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STUDIES ON TERPENES

III. GAS CHROMATOGRAPHY OF ACYCLIC MONOTERPENE ALCOHOLS

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SUMMARY

The retention indices of 22 acyclic monoterpene alcohols, determined on Apiezon L and Carbowax 20M as stationary phases, are discussed in relationship to the structure of these compounds. So-called homomorphy factors were used to examine the effect of the introduction of double bonds on the retention index and ΔI values. Intramolecular hydrogen bonding in some unsaturated alcohols, as measured in the near-infrared region, was correlated to retention behaviour.

INTRODUCTION

The advantage of the retention index system introduced by Kováts[1] in 1958 for qualitative measurements in gas chromatography has been demonstrated by Wehrli and Kováts[2–5]. As part of our work on terpenes the analysis of the hydrocarbons[6] and esters[7] has been reported. To characterize these compounds an effort was made to evaluate the influence of variations in chemical structures on gas chromatographic retention, and the use of columns of different polarity provided a method for the classification of terpene compounds. Although numerous publications have supplied gas chromatographic retention data for monoterpene alcohols, none is concerned with a systematic study with regard to the relationship between retention index values and structure of these compounds. In most of these studies only a few compounds were simultaneously analyzed.

With respect to acyclic monoterpene alcohols, the retention indices of linalool, citronellol, nerol, geraniol and some of their hydrogenated products have been reported[8–24]; also mentioned were the index values of myrcenol[12,24], dihydromyrcenol[14], ocimenol isomers[12,24] and lavandulol[24].

This paper reports a systematic investigation of 22 acyclic monoterpene alcohols chromatographed on Apiezon L and Carbowax 20M as stationary phases. As an aid in discussing structure–retention index correlations, use was made of homomorphy factors and infrared spectra. Results of the analysis of monocyclic and bicyclic terpene alcohols will be reported elsewhere.

TABLE I

## RETENTION INDICES, HOMOMORPHY FACTORS AND HYDROXYL FREQUENCIES OF PRIMARY ACYCLIC MONOTERPENE ALCOHOLS

AP = Apiezon L; CW = Carbowax 20M; sh = shoulder; m = band of medium intensity; w = weak band.
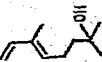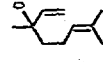
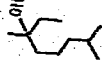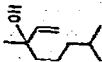| No.	Structure	Name	Retention indices			Homomorphy factors with reference to					Homomorphy factors of ethyl ethers with reference to ethyl ether of 3,7-dimethyl-1-octanol[28]		OH-frequencies, 0.01% solution in CCl$_4$ (cm^{-1})	
						3,7-Dimethyl-1-octanol (= 0)			Citronellol (= 0)					
			AP	CW	ΔI	H^{AP}	H^{CW}	$\Delta\Delta I$	H^{AP}	H^{CW}	H^{AP}	H^{CW}	ν Free	ν Bonded
1	CH$_2$OH	3,7-Dimethyl-1-octanol; tetrahydrogeraniol	1145	1675	530	0	0	0			0	0	3640(m) 3633(sh)	0
2	CH$_2$OH	(Z)-3,7-Dimethyl-2-octen-1-ol; dihydronerol	1151	1725	574	+6	+50	+44			+20	+97	3622(m)	
3	CH$_2$OH	(E)-3,7-Dimethyl-2-octen-1-ol; dihydrogeraniol	1172	1759	587	+27	+84	+57			+43	+132	3624(m)	
4	CH$_2$OH	3,7-Dimethyl-6-octen-1-ol; citronellol	1173	1765	592	+28	+90	+62	0	0	+28	+111	3640(m) 3628(sh)	0
5	CH$_2$OH	3,7-Dimethyl-7-octen-1-ol; α-citronellol	1164	1760	596	+19	+85	+66						

No.	Compound											
6	(Z)-3,7-Dimethyl-2,6-octadien-1-ol; nerol	1175	1808	633	+30	+133	+103	+2	+43	+43	+208	3623(m) 3562(w)
7	(E)-3,7-Dimethyl-2,6-octadien-1-ol; geraniol	1189	1842	653	+44	+167	+123	+16	+77	+71	+243	3625(m) 3540(w)
8	(Z)-3,7-Dimethyl-3,6-octadien-1-ol; cis-isogeraniol	1179	1812	633	+34	+137	+103	+6	+47			
9	(E)-3,7-Dimethyl-3,6-octadien-1-ol; trans-isogeraniol	1184	1812	628	+39	+137	+98	+11	+47			
10	7-Methyl-3-methylene-6-octen-1-ol; γ-isogeraniol	1169	1800	631	+24	+125	+101	−4	+35			
11	(E)-2-Methyl-6-methylene-2,7-octadien-1-ol; myrcenol-8	1196	1919	727								
12	2-Isopropyl-5-methyl-1-hexanol; tetrahydrolavandulol	1123	1600	477								
13	2-Isopropenyl-5-methyl-4-hexen-1-ol; lavandulol	1135	1707	572								

TABLE II

RETENTION INDICES, HOMOMORPHY FACTORS AND HYDROXYL FREQUENCIES OF TERTIARY ACYCLIC MONOTERPENE ALCOHOLS

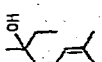AP = Apiezon L; CW = Carbowax 20M; sh = shoulder; m = band of medium intensity; w = weak band.

Monoterpene alcohol		Retention indices			Homomorphy factors with reference to						OH-frequencies, 0.01% solution in CCl_4 (cm^{-1})	
					2,6-Dimethyl-2-octanol (= 0)			3,7-Dimethyl-3-octanol (= 0)				
No.	Structure / Name	AP	CW	ΔI	H^{AP}	H^{CW}	ΔΔI	H^{AP}	H^{CW}	ΔΔI	v Free	v Bonded
14	2,6-Dimethyl-2-octanol; tetrahydromyrcenol	1067	1449	382	0	0	0				3625(sh) 3619(m)	
15	2,6-Dimethyl-7-octen-2-ol; 6(10)-dihydro myrcenol	1036	1473	437	−31	+24	+55				3620(m)	
16	2-Methyl-6-methylene-7-octen-2-ol; mycenol	1084	1631	547	+17	+182	+165				3620(m)	
17	(Z)-2,6-Dimethyl-5,7-octadien-2-ol; cis-ocimenol	1115	1660	545	+48	+211	+163					

#	Compound							IR
18	(E)-2,6-Dimethyl-5,7-octadien-2-ol; *trans*-ocimenol	1132	1685	553	+65	+236	+171	
19	3,7-Dimethyl-3-octanol; tetrahydrolinalool	1076	1431	355	0	0		3617(m)
20	3,7-Dimethyl-1-octen-3-ol; 6,7-dihydrolinalool	1035	1449	414	−41	+18	+59	3611(m)
21	3,7-Dimethyl-6-octen-3-ol; 1,2-dihydrolinalool	1104	1537	433	+28	+106	+78	3618(m) 3555(w)
22	3,7-Dimethyl-1,6-octadien-3-ol; linalool	1064	1555	491	−12	+124	+136	3609(m) 3548(w)

Nomenclature
    The chemical structures of the alcohols investigated, with systematic names based on official rules[25] and trivial names are given in Tables I and II. In instances of isomerism around a double bond, the designations Z and E are added as proposed by IUPAC[26].

Reference substances
    The terpene alcohols were obtained either from commercial sources, or were synthesized or isolated from appropriate essential oils by preparative gas chromatography. The purity and identity of the samples were verified by gas–liquid chromatography, infrared and nuclear magnetic resonance spectroscopy and mass spectrometric analysis.

EXPERIMENTAL

    The alcohols were chromatographed on a modified Becker gas chromatograph with two flame ionization detectors. The instrument was equipped with two electrometers and two recorders (1 mV). Two glass columns (2 m × 2 mm I.D.) of different polarities were fitted in the oven.

Column I (non-polar)
    This column was filled with Apiezon L (purified by percolation over alumina) coated on 60–80-mesh Embacel support (May & Baker, Dagenham, Great-Britain) in a weight ratio 20:80 from dichloromethane.

Column II (polar)
    This column was filled with Carbowax 20M, coated on 60–80-mesh Embacel support in a weight ratio 20:80.
    After conditioning the columns overnight at 225°, the non-polar column was silanized *in situ* by injecting 100 μl of hexamethyldisilazane in four equal portions of 25 μl, at 87°, using a nitrogen flow-rate of 20 ml/min. During analysis the oven temperature was maintained at 150° and the detector and injector temperatures at 250°; the nitrogen carrier gas flow-rate was 20 ml/min.
    The retention indices were calculated by using the following equation:

$$I_x = 100 \cdot \frac{\log t'_r(x) - \log t'_r(P_z)}{\log t'_r(P_{z+1}) - \log t'_r(P_z)} + 100\,z$$

where t'_r is the adjusted retention time (methane was used as dead volume marker); x the compound to be indexed; z the carbon number of reference *n*-alkane P_z; and $z+1$ the carbon number of reference *n*-alkane P_{z+1}.
    Alteration of the column packing was checked by periodical determination of the retention index of citronellol. The temperature coefficients for citronellol in the range 150–170° were: $10\delta I^A/\delta T = +3.0$; $10\delta I^P/\delta T = -1.0$; $10\delta \Delta I/\delta T = -4.0$. Each index value given in Tables I, II and III was the average of four consecutive runs, the coefficient of variation being $\pm 0.3\%$ for the Carbowax 20M column and $\pm 0.2\%$ for the Apiezon L column.

TABLE III

CLASSIFICATION OF ACYCLIC MONOTERPENE ALCOHOLS BY MEANS OF THE RETENTION INDEX SYSTEM

Class of terpene alcohols*	No. of alcohols investigated	Retention index range		ΔI-range
		Apiezon L	Carbowax 20M	
Saturated tertiary	2	1067–1076	1431–1449	355–382
Mono-unsaturated tertiary	3	1035–1104	1449–1537	414–437
Di-unsaturated tertiary (not conjugated)	1	1064	1555	491
Di-unsaturated tertiary (conjugated)	3	1084–1132	1600–1685	545–553
Saturated primary	1	1145	1675	530
Mono-unsaturated primary	4	1151–1173	1725–1765	574–596
Di-unsaturated primary	5	1169–1189	1800–1842	622–653
Tri-unsaturated	1	1196	1919	727

* Tetrahydrolavandulol and lavandulol are not included.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. The alcohols were run in the 2500–4000 cm^{-1} range as solutions in carbon tetrachloride, 0.01 % by weight. The chart abscissa was expanded 10-fold. Quartz cells of 50-mm pathlength were used. The wavelength accuracy was within ± 4 cm^{-1}, and was checked by calibration with indene.

RESULTS AND DISCUSSION

Kováts' retention indices can be of assistance in the identification of compounds. The indices and ΔI values of monoterpene alcohols depend on the stationary phase, on the structure of the parent hydrocarbon, the number and the position of double bonds and the position of the hydroxyl group in the molecule.

To study relationships between structure and retention behaviour, the alcohols were analyzed on phases in which the solute–stationary phase interactions were very dissimilar, i.e., on Apiezon L (a non-polar paraffin grease), and on Carbowax 20M (a polyethylene glycol). Adsorption effects due to the solid support were minimized by silanizing the Apiezon L column and by coating a relatively large amount of stationary phase on the support. By using an all-glass system in the gas chromatograph, destruction and isomerization of labile alcohols were avoided. The retention indices (average of four determinations) of 22 acyclic monoterpene alcohols are listed in Tables I and II.

The position of the hydroxyl group in the dimethyloctane skeleton has a marked influence on the retention behaviour. A shift of the OH group from carbon atom 1 (structure 1, Table I) to carbon atom 7 (structure 14, Table II) reduces the ΔI value by 148 units, a further decrease of 27 units being observed for tetrahydrolinalool (structure 19, Table II). The different alkyl substituents at the carbon atom carrying the OH group, did not result in a difference of the dispersion forces, because tetrahydrolinalool and tetrahydromyrcenol were barely separated on the Apiezon L column. Shielding of a primary OH group by an isopropyl substituent, as occurs with tetrahydrolavandulol (12), an alcohol with an unusual arrangement of isoprene units, causes a decrease of 53 ΔI units compared with 3,7-dimethyl-1-octanol (1).

Eighteen unsaturated acyclic alcohols, the retention behaviour of which has not so far been discussed in the literature, were analyzed. The effect of the introduction of double bonds on retention values was determined by comparison with the corresponding retention data of their saturated counterparts on the same stationary phase. I^{AP} (unsaturated alcohol) $- I^{AP}$ (saturated alcohol) $= H^{AP}$, which is called the homomorphy factor[27] for the Apiezon L column. Also, the homomorphy factors for the Carbowax 20M column (H^{CW}) were calculated. The H values reflect the sum of the effects, caused by the introduction of double bonds, on gas chromatographic retention. The retention indices and the homomorphy factors are given in Tables I and II.

The double bond in the 2,3-position in (Z)- and (E)-3,7-dimethyl-2-octen-1-ol (structures 2 and 3, Table I) increased the retention indices by 50 and 84 index units, respectively (Carbowax 20M column). The corresponding ethyl ethers, the homomorphy factors of which were calculated by subtraction of the H^{CW} value of citronellyl ethyl ether from those of the neryl ethyl and geranyl ethyl ethers[28] (given in Table I), showed H^{CW} values of $+ 97$ and $+132$, respectively. The much lower H values of the corresponding alcohols may be caused by intramolecular hydrogen bonding between the hydroxyl group and the π electrons of the double bond in the 2,3-position.

Intramolecular bonded hydroxyl groups do not tend to form intermolecular bonds with the Carbowax 20M phase and therefore display H^{CW} values that are lower than those of the corresponding non-intramolecular bonded ethyl ethers. In the gas chromatographic system, self-association of the alcohol molecules can be excluded because of the high degree of dilution[29]. Support for the intramolecular interaction was obtained by investigation of the infrared spectra of these unsaturated alcohols in the 3500–3700 cm^{-1} region. The alcohols were diluted with carbon tetrachloride to give a concentration of 0.01 %, low enough to eliminate intermolecular association. The main absorption band of dihydronerol (2) was located at 3622 cm^{-1} and that of dihydrogeraniol (3) at 3624 cm^{-1}, which corresponds to a spectral shift of about 15 cm^{-1} when compared with the absorption maximum of 3,7-dimethyl-1-octanol (1), having an asymmetrical band at 3640/3633 cm^{-1} due to conformational heterogeneity. Other workers reported similar shifts for 3-substituted allylic alcohols[30,31]. The spectral data of the alcohols are listed in Table I and II.

The relationship of OH-π intramolecular bonding to retention time in gas chromatography on polar phases has been referred to by various workers[32–35].

The H^{CW} value of citronellol (4) is 21 units lower than that of the corresponding ethyl ether (see Table I and ref. 28). Some intramolecular OH-π interaction[30] may exist, but this could not be proved by infrared analysis, no band being found at the expected frequency near 3560 cm^{-1}. The isomer with a terminal double bond (5) elutes on both columns just before citronellol. Analogous observations have also been reported[36–38].

Six primary alcohols with two olefinic bonds were analysed. The introduction of a second double bond resulted in an increase in the H^{CW} and ΔI values. By a comparison of the H^{CW} values of nerol (6) and geraniol (7) with those of their ethyl ethers[28], and from a study of the infrared spectra of these alcohols in the near-infrared region, it can be concluded that intramolecular interaction exists. Nerol eluted before geraniol on both columns. Their structures, questioned by Rummens[39], have now unambiguously been established by nuclear magnetic resonance analysis[28,40]. The double bond in the 3,4-position with respect to the OH group in the so-called iso-

geraniols (8–10) caused an increase in the H^{CW} values of 35–47 units when citronellol (4) is taken as the reference alcohol (see Table I). The separation of these isogeraniol isomers in particular was difficult on the polar phase. Other workers had similar experiences[41–44]. It is reasonable to assume that the hydroxyl group in the isogeraniols is also intramolecularly bonded, although this has not so far been proved by means of infrared spectroscopy.

One primary alcohol with three double bonds (11) was analyzed, only the synthetic (E)-isomer being available, which alcohol, also chromatographed by other workers[45,46], has the highest polarity of the alcohols investigated.

The retention characteristics of the tertiary unsaturated alcohols are given in Table II. Dihydromyrcenol (15) and 6,7-dihydrolinalool (20) possess a vinylic double bond with a methyl group in the α-position. In spite of the different position of the double bond with respect to the hydroxyl group, the homomorphy factors and the ΔI values of these alcohols do not differ markedly. Infrared analysis revealed that, at room temperature, 6,7-dihydrolinalool (20) is intramolecularly bonded (see Table II) and dihydromyrcenol (15) is not. It is known that the OH-π bond in tertiary alcohols with a double bond in the 2,3-position is very weak[31] and that the population of the bonded molecules diminishes with increasing temperature[31,47–49]. Therefore, the retention indices of these alcohols (Carbowax 20M column) were also compared at 80, 100 and 120° with their saturated analogues. The homomorphy factors at these temperatures were identical with those at 150° (temperature coefficient, $10\delta I^P/\delta T$ (80–150°), −2). It is likely that, even at 80°, the intramolecular bond in 6,7-dihydrolinalool (20) does not exist. The H^{CW} values of these unsaturated alcohols were the lowest found in this study. It is further interesting to note that these alcohols (15 and 20) showed negative H^{AP} values by 31 and 41 units compared with their saturated analogues (14 and 19), respectively. These high values were not observed with any of the other acyclic alcohols studied. A similar trend has been reported for 3-methyl-1-alkenes on non-polar phases[27,50] and for 2-methyl-3-buten-2-ol[51]. The double bond in 1,2-dihydrolinalool (21) behaves like a much more polar one ($H^{CW} = +106$). Our observations are analogous to those reported for substituted olefins, which showed the higher degree of interaction of 2-methyl-2-alkenes with polar column liquids compared with 3-methyl-1-alkenes[50,52–54].

In the infrared spectra of 1,2-dihydrolinalool (21) and linalool (structure 22), a weak absorption band was observed at 3555 and 3548 cm^{-1}, respectively, which might have originated from a weak interaction between the hydroxyl group and the π electrons of the double bond located at the 4,5-position[31]. However, a significant reduction of the retention indices on Carbowax 20M because of this interaction was not observed. Gas chromatographic analysis of linalool (22) and the three products obtained by partial and complete hydrogenation has also been carried out by Holmgren[55], who obtained comparable results.

A system with conjugated double bonds gave rise to an additional increase in the polarity of the alcohols. The ΔI values of myrcenol (16) and the ocimenol isomers (17 and 18) were found to be in the range 545–553, the more open form of (E)-ocimenol (18) ensuring greater possibilities of interaction with the stationary phases than the (Z)-isomer (17). The homomorphy factors of myrcenol and ocimenol differ markedly, which is in agreement with observations reported by Widmer[50] on the conjugated olefins 2-ethyl-1,3-butadiene and 3-methyl-1,3-pentadiene. The gas chromatographic

TABLE IV

ADDITIVE PROPERTIES OF HOMOMORPHY FACTORS RELATED TO DOUBLE BONDS

Alcohol	Retention index			
	Apiezon L		Carbowax 20M	
	Calculated	Measured	Calculated	Measured
Nerol	1179	1175	1815	1808
	(1145 + 6 + 28)		(1675 + 50 + 90)	
Geraniol	1200	1189	1849	1842
	(1145 + 27 + 28)		(1675 + 84 + 90)	
Linalool	1063	1064	1555	1555
	(1076 − 41 + 28)		(1431 + 18 + 106)	

analysis of the ocimenol isomers has been carried out by various workers[12,24,56-58].

The additive properties of homomorphy factors related to double bonds were examined by comparing the measured retention indices of nerol, geraniol and linalool with those calculated by addition of the homomorphy factors of the mono-unsaturated alcohols to the retention index of the saturated alcohols. The results obtained are given in Table IV.

The additivity rules can be applied to the calculation of retention indices of alcohols that are not available as reference compounds.

CONCLUSIONS

Most of the acyclic alcohols were separated much more easily on Carbowax 20M than on Apiezon L. On the former, all of the tertiary alcohols investigated, except (Z)-ocimenol, eluted before the primary alcohols (excluding tetrahydrolavandulol).

If the ΔI values, and also to a lesser extent the retention indices, are listed in order of magnitude, a classification of the acyclic terpene alcohols in well defined groups can be obtained (see Table III).

Homomorphy factors can be used with advantage for the determination of retention values of terpene alcohols.

Reduction of retention indices of 2,3- and 3,4-unsaturated primary alcohols may be caused by intramolecular interaction between the hydroxyl group and π electrons. Support for this view may be obtained from infrared spectra recorded in the near-infrared region in highly dilute solution.

ACKNOWLEDGEMENTS

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