CHROM. 5653

CHROMATOGRAPHIC BEHAVIOUR AND THE STRUCTURE OF SECONDARY ALIPHATIC ALCOHOLS

M. ŠINGLIAR
Research Institute for Petrochemistry, Nováky (Czechoslovakia)

SUMMARY

A mixture of secondary alcohols obtained by the indirect hydration of 1-alkenes was analysed by gas chromatography. The individual alcohols were identified by means of standard substances, using the retention index system. It was found that the retention of secondary alcohols as well as their acetates was the lower, the closer was the hydroxyl group to the centre of the molecule.

INTRODUCTION

One of the methods for the preparation of higher aliphatic alcohols is the indirect hydration of 1-alkenes by sulphuric acid. Under suitable conditions, the major product of the reaction is the secondary alcohol with the hydroxyl group on the second carbon atom of the 1-alkene. However, owing to the isomerization of 1-alkenes in sulphuric acid[1], some secondary alcohols with the hydroxyl group on the third, fourth or other carbon atoms are produced. The above reaction is illustrated schematically in Fig. 1. Besides the substances mentioned, ethers, polymers and non-hydrated olefins are also present in the reaction product; this will not be taken into account in this work[2].

Since the presence of secondary alcohols with the hydroxyl group shifted towards the centre of the molecule is unsuitable for the production of surfactants[3], they must be determined in the product. The most advantageous method for the determination of the above substances is gas chromatography (GC).

There are a number of papers on the GC of secondary alcohols[4–7,9]. SIVARAMA KRISHNAN *et al.*[7] investigated the dependence of the retention times of the secondary

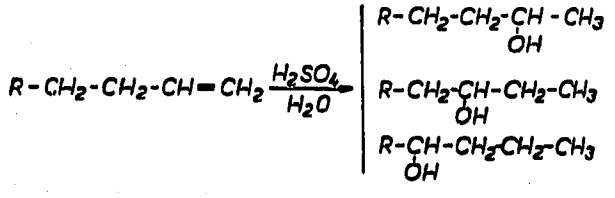


Fig. 1. Reaction scheme for the indirect hydration of 1-alkenes.

C_{18} alcohols on the position of the hydroxyl group in the molecule. The elution sequence of the individual isomers on different stationary phases was shown to be different and irregular. As none of the stationary phases investigated afforded satisfactory separation of isomeric alcohols, we investigated other column packings that would permit a better separation to be attained of the secondary alcohols prepared by us. At the same time, we studied the effect of the structure of the secondary alcohols on their retention properties.

EXPERIMENTAL

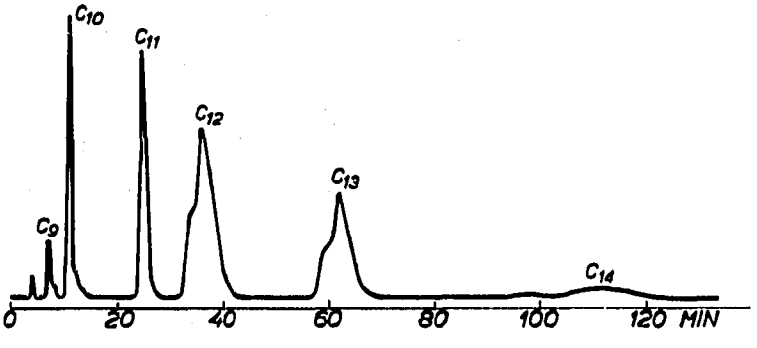
The measurements were carried out on a CHROM 2 gas chromatograph (Laboratory Instruments N.E., Prague, Czechoslovakia). The column was made of stainless steel, with length 2.55 m and I.D. 3 mm. The work was carried out under isothermal conditions while continuously heating the injection port. The following substances were used as stationary phases: Apiezon L, neopentyl glycol adipate–polyester, Carbowax 20 M and poly(oxyethylene)glycols 4000, 1500 and 1000. All these substances were the products of Lachema N.E., Brno, Czechoslovakia. The flow-rates of the gases were nitrogen, 21 ml/min; hydrogen, 75 ml/min and air, 470 ml/min. Sample volumes of 0.2–0.5 μl were injected with a Hamilton injection syringe.

The standard compounds were primary C_8–C_{12} alcohols, 2-octanol and 3-octanol (products of Koch-Light, Great Britain).

RESULTS

Figs. 2–7 show the chromatograms of a mixture of the secondary alcohols obtained by the indirect hydration of C_9–C_{15} 1-alkenes. It can be seen that Apiezon L and the polyester are the least suitable phases for the separation of these compounds. Much better separation was achieved on the polyethylene glycols. At a temperature of 146° or, if necessary, 130°, the best separation was attained on polyethylene glycols 1500 and 1000.

Triplets of peaks are observed in chromatograms 4–7, of which one is always



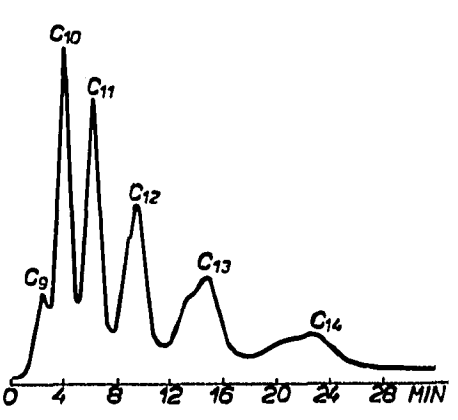


Fig. 2. Chromatogram on Apiezon L of the products of the indirect hydration of 1-alkenes. Column temperature, 135°.

Fig. 3. Chromatogram on poly(neopentyl glycol adipate) of the products of the indirect hydration of 1-alkenes. Column temperature, 164°.

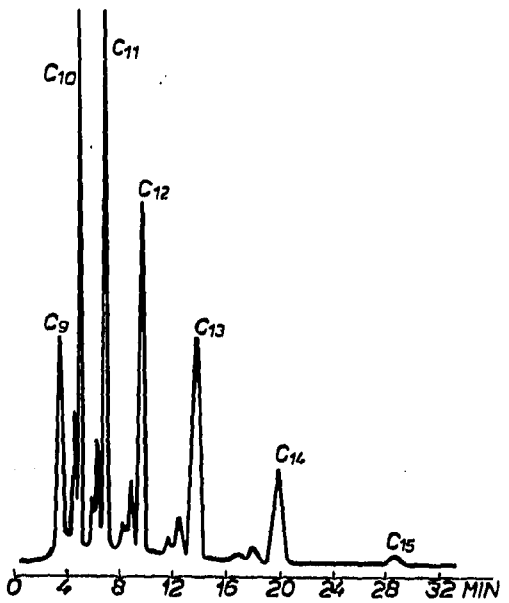


Fig. 4. Chromatogram on Carbowax 20 M of the products of the hydration of 1-alkenes. Column temperature, 165°.

larger than the other two. When comparing these chromatograms with that of the initial material (Fig. 8), it is justifiable to assume that the peak triplets correspond to three isomeric alcohols with the same carbon chain-length.

In order to be able to identify the individual peaks, we prepared, in the same way, secondary alcohols from pure 1-heptene, 1-octene and 1-nonene. Heptene and octene can produce at most three isomers, while nonene can give four secondary alcohols. The purified preparations were analysed on the polyethylene glycol phases. Fig. 9 shows chromatograms of the octanols obtained by the hydration and of 2-octanol and 3-octanol as standard substances. In the chromatogram of the octanols prepared by hydration, a peak of 4-octanol is present. In the chromatography of

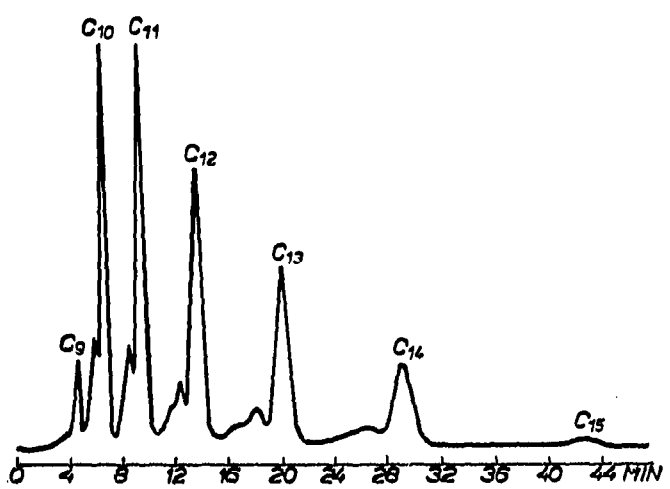


Fig. 5. Chromatogram on polyethylene glycol 4000 of the products of the hydration of 1-alkenes. Column temperature, 164°.

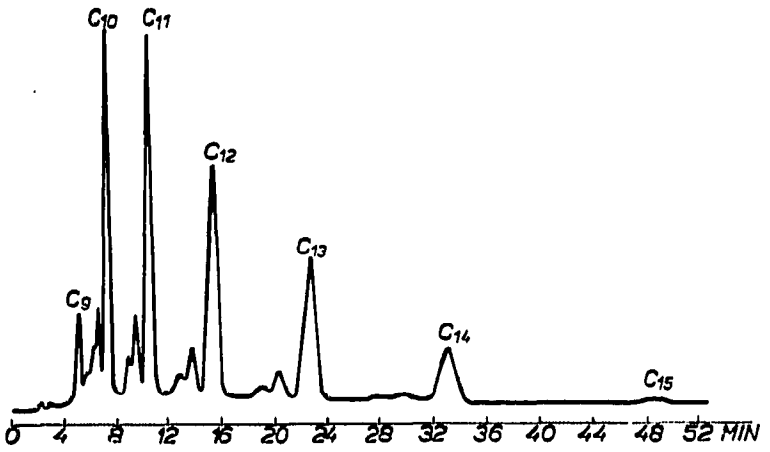


Fig. 6. Chromatogram on polyethylene glycol 1500 of the products of the hydration of 1-alkenes. Column temperature, 165°.

nonanols on packed columns, the separation of 5-nonanol and 4-nonanol was not satisfactory, but the other isomers were separated well.

The retention times were measured and the retention indices calculated for the above alcohols on two stationary phases. It can be seen from Table I that the retention indices increase in the homologous series by 100 index units. Upon shifting the hydroxyl group towards the centre of the molecule, the retention indices decrease by 30 or 20 units on passing from position 2 to position 3, and by 12 or 13 units on passing from position 3 to position 4.

The functional retention indices calculated after SVOBODA[8] agree with the data of CAROFF *et al.*[15], who measured the retention indices on polyethylene glycol 1540 and obtained values of 635 and 605 for 2-pentanol and 3-pentanol, respectively.

It is possible to conclude from the above results that the elution sequence of secondary alcohols on polyethylene glycol stationary phases is: 5, 4, 3, 2.

The acetates were prepared by the esterification of the alcohols with acetic

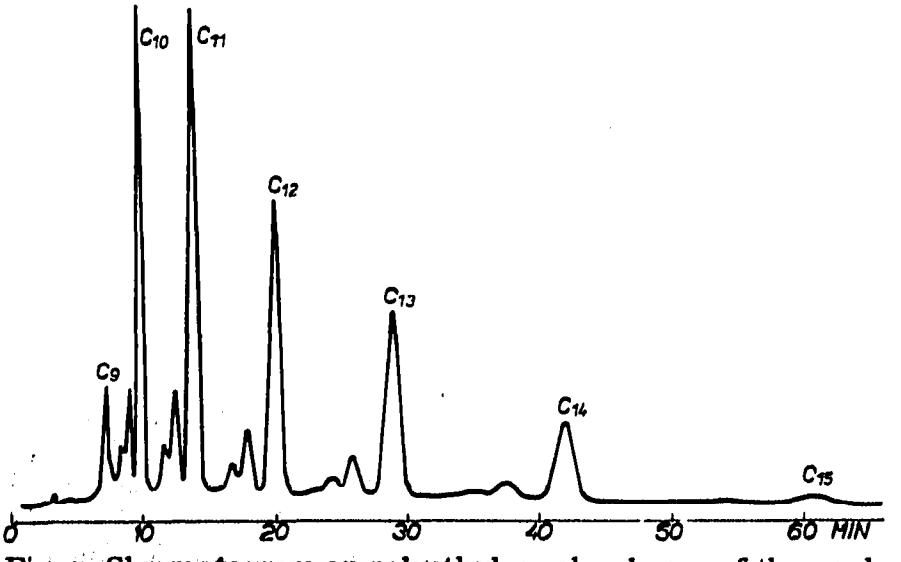
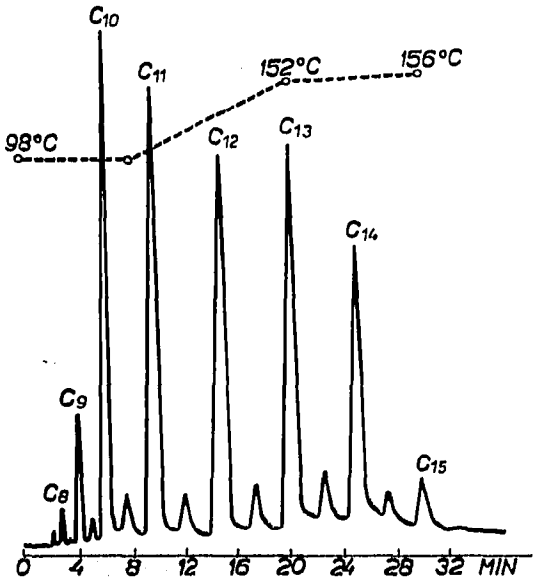


Fig. 7. Chromatogram on polyethylene glycol 1000 of the products of the hydration of 1-alkenes. Column temperature, 165°.



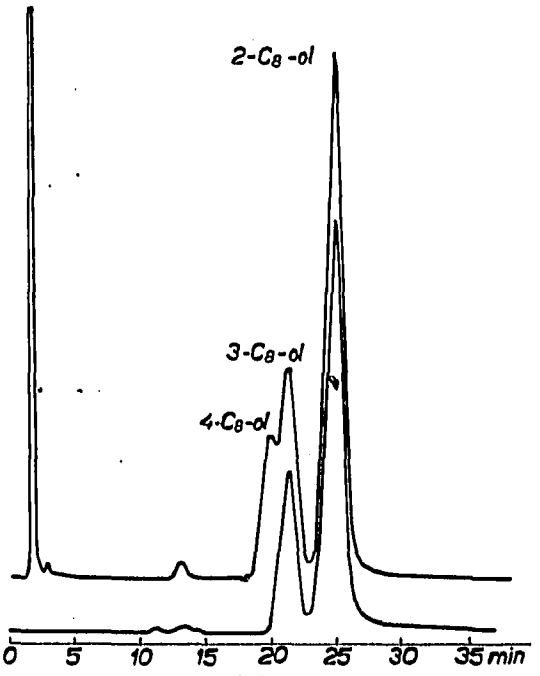


Fig. 8. Chromatogram of C_9–C_{15} 1-alkenes on polyethylene glycol 1500 with temperature programming of the column.

Fig. 9. Chromatogram of the secondary octanols prepared by the hydration of 1-octene (upper curve) and of 2-octanol and 3-octanol as standard compounds (lower curve). Stationary phase, polyethylene glycol 1500; column temperature, 100°.

anhydride and the retention times of the acetates were measured on polyethylene glycol 1500 and Apiezon L. The retention indices are given in Table II. It is evident that the separation of esters on Apiezon L is much better than that of free alcohols. It can also be stated that the elution order of the esters of secondary alcohols is the same as that of free alcohols on both polar and non-polar stationary phases. This finding is in compliance with the data of SCHOMBURG[9], who determined the retention indices for the acetates of heptanols.

TABLE I

RETENTION INDICES (*I*) AND FUNCTIONAL RETENTION INDICES (*FRI*) OF THE SECONDARY C_7–C_9 ALCOHOLS ON POLYETHYLENE GLYCOLS 1500 AND 1000 (P-1500, P-1000) AT 100°

FRI = *I* (alcohol) — *I* (*n*-alkane).

Alcohol	*Boiling point (°C)*[11]	*I*		*FRI*	
		P-1500	*P-1000*	*P-1500*	*P-1000*
2-C_7-ol	158.7	1335	1343	635	643
3-C_7-ol	156.5-7	1305	1323	605	623
4-C_7-ol	155.4	1291	1311	591	611
2-C_8-ol	179.0	1433	1443	633	642
3-C_8-ol	177.0	1404	1422	604	622
4-C_8-ol	176.3	1393	1409	593	609
2-C_9-ol	198.3	1538	1544	638	644
3-C_9-ol	194.5-5	1507	1524	607	624
4-C_9-ol	192-3	1492	1511	592	611
5-C_9-ol	193-4	1482	1500	582	600

TABLE II

RETENTION INDICES AND FUNCTIONAL RETENTION INDICES OF THE ACETATES OF SECONDARY ALCOHOLS ON POLYETHYLENE GLYCOL 1500 AND APIEZON L AT 100°

Symbols as in Table I.

Acetate of	*I*		*FRI*	
	P-1500	*Apiezon L*	*P-1500*	*Apiezon L*
2-C_7-ol	1280	985	580	285
3-C_7-ol	1252	—	552	—
2-C_8-ol	1379	1082	579	282
3-C_8-ol	1354	1665	554	265
4-C_8-ol	1332	1040	532	240
2-C_9-ol	1479	1186	579	286
3-C_9-ol	1455	1165	555	265
4-C_9-ol	1433	1139	533	239
5-C_9-ol	1411		511	

We measured the retention times of all the alcohols obtained by hydration of C_9–C_{15} 1-alkenes. The logarithms of the net retention times were correlated with the number of carbon atoms. It can be seen from Fig. 10 that the dependence is linear in all cases. Line *a* corresponds to the retention times of primary alcohols used as standards. On line *b* are the retention times of the major peaks of the above chromatograms, which are of 2-alkanols. The retention time of the standard 2-octanol is also on line *b*. On line *c* are the retention times of 3-alkanols, which is also confirmed by the retention time of 3-octanol on this line. The retention times of 4-alkanols, or the other isomers, lie on line *d*.

It is known from the analogous reactions of olefins in acidic media that all the possible isomers are produced in the reaction[10]. Hence, it can be assumed that the high peaks of the 4-alkanols in the chromatogram in Fig. 11 overlap with those of other isomers.

The above assumption was proved as follows: the C_{10} alcohols were isolated on a preparative chromatograph, and the fraction so obtained was re-analysed on an

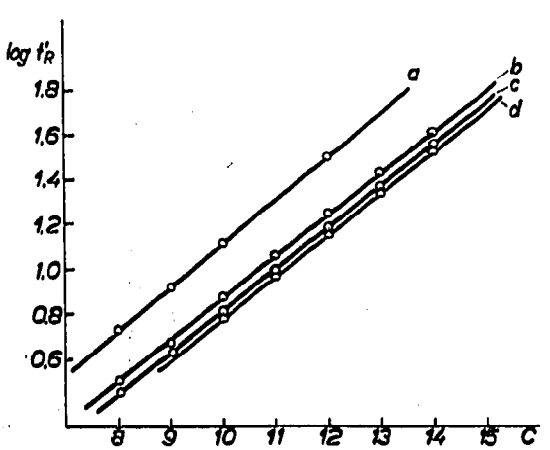


Fig. 10. Dependence of retention time on carbon number. Stationary phase, Carbowax 20 M; column temperature, 146°.

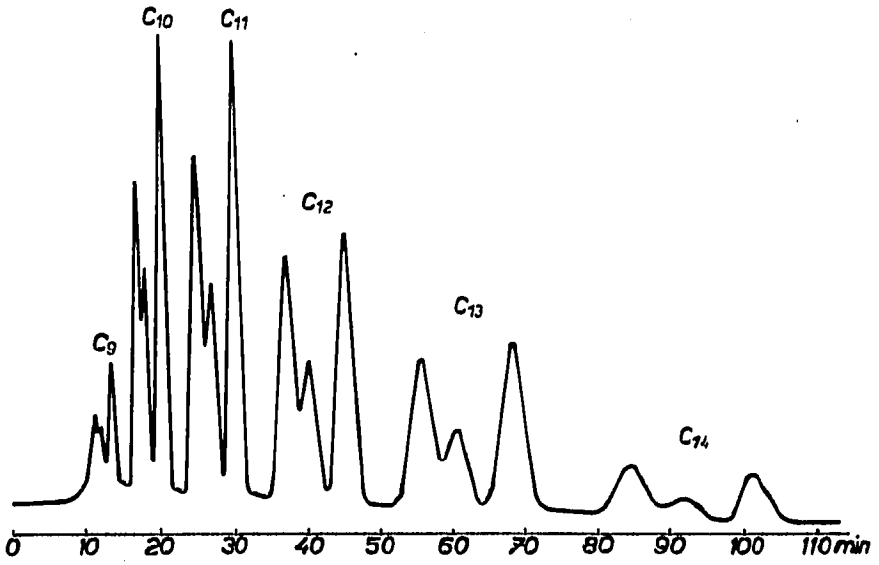
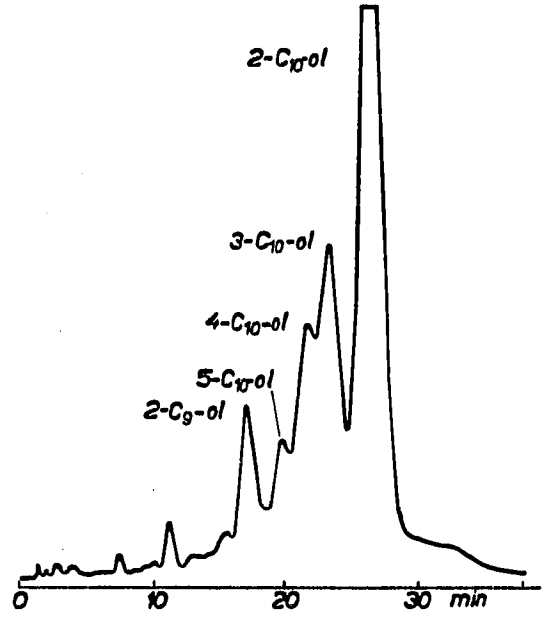


Fig. 11. Chromatogram of the products of the hydration of C_9–C_{15} 1-alkenes. Stationary phase, polyethylene glycol 1000; column temperature, 150°.

analytical column. It can be seen from Fig. 12 that 5-decanol appeared in the peak of 4-decanol. It follows that a more detailed analysis of the hydration product requires a more efficient column. Fig. 13 shows a chromatogram of a mixture of secondary alcohols, obtained on a capillary column with polyethylene glycol 1500 as the stationary phase. The peaks of 5- and 6-alkanols are evident in this chromatogram.

It follows from the above results that a complete separation of the isomers of higher aliphatic alcohols may be attained on a high-efficiency capillary column or by chromatographing the alcohols in the form of acetates.



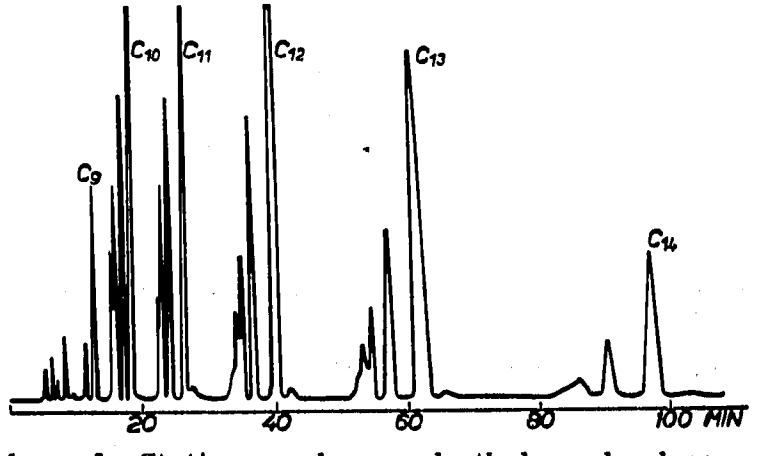


Fig. 12. Chromatogram of the secondary decanols. Stationary phase, polyethylene glycol 1500; column temperature, 146°.

Fig. 13. Chromatogram of the products of the hydration of 1-alkenes, obtained on a capillary column. Stationary phase, polyethylene glycol 1500; column temperature, 150°.

TABLE III

RETENTION INDICES OF SECONDARY AND SOME PRIMARY ALCOHOLS

Alcohol	*Stationary phase*			
	Carbowax 20 M		*PEG-1000*	
	130°	*165°*	*135°*	*165°*
1-C_8-ol	1518	1522	1588	1585
2-C_8-ol	1385	1385	1445	1443
3-C_8-ol	1356	1359	1423	1422
1-C_9-ol	1624	1629	1697	1690
2-C_9-ol	1488	1489	1545	1542
3-C_9-ol	1459	1461	1525	1523
1-C_{10}-ol	1732	1736	1799	1788
2-C_{10}-ol	1592	1596	1649	1645
3-C_{10}-ol	1563	1570	1623	1618
4-C_{10}-ol	1545	1544	1609	1598
2-C_{11}-ol	1697	1706	1753	1750
3-C_{11}-ol	1665	1673	1723	1719
4-C_{11}-ol	1648	1651	1704	1700
1-C_{12}-ol	1943	1952	2004	1996
2-C_{12}-ol	1801	1806	1855	1855
3-C_{12}-ol	1769	1779	1826	1826
4-C_{12}-ol	1752	1763	1808	1806
2-C_{13}-ol	1903	1906	1953	1957
3-C_{13}-ol	1872	1879	1926	1928
4-C_{13}-ol	1856	1862	1910	1908
2-C_{14}-ol	2005	2013	2055	2059
3-C_{14}-ol	1981	1988	2029	2029
4-C_{14}-ol	—	1967	2008	2012
2-C_{15}-ol	—	2118	—	—

For the sake of a quantitative assay of the individual stationary phases, retention indices on Carbowax 20 M and on polyethylene glycol 1000 (Table III) were measured at two temperatures. Although the values measured are rather scattered, the large number of results allows certain regularities to be found. It can be seen from Table IV that the shift of the hydroxyl group from the first to the second carbon atom manifests itself in a decrease of the retention index by about 140 units, the shift from position 2 to position 3 results in a decrease of the retention index by about 27 units and the shift from position 3 to position 4 decreases the retention index by about 18 units. It can be inferred from these results that a further shift in the hydroxyl

TABLE IV

DECREASES IN THE RETENTION INDEX BROUGHT ABOUT BY A CHANGE IN THE POSITION OF THE HYDROXYL GROUP

Change of position	*Carbowax 20 M*			*PEG-1000*		
	130°	*146°*	*165°*	*135°*	*150°*	*165°*
1 → 2	−138	−139	−141	−143	−144	−143
2 → 3	− 29	− 27	− 29	− 27	− 27	− 26
3 → 4	− 17	− 18	− 18	− 18	− 20	− 19

TABLE V

FUNCTIONAL RETENTION INDICES OF SECONDARY ALCOHOLS

A = Apiezon L; C-20 M = Carbowax 20 M; P-1000 = polyethylene glycol 1000.

Alcohols	*135°*			*165°*		
	A	*C-20 M*	*P-1000*	*A*	*C-20 M*	*P-1000*
1-ols	240	735	795	238	738	790
2-ols	171	595	648	172	600	650
3-ols	167	565	624	167	570	622
4-ols	167	550	608	167	565	604

group towards the centre of the molecule will result in a decrease in the difference between the retention indices and the separation of such isomers will be more difficult. The separation of the above isomers may be achieved only on stationary phases that have sufficiently high interactions with the substance being separated. The extent of this interaction is expressed quantitatively by the functional retention index. It is apparent from Table V that the functional retention indices on Apiezon L are relatively low. On the polyethylene glycols, the above values are much higher, being still higher on polyethylene glycol 1000 than on Carbowax 20 M. This difference is connected with the relatively higher content of hydroxyl groups, which form hydrogen bonds with the alcohols being analysed, thus increasing the interaction. The retention times measured on polyethylene glycols 1500 and 400 and on polypropylene glycol confirm the above concept. On polyethylene glycol 400, the functional retention indices were the highest, while on polypropylene glycol 3040 these values were only a little higher than on Apiezon L. At the same time, the separation of isomers was much worse on the propylene glycol phase.

The interaction of the stationary phase with the alcohols being analysed is shown by a large change of the relative volatility of the alcohols. Thus, for instance,

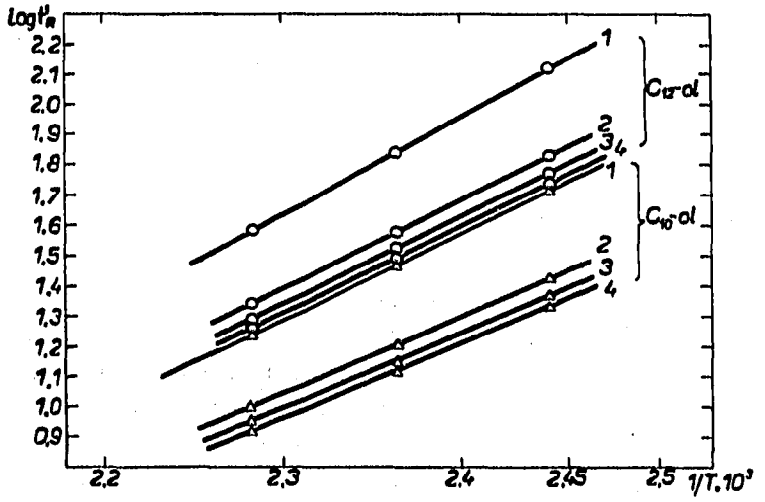


Fig. 14. Dependence of the net retention time on the column temperature for C_{10}–C_{12} alcohol Stationary phase, polyethylene glycol 1000.

the boiling point of 3-decanol (213°) is 3° higher than that of 2-decanol (210°) (ref. 11), but the elution sequence is the opposite. A decreased interaction in the case of 3-decanol and other similar cases may be explained by the fact that the shifting of the hydroxyl group towards the centre of the molecule enhances the shielding of the hydroxyl group by the remaining part of the molecule, thus increasing the steric hindrance to the formation of hydrogen bonds. This is in agreement with the results of JANÁK *et al.*[12], who studied the elution sequence of monofunctional phenols on stationary phases capable of forming hydrogen bonds.

We also investigated the effect of temperature on the elution sequence of the C_{10} and C_{12} alcohols. It is apparent from Fig. 14 that the dependence is linear for all the alcohols. This means that no change in the elution order is produced on changing the temperature.

It can be assumed from the above results as well as from the dependence in Fig. 10 that the correlations obtained will apply also to alcohols with longer chains.

CONCLUSIONS

It can be concluded that the C_{18} alcohols are eluted in the sequence 6, 5, 4, 3, 2, the primary alcohol being eluted last.

We searched the literature for the elution sequences of other isomeric substances. Methylalkanes, with the methyl group shifted along the molecule, are eluted in the sequence 5, 4, 2, 3, 1, *i.e.*, in the order of increasing boiling point, on both polar and non-polar stationary phases[9,13].

Olefins on squalane are eluted in the sequence 1, 4, 3, 2, *i.e.*, in the order of increasing boiling points, but on polyethylene glycol the elution order is 1, 2, 3, regardless of the boiling point[14].

Primary esters, with the methyl group shifted along the carbon chain of the acid portion, are eluted on a non-polar stationary phase in the sequence 1, 2, 3, 4, 5, 6, while on polar stationary phases the elution sequence is[9] 1, 2, 3, (4 + 6), 5.

The esters of secondary alcohols are eluted in the same order as the secondary alcohols[9] on both polar and non-polar stationary phases, *i.e.*, 5, 4, 3, 2. The same elution order also occurs for tertiary alcohols and ketones[7].

From the above results, it is possible to conclude that if an alkyl group is situated near a polar group in the molecule, the retention time will be decreased owing to shielding of the polar group by the alkyl group. When the distance between the alkyl and polar groups is increased, the retention time also increases since the degree of steric hindrance decreases.

However, if the polar group is shifted towards the centre of the molecule, the opposite occurs, as the steric hindrance due to the remaining part of the molecule starts to have an influence. The steric hindrance becomes greater as the functional group moves towards the centre of the molecule. When the functional group is in the centre of the molecule, *i.e.*, for a symmetrical molecule, this isomer is eluted first as it has the greatest possibility of shielding the functional group, despite the fact that its boiling point is relatively high. This applies mainly to polar stationary phases. With non-polar stationary phases, the situation is similar, although the differences are not as great owing to the lower interaction of the stationary phase with the substances being separated.

REFERENCES

1 S. PATAI, *The Chemistry of Alkanes*, Interscience Publisher, New York, 1964, p. 419.
2 B. A. KRENCEL, *Osnovy Synteza Alifaticheskikh Spirtov iz Neftyannykh Uglevodorodov*, Iz. AN SSSR, Moscow, 1954.
3 B. M. FINGER, G. A. GILLIES, G. M. HARTWIG, W. W. RYDER AND W. A. SAWYER, *J. Amer. Oil Chem. Soc.*, 44 (1967) 525.
4 E. GIL-AV AND D. NUROK, *Proc. Chem. Soc.*, (1962) 146.
5 E. GIL-AV, R. CHARLES-SIGLER, G. FISCHER AND D. NUROK, *J. Gas Chromatogr.*, 4 (1966) 51.
6 J. M. GROSS, B. F. DUTNEY AND J. BERNSTEIN, *J. Chromatogr. Sci.*, 8 (1970) 679.
7 R. SIVARAMA KRISHNAN, L. A. WITTING AND M. K. HORWITT, *J. Chromatogr.*, 13 (1964) 22.
8 P. A. T. SWOBODA, in M. VAN SWAAY (Editor), *Gas Chromatography*, Butterworths, London, 1962, p. 273.
9 G. SCHOMBURG, *Sep. Sci.*, 1 (1966) 339.
10 M. MARQUIS, *Hydrocarbon Process.*, 47, No. 3 (1966) 109.
11 F. RICHTER (Editor), *Beilsteins Handbuch der Organische Chemie*, Ergänzungswerk I–III, System No. 24, Springer Verlag, Berlin–Gottingen–Heidelberg.
12 J. JANÁK, R. KOMERS AND J. ŠÍMA, *Chem. Listy*, 52 (1958) 2296. *Collect. Czech. Chem. Commun.*, 24 (1959) 1492.
13 G. D. MITRA AND N. G. SAHA, *J. Chromatogr. Sci.*, 8 (1970) 95.
14 B. BLOURI, J. FAUVET AND P. RUMPF, *Bull. Soc. Chim. Fr.*, (1963) 1855.
15 J. N. CAROFF, I. BAHURELL AND I. VERNON, *J. Gas Chromatogr.*, 4 (1966) 234.