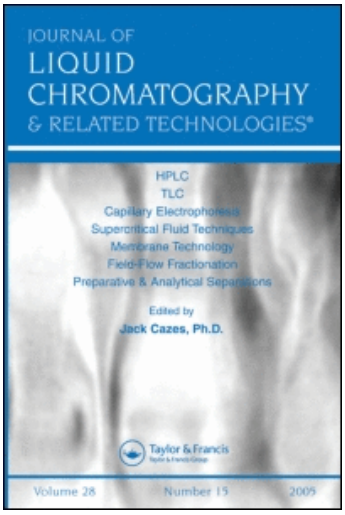

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Atypic Gel Permeation Chromatography of Alcohols

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ATYPIC GEL PERMEATION CHROMATOGRAPHY OF ALCOHOLS

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ABSTRACT

The elution behaviour of alcohols in the systems Bio Beads SX-8/dichloromethane and Sephadex LH-20/dichloromethane is investigated. On Bio Beads SX-8 the elution volumes are lower than expected for normal GPC behaviour, which is perhaps due to hydrogen bonding in solution. On Sephadex LH-20 adsorption takes place by means of hydrogen bonding, which can be used for very selective separations.

INTRODUCTION

In previous publications (1,2) the separation of lower acyclic oligomers of isoprene by gel permeation chromatography (GPC) was described. It could be shown (1) that there exists a linear relationship between the logarithms of the molecular refraction R_{M_D} (which can

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be calculated from the increments found in literature) and the elution volumes V_e. In this way a universal calibration is given for the alkanes, alkenes, polyalkenes and alkyl halides. When trying to separate mixtures of isoprene oligomers and dimethyl octadienols from the homogeneously catalyzed telomerization of isoprene (3,4) deviations were observed for the alcohols, which are described here and employed for separating them. Since also smaller molecules can advantageously be separated especially for preparative purposes by means of GPC, the knowledge of these facts seems to be of common interest.

EXPERIMENTAL

The apparatus consisted of an eluent reservoir, a sintered glass filter, a micropump MC 300 with a pump head 2D (Mikrotechna Praha/CSSR), PTFE tubing, a 500 x 15 mm or 1000 x 15 mm glass column (VEB Technisches Glas Ilmenau/GDR) with home-made adapters and a differential refractometer RIDK 101 (Laboratorni Pristroje Praha/CSSR). All further details concerning the purification of dichloromethane and the filling of the column with Bio Beads SX-8 (Bio-Rad Laboratories, Richmond/USA) or Sephadex LH-20, particle size 0.025-0.100 mm (Pharmacia Fine Chemicals, Uppsala/Sweden), are to be found in (1,2). The technique of recycling is described in (2).

The samples for analytical separations (0.005-0.05 ml) were directly introduced into the column through the inlet tube. The flow velocity was 55-60 ml/h and the observed average number of theoretical

plates $N = 16\left(\frac{V_e}{w}\right)^2$ for pure substances with K_D of about 1 was 2700. V_m was determined from V_e of isoprene polymers and $V_m + V_s$ from V_e of chloroform. The temperature was 23 $\pm$ 2°C.

Some of the experiments with Sephadex LH-20 were made with a column using only the gravity flow of the eluent (difference in level 3 m max., v = 70-90 ml/h, average N 2000-3000). In this way it was found that the bed of the column, which was connected to the pump (at about $2\text{-}3 \cdot 10^5$ Pascal), had been compressed considerably.

Column with gravity flow 811 x 15 mm
V_m = 35.4 ml V_s = 64.5 ml
Column with pump 920 x 15 mm
V_m = 22.0 ml V_s = 82.4 ml

The distribution coefficients K_D of tables 2 and 3 were determined by at least three measurements by weighing the eluent and simultaneously using chloroform as a reference substance. They were in good agreement with the K_D values found with gravity flow. The compression of the column bed did not influence the values of K_D, but has the advantage of increasing the peak capacity, which is proportional to V_s.

The molecular refractions R_{M_D} (in relation to the sodium D line) were calculated with the following increments: C 2.418; H 1.1; hydroxyl oxygen 1.525; I 13.9; double bond 1.733 (1).

The isoprene oligomers employed were isolated from oligomer mixtures (5) by preparative GLC according to (2). The dimethyl octadienols were isolated from

TABLE 1

V_e (ml) on 437 x 15 mm Bio Beads SX-8 in CH_2Cl_2

x) sample amount

		ml
Squalane		33.3
Hexadecane		39.1
n-Decane		44.0
n-Hexane		48.6
Chloroform		53.2
V_m		29.7
1-Octadecyl iodide		37.5
1-Decyl iodide		42.0
Tetramers of isoprene		36.7
Trimers of isoprene		39.7
Dimers of isoprene		43.7
Mixture of dimethyl octadienols		40.7
1-Butanol 0.01 ml x)		45.9
0.02 ml		45.5
0.05 ml		44.5
0.2 ml		42.7
2-Butanol 0.02 ml		45.8
1-Pentanol		44.3
1-Hexanol		43.7
1-Heptanol		42.7
1-Decanol		40.1
1-Dodecanol		39.5
1-Octadecanol		36.5
E-3,7-Dimethyl-2,6-octadiene-1-ol	Subst.6	40.6
3,7-Dimethyl-1,6-octadiene-3-ol	Subst.1	41.2
3,7-Dimethyl-7-octene-1-ol	Subst.9	40.7

TABLE 2

Elution volumes V_e (ml) and distribution coefficients $K_D = \frac{V_e - V_m}{V_s}$ on 920 x 15 mm Sephadex LH-20 in CH_2Cl_2

	ml	K_D
Chloroform	104.4	1
Squalane	39.5	0.212
Hexadecane	51.8	0.362
Decane	64.4	0.514
V_m	22.0	0
Tetramers of isoprene	49.5	0.334
Trimers of isoprene	55.1	0.402
Dimers of isoprene	63.8	0.507
1-Octadecanol	95.5	0.892
1-Dodecanol	128.5	1.292
1-Decanol	143	1.47
1-Octanol	157.6	1.646
2-Ethyl-1-hexanol	141.8	1.454
1-Heptanol	171.2	1.811
1-Hexanol	179.8	1.915
2-Methyl-2-butanol	136.7	1.392
2-Pentanol	155.3	1.618
3-Methyl-1-butanol	193	2.08
2-Methyl-1-butanol	188	2.02
1-Pentanol	196.8	2.12
2-Methyl-2-propanol	155.3	1.618
2-Butanol	167.4	1.765
2-Methyl-1-propanol	199.1	2.149
1-Butanol	210	2.28
2-Propanol	201	2.17
1-Propanol	235	2.59

TABLE 3

Elution volumes V_e (ml) and distribution coefficients $K_D = \frac{V_e - V_m}{V_s}$ on 920 x 15 mm Sephadex LH-20 in CH_2Cl_2

	Substance	ml	K_D
1	3,7-Dimethyl-1,6-octadiene-3-ol	98.1	0.924
2	3,7-Dimethyl-1,7-octadiene-3-ol	105	1.01
3	2,7-Dimethyl-1,7-octadiene-3-ol	117.3	1.157
4	2,6-Dimethyl-1,7-octadiene-3-ol	117.6	1.160
5	Z-3,7-Dimethyl-2,6-octadiene-1-ol	128	1.29
6	E-3,7-Dimethyl-2,6-octadiene-1-ol	135.7	1.38
7	Z-2,7-Dimethyl-2,7-octadiene-1-ol	140.7	1.441
8	E-2,7-Dimethyl-2,7-octadiene-1-ol	134	1.36
9	3,7-Dimethyl-3,6-octadiene-1-ol (presumably Z)	141.2	1.447
10	3,7-Dimethyl-7-octene-1-ol	141.1	1.445

samples of VEB Chemisches Kombinat Miltitz/GDR (substances 1,5,6,9 and 10 of table 3) or products of the palladium catalyzed telomerization of isoprene (3,4) by means of preparative gas chromatography. In a gas chromatograph Model 2868 (Varian Aerograph, Walnut Creek/USA) 0.2 ml portions of mixture were repeatedly separated on a commercial column, 15 m x 9.5 mm, filled with 20% m-bis(m-phenoxyphenoxy) benzene (5-ring PMPE) on Chromosorb W 30/60 mesh preparative grade in an isothermal way at 190°C (sample inlet 250°C).
From substances 1, 5 and 10, i.e., β-linalool, nerol and citronellol resp., all by-products were re-

moved, whereas from geraniol 6 and 9 were isolated, 6 being present in higher amounts and showing a longer retention time. Identifications were based upon their IR spectra, which were taken between KBr discs and compared with known IR spectra (3,6,7). The analysis of the fractions of the separation of the telomerization mixtures on the system Sephadex LH-20/dichloromethane was made by capillary gas chromatography. In a chromatograph Chrom 4 (Laboratorni Pristroje Praha/CSSR) 0.5 μl portions with a splitting ratio of about 1:90 were separated at 150°C on a metal capillary (50m x 0.25 mm) coated with nitrile silicone oil OE 4178 (20% solution in acetone). The identification of peaks was in agreement with another investigation (3).

RESULTS AND DISCUSSION

In the system Bio Beads SX-8/CH_2Cl_2 dimethyl octadienols are eluted at a longer distance before the isoprene dimers than could be expected on the basis of the above-mentioned calibration of log R_{M_D} against V_e. The incorporation of simple alcohols shows these deviations to increase with decreasing alkyl chain length. A reasonable explanation would be an increasing association of alcohols with decreasing alkyl chain length due to hydrogen bonding in solution. This explanation is supported by the observation that the above-mentioned deviation will increase with increasing concentration of n-butanol in the sample. Freeman and Angeles (8) used the same explanation in an extensive investigation and literature research on the system Styragel/CCl_4 for methanol.

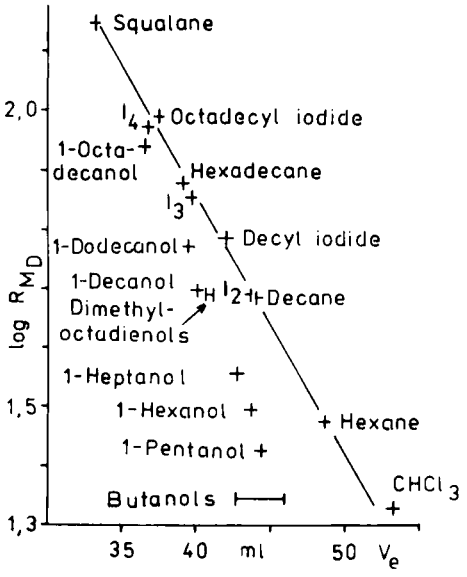

FIGURE 1

Correlations between log R_{M_D} and V_e on 437 x 15 mm Bio Beads SX-8 in CH_2Cl_2. I_4, I_3 and I_2 mean tetramers, trimers and dimers of isoprene, resp.

In contrast to the system Bio Beads SX-8/CH_2Cl_2 more advantageous selectivity relations are to be expected with the system Sephadex LH-20/CH_2Cl_2.
Joustra et al. (9) noticed "that on Sephadex LH-20 in $CHCl_3$ solutions substances containing carboxyl groups or hydroxyl groups are retarded relative to the corresponding substances not containing these groups".
Brooks et al. (10) observed the same in benzene on a conversion product of Sephadex LH-20 bearing hydroxyl and ether groups and they found that by addition of alcohol to the eluent this effect is eliminated. They

write: "..it appears that a hydrogen bonding effect is operating with the gel acting exclusively as the basic compound".

Determann and Walter (11) found an increased affinity of phenols to a solution of polyethylene glycol, when compared with a solution of dextran . It seems to be interesting that the adsorption of phenol on Sephadex LH-20 is eliminated by an ether like monoethyl-diglycol ether as eluent (12). All effects seem to indicate that oxygen atoms of ether favour the formation of hydrogen bonds. Streuli (13) found indications for the adsorption of phenol by hydrogen bonding on Sephadex LH-20 even in methanol as an eluent. When comparing the eluents methanol, dimethyl formamide, THF and acetonitrile (14) he noticed a particularly high adsorption of methanol, benzyl alcohol, phenols and aromatic carboxylic acids in the latter.

Adsorption of phenols due to hydrogen bonding was also observed by Determann and Lampert (15) in n-butanol, by Concin et al. (16) even in dioxane and by Johnels et al. (17) in $CHCl_3$. It should be noticed that the adsorption of aromatic compounds from alcohols as eluents was the starting point of the investigations in all publications cited and not the attempt to separate compounds having hydroxyl groups.

Barth et al. (18) developed a group separation by means of a stepwise gradient $CHCl_3$, $CHCl_3$ + methanol, $CHCl_3$ + THF, in which hydrocarbons, alcohols, phenols, polyhydroxy compounds and fatty acids are eluted in the order mentioned; the alcohols being en bloc isolated after the alkanes. Their results are interesting in that hydroperoxides were more strongly adsorbed than alcohols of comparable molar mass .

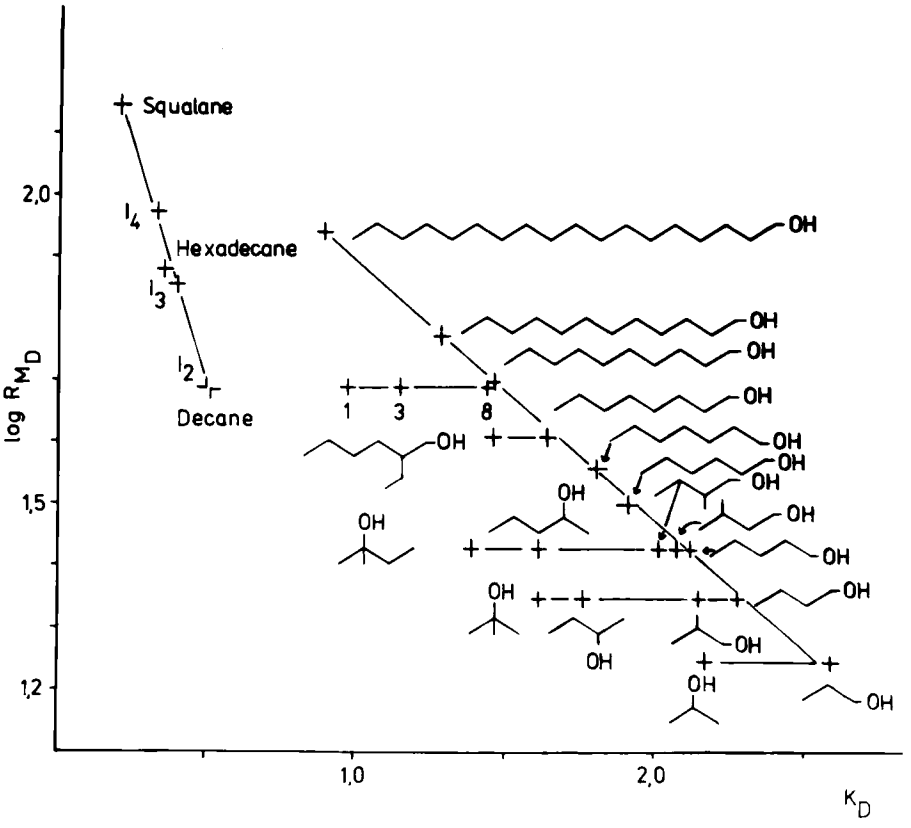

FIGURE 2

Correlation between log R_{M_D} and K_D on 920 x 15 mm Sephadex LH-20 in CH_2Cl_2. Nos.of substances cf. Table 3

All observations summarized it is not astonishing that in the system Sephadex LH-20/CH_2Cl_2 the dimethyl octadienols to be separated were eluted long after the isoprene oligomers which were eluted via typical GPC. To study this effect in detail a number of well-known alcohols were included into the investigation.

Except 1-octadecanol the K_D values are all larger than one and indicate adsorption, which is practically only due to hydrogen bonding. On the other hand there is a certain course of the K_D values clearly recognizable in the order of primary straight chain alcohols, which can be explained with a smaller surface of the adsorbent being available to the larger alcohol molecules than to the smaller ones.

A second explanation, which does not exclude the first one, would be hydrophobic interaction with the eluent, which increases with the size of the molecules of these alcohols. If hydrophobic interaction in hydrous systems is thought of being so important in this connection (15,19,20), it should be paid due attention in anhydrous systems, too.

Therefore it is interesting and emphasizing the first explanation that the separation of the alcohols proceeds strongly according to their specific structure

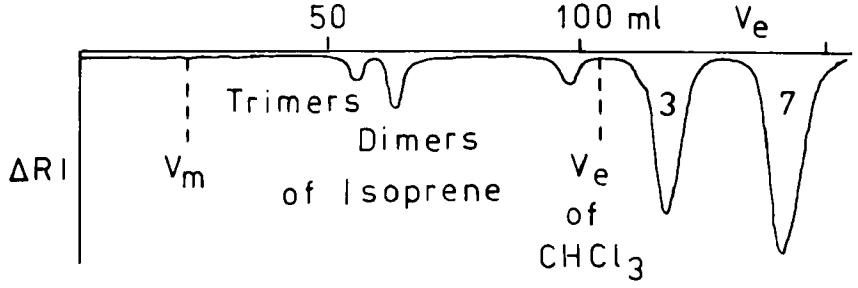

FIGURE 3

Separation of 0.04 ml of a mixture of oligomers of isoprene and dimethyl octadienols on 920 x 15 mm Sephadex LH-20 in CH_2Cl_2, v = 54.5 ml/h. Sensitivity of the RI detector E = 4. Nos. of substances cf. Table 3.

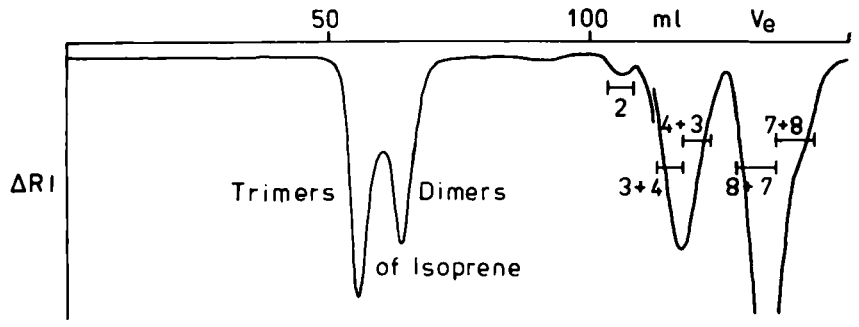

FIGURE 4

Separation of 0.225 ml of a mixture of oligomers of isoprene and dimethyl octadienols. v = 42.8 ml/h. E = 4 up to the first fraction = subst. 2, afterwards E = 8. The horizontal lines mean fractions, the first number means the dominating substance. Nos. of substances cf. Table 3.

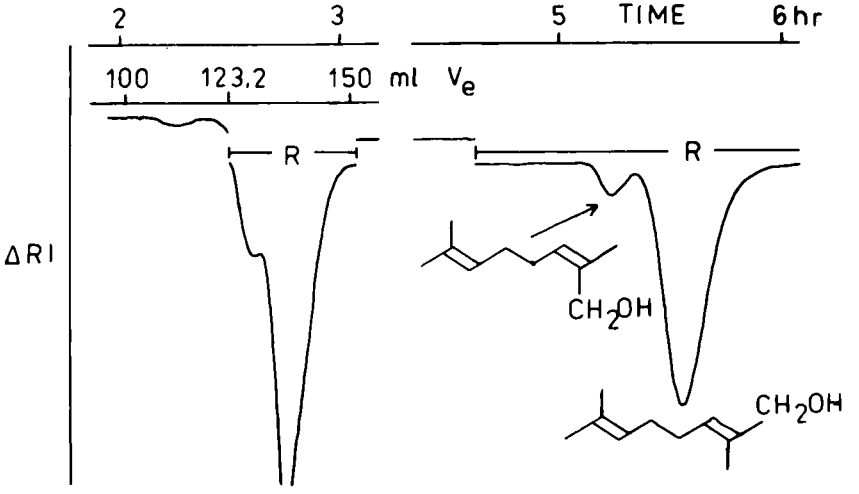

FIGURE 5

Separation of 0.02 ml geraniol (subst.6) and 0.003 ml nerol (subst.5) by one recycling step. v = 49.3 ml/h, E = 2. R means recycling (involving some baseline shift)

in such a way that at first tertiary alcohols, then secondary and at last primary ones are eluted. In this way from simple mixtures of telomerization the separation of pure dimethyl octadienols (Fig.3) and from more domplex mixtures a group separation into tertiary, secondary and primary dimethyl octadienols (Fig.4) will be possible.

Both with the saturated primary alcohols and the primary dimethyl octadienols the remaining alkyl or alkenyl group has an unexpectedly strong influence on the elution behaviour so that even the E,Z isomers nerol and geraniol could be separated after a single recycling step (Fig.5).

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