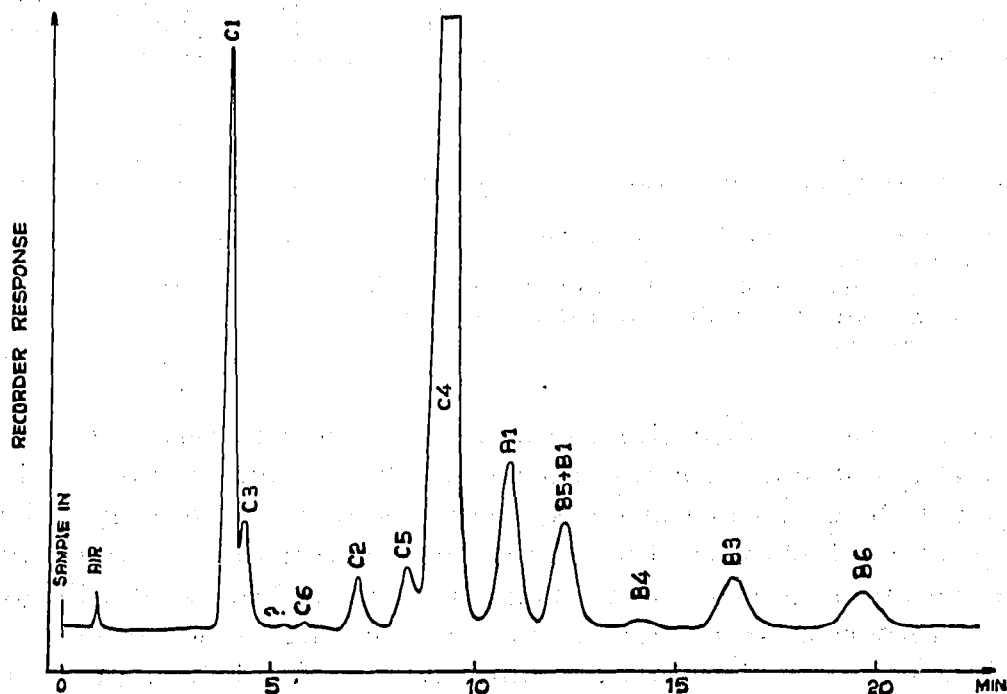


Fig. 5. Separation of the monoterpene hydrocarbons of a sample of savin oil on  $\beta,\beta'$ -oxydipropionitrile. Operating conditions: see Table I. Code: see Table III.

TABLE IV  
 PHYSICAL CONSTANTS OF TERPENE HYDROCARBONS

Compounds	Code	Boiling point* (760 mm Hg)	Refractive index* ( <i>n</i> <sub>20/D</sub> )	Density* ( <i>d</i> <sub>20/4</sub> )	Molecular refraction** (theoretical)	Molecular refraction*** (calculated)	Exaltation
<i>Aliphatic terpenes</i>							
	A						
Myrcene	1	167	1.4701	0.7869	46.98	48.20	+ 1.22
Ocimene X	2	± 176 <sup>§</sup>	—	—	—	—	—
Ocimene Y	3	± 179 <sup>§</sup>	—	—	—	—	—
<i>trans</i> -4,5- <i>cis</i> -6,7-Allo-ocimene	4	199	1.5438	0.8161	46.98	52.59	+ 5.61
<i>trans</i> -4,5- <i>trans</i> -6,7-Allo-ocimene	5	201	1.5438	0.8106	46.98	52.94	+ 5.96
<i>Monocyclic terpenes</i>							
	B						
α-Terpinene	1	173.4	1.4780	0.8400	45.24	45.89	+ 0.65
α-Phellandrene	2	171.5	1.4700	0.8324	45.24	45.71	+ 0.47
γ-Terpinene	3	183	1.4732	0.8490	45.24	45.02	— 0.22
β-Phellandrene	4	178	1.4800	0.8400	45.24	46.06	+ 0.82
Limonene	5	177.7	1.4725	0.8422	45.24	45.30	+ 0.06
Terpinolene	6	186	1.4886	0.8600	45.24	45.96	+ 0.72
<i>p</i> -Cymene	7	176.7	1.4907	0.8565	44.78	45.30	+ 0.52
<i>Bicyclic terpenes</i>							
	C						
α-Pinene	1	156	1.4653	0.8582	43.51	43.93	+ 0.42
β-Pinene	2	164	1.4780	0.8706	43.51	44.29	+ 0.78
α-Thujene	3	152	1.4509	0.8306	43.51	44.10	+ 0.59
Sabinene	4	164	1.4670	0.8436	43.51	44.80	+ 1.29
Δ <sup>3</sup> -Carene	5	171	1.4722	0.8643	43.51	44.16	+ 0.65
Camphene	6	159.6	1.4565 (54°)	0.8421 (54/4)	43.51	43.99	+ 0.58
β-Fenchene	7	157	1.4696	0.8611	43.51	44.10	+ 0.59
α-Fenchene	8	158.6	1.4740	0.8697	43.51	44.02	+ 0.51
Santene*	9	139	1.4666	0.8678	38.89	39.00	+ 0.11
Tricyclene (tricyclic)	10	153	1.4405 (66°)	0.8440 (66/4)	41.78	42.39	+ 0.61

\* The data were selected from the literature. The constants for santene were kindly provided by Prof. Dr. N. J. TOIVONEN.

\*\* The theoretical values were calculated from the atomic refractions for the sodium D-line as determined by BRÜHL AND CONRADY.

\*\*\* These data were obtained by applying the formula of LORENTZ AND LORENZ  $[(n^2 - 1)/(n^2 + 2) M/d]$ . We used the densities and refractive indices mentioned in this table.

§ Interpolated from Fig. 6.

for one stationary phase against those in another stationary phase. It is surprising that this method is not applied more extensively. Figs. 7 and 8 show such plots for Apiezon-L against Reoplex 100 and for Apiezon-L against β,β'-oxydipropionitrile.

A new type of plot is shown in Fig. 9. It has no theoretical basis, but it has proved to be extremely useful in practice to distinguish between the acyclic, the monocyclic and the bicyclic terpenes. We termed the lines connecting the log retention volumes for five stationary phases "chromatographic diagrams". The slope of the curve between Apiezon-L and β,β'-oxydipropionitrile gives a clear indication of the selectivity of the latter.



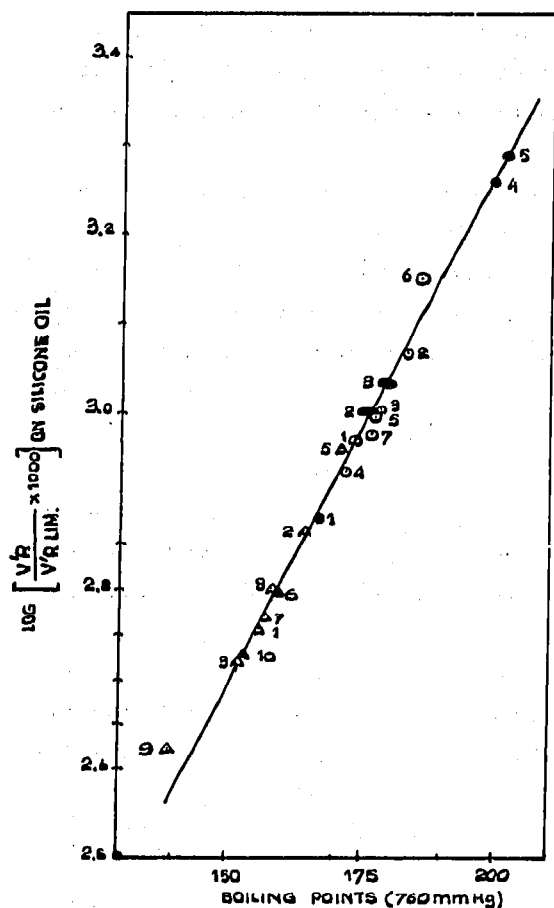


Fig. 6. Correlation between the logarithms of the relative retention volumes and boiling points of the monoterpene hydrocarbons at 100° on silicone oil. (●) Aliphatic; (⊙) monocyclic; (Δ) bicyclic. Operating conditions: see Table I.

Fig. 8. Log (relative retention volumes) for Apiezon-L against those for  $\beta, \beta'$ -oxydipropionitrile. A = aliphatic (●); B = monocyclic (+); C = bicyclic (Δ). Operating conditions: see Table I. Code: see Table III.

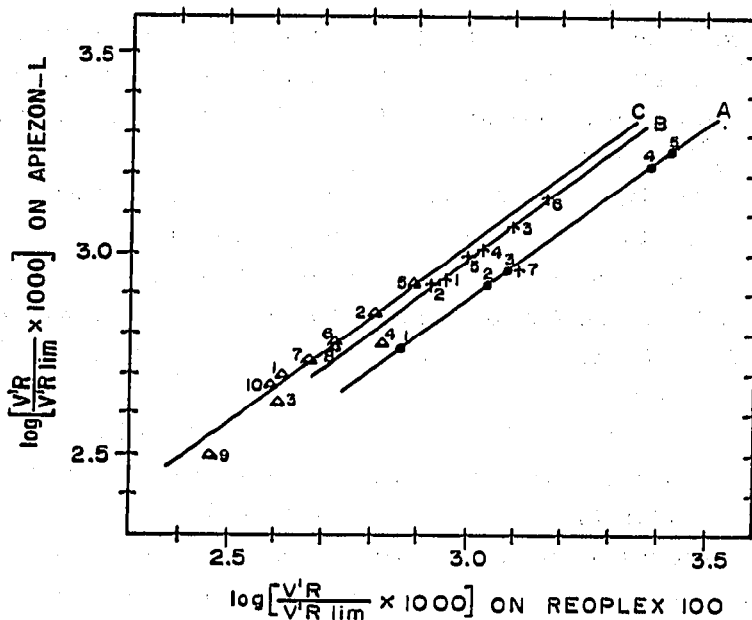
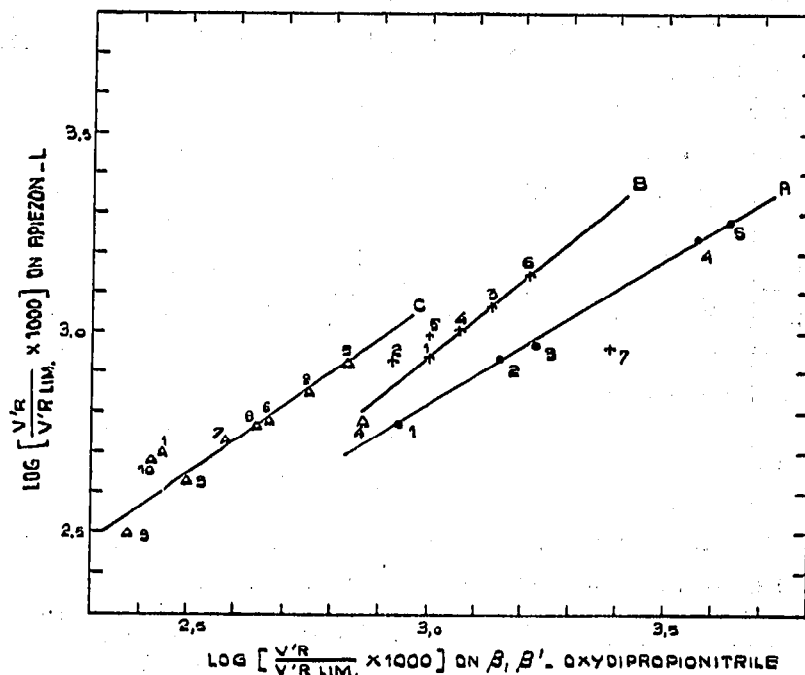


Fig. 7. Log (relative retention volumes) for Apiezon-L against those for Reoplex 100. A = aliphatic (●); B = monocyclic (+); C = bicyclic (Δ). Operating conditions: see Table I. Code: see Table III.



#### RELATION BETWEEN STRUCTURE AND SOLUTE-SOLVENT INTERACTION

The retention time of a solute in a liquid phase is determined by the forces and energy of interaction between solute and solvent. The forces of attraction which play a role in gas chromatographic separations have among others been discussed by KEULEMANS

*et al.*<sup>27</sup> in 1955. WEHRLI AND KOVATS<sup>28</sup> formulated the cohesive forces as follows:  
 I. In a non-polar solvent the dissolved molecules are only affected by dispersion (London) forces and in dilute solutions non-polar solutes are retained in such solvents by these forces only.

II. In a polar solvent additional forces are working on the dissolved molecules:

(a) Forces based on polar properties.

(a. 1) Attraction between permanent dipoles (and higher poles) of the dissolved molecules on the one hand and those of the stationary phase on the other.

(a. 2) Attraction of the polarizable "zones", in which charge displacement occurs by induction.

(b) Chemical bonds ("hydrogen bonding" and complex formation).

(c) Sterical effects, influencing the forces described under *a* and *b*.

WEHRLI AND KOVATS<sup>28</sup> studied extensively the relation between structure and "retention indices" (increments) on a polar and a non-polar stationary phase. In the case of isomers this method was not always applicable. Of the isomeric terpene hydrocarbons only limonene was mentioned.

Regarding the terpenes, especially the cyclic ones, we have to take into account chiefly the unequal polarizabilities, caused by the different effects of the polarizable substituents on the neighbouring double bonds. It is beyond the scope of this study to

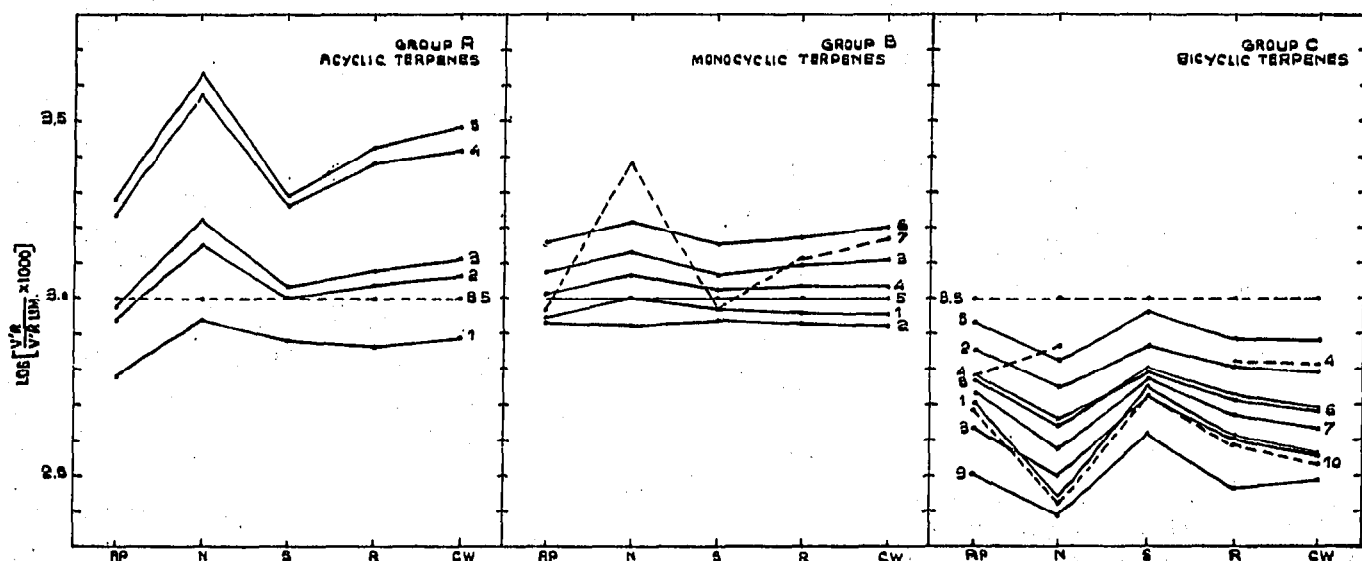


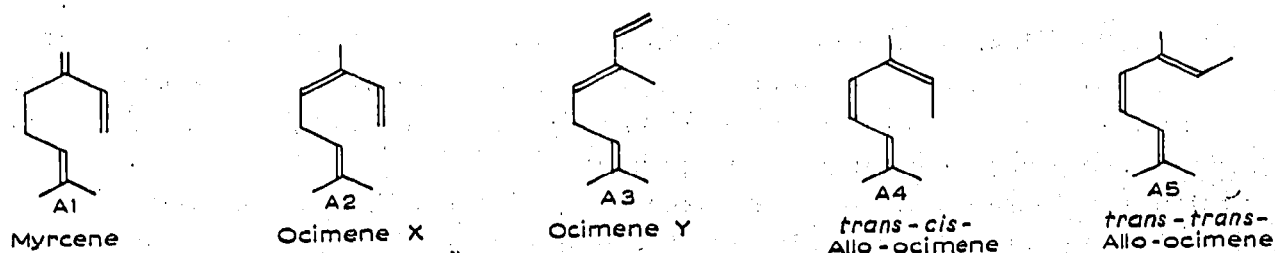
Fig. 9. Plots of the logarithms of the relative retention volumes on 5 stationary phases. The graphs are termed "chromatographic diagrams". AP = Apiezon-L; N =  $\beta, \beta'$ -oxydipropionitrile; S = silicone oil; R = Reoplex 100; CW = Carbowax 4000. Operating conditions: see Table I. Code: see Table III.

discuss the electron migrations with regard to the inductive effects (I effect) and to the hyperconjugative effects of the substituents attached to an unsaturated carbon atom. In the following sections the three classes of monoterpenes are separately discussed. We investigated whether comparison of the different chromatographic diagrams (Fig. 9) and especially the slope of the connecting lines between a non-

polar and a polar solvent could give information about the position of the double bonds. The definition of *cis-trans* isomers is based on the relative position of the substituents with the greatest number of C-atoms at the ethylenic bond.

### I. Aliphatic terpenes

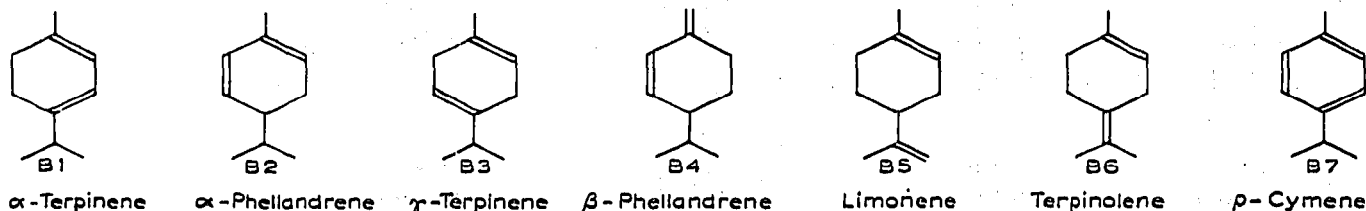
The chromatographic diagrams of the acyclic monoterpenes myrcene (A1), ocimene X (A2), ocimene Y (A3) and allo-ocimene (A4 and A5) are shown in Fig. 9. From the slope of the connecting lines of the diagrams it can be deduced that the polarizability of the aliphatic terpenes increases in the order A1  $\rightarrow$  A5. Comparing the formulas A1, A2 and A3 it is seen that ocimene Y (A3) possesses the most elongated system of



double bonds. Therefore we may expect that the forces of interaction with a polar solvent are stronger for A3 than for A1 and A2<sup>29</sup>. Consequently A3 has the larger retention volume. Using similar arguments, the larger retention volume of A2 as compared with A1 may be explained. The stronger polarity of allo-ocimene must be attributed to the conjugated triene structure. Comparing both isomers (A4 and A5) it can be expected that the all-*trans* configuration (A5) will be retained longer on a polar phase, an observation which agrees with the results reported by THEIMER<sup>30</sup>.

### II. Monocyclic terpenes

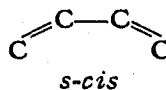
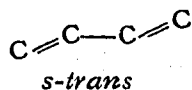
As is clearly illustrated in Fig. 9, not all members of this group behave similarly. We studied the influence of the position of the double bonds on the gas chromatographic behaviour and in spite of the fact that a clear interpretation was not possible in every case, some very interesting conclusions could be drawn.



The cyclohexadiene derivatives with conjugated double bonds inside the six-membered ring ( $\alpha$ -terpinene (B1) and  $\alpha$ -phellandrene (B2)) show a lower polarity than the isomer with isolated ethylenic linkages in the ring, *i.e.*  $\gamma$ -terpinene (B3). This is in striking contrast to what is found in the aliphatic series, where the conjugated system has not the lower but the higher polarity. In acyclic dienes MULLIKEN<sup>31</sup>

has introduced the terms *s-cis* and *s-trans*. In butadiene for instance the forms have a different polar character and the *s-trans* form is energetically more favoured<sup>32</sup>.

The same must be true for the forced *s-cis* configuration of the conjugated system inside the ring and the "free" *s-trans* configuration of the conjugated system in an open chain.  $\alpha$ -Phellandrene (B2) is less polarizable than  $\alpha$ -terpinene (B1). Both terpenes have a conjugated system inside the ring. The greater polar character of  $\alpha$ -terpinene can be due to the effect of the isopropyl substituent on the neighbouring



double bond. This bond is activated and hence more polarizable<sup>33</sup>.  $\gamma$ -Terpinene (B3) is more polarizable than the  $\alpha$ -isomer (B1). Our observations are in good agreement with comparable results obtained by Hively<sup>34</sup> who separated 1,3- and 1,4-cyclohexadiene on liquid phases of different polarity.

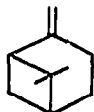
Shifting a double bond into an exocyclic position causes a marked increase in polarizability ( $\alpha$ - and  $\beta$ -phellandrene).  $\beta$ -Phellandrene (B4) possesses an exocyclic ethylenic bond, in *s-trans* position towards the double bond inside the ring, which is a more polarizable system than the *s-cis* configuration in  $\alpha$ -phellandrene (B2). Comparing the results obtained for the other cyclohexene derivatives it became clear that terpinolene (B6) is much more polarizable than limonene (B5). This must be ascribed to the exocyclic double bond in B6, which is strongly activated by the presence of the attached substituents. *p*-Cymene (B7) a non-terpenoid compound with the same carbon skeleton as the other B-members does not "fit" in diagram B (Fig. 9) and resembles much more the chromatographic diagrams characteristic for group A (aliphatic terpenes).

### III. Bicyclic terpenes

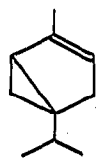
Most of the bicyclic members of the terpenes do not differ much in polar character. A marked exception is sabinene (C4), which shows similar behaviour as some mono-



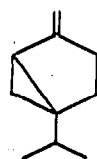
C1  
 $\alpha$ -Pinene



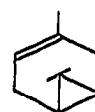
C2  
 $\beta$ -Pinene



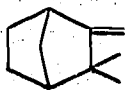
C3  
 $\alpha$ -Thujene



C4  
Sabinene



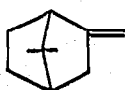
C5  
 $\Delta^3$ -Carene



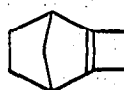
C6  
Camphene



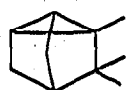
C7  
 $\beta$ -Fenchene



C8  
 $\alpha$ -Fenchene



C9  
Santene



C10  
Tricyclene

cyclic terpenes. From the chromatographic diagrams in Fig. 9 we can draw the following conclusions:

a. Members with an exocyclic ethylenic bond are more easily polarized than those with an endocyclic double bond. *Cf.*  $\alpha$ - and  $\beta$ -pinene (C1, C2) on the one hand and  $\alpha$ -thujene (C3) and sabinene (C4) on the other.

b. As regards the bicyclic terpenes possessing an ethylene linkage in conjugation with a cycle, it can be stated that conjugation of an ethylenic bond causes a stronger polar character with a cyclopropane ring than with a cyclobutane ring (sabinene (C4) and  $\beta$ -pinene (C2) and to a lesser extent  $\alpha$ -thujene (C3) and  $\alpha$ -pinene (C1)).

With compounds possessing an exocyclic bond the differences are much more striking compared with those having an endocyclic double bond in conjugation with a cycle. This can be attributed to the *trans* disposition of the exocyclic bond with regard to the cycle.

c. The terpenes possessing an exocyclic ethylenic bond attached to a cyclopentane ring show mutually no significant differences in their gas chromatographic behaviour (camphene (C6), and  $\beta$ - and  $\alpha$ -fenchene (C7 and C8)). For santene (C9), a  $C_9H_{14}$  terpene, we observed a somewhat greater selectivity (see also Fig. 9).

When analysing camphene an impurity was found of which a chromatographic diagram is presented in Fig. 9. It can immediately be seen that this compound is very little polarizable. According to Fig. 6, this product must have a boiling point of about  $153^\circ$ . It is reported<sup>35</sup> that camphene prepared from isborneol, contains a tricyclic hydrocarbon  $C_{10}H_{16}$  as impurity. The structure and boiling point of tricyclene (C10) agree well with those for the detected byproduct.

#### ACKNOWLEDGEMENTS

The authors wish to thank the Directors of the Chemische Fabriek "Naarden" for permission to publish these results. We express our thanks to Prof. Dr. Ir. A. I. M. KEULEMANS and Prof. Dr. TH. J. DE BOER for valuable comments during the course of this work. The authors are indebted to Dr. Y. R. NAVES of Givaudan et Cie., Vernier-Genève, for a sample of pure  $\Delta^3$ -carene and to Prof. Dr. N. J. TOIVONEN of the Chemical Institute of the University of Helsinki, who supplied them with a sample of pure santene. We should also like to acknowledge the able technical assistance of Mr. W. N. VERHOEVEN and Mr. H. BOELENS, who prepared the ocimene mixture.

#### SUMMARY

A systematic study was undertaken with 22 monoterpene hydrocarbons  $C_{10}H_{16}$  (including santene and *p*-cymene). They were separated by gas-liquid partition chromatography, using five stationary phases of different polarity.

It was found that a fairly good linear relationship exists when the log relative retention volumes on silicone oil are plotted *versus* the boiling points.

On the basis of characteristic "chromatographic diagrams" the terpenes can be divided into three distinct groups A, B and C.

Plotting the log retention volumes on a polar stationary phase *versus* those on a non-polar one also results in distinct group separations. In a special section structural phenomena are discussed and for some terpenes formulas are proposed.

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