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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF ADAMANTANOLS AND OTHER CYCLIC ALCOHOLS

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SUMMARY

Chromatographic elution data for 28 monocyclic and polycyclic alcohols of the adamantane type have been measured, using silica gel as the stationary phase and mixed mobile phases in different concentration ratios.

The position of the hydroxyl group has the largest effect on the chromatographic behaviour of polycyclic alcohols. The introduction of an alkyl group into alcohols such as adamantanol results in a decrease in retention time. This decrease is larger when the adamantanol is substituted by several small alkyl substituents ($-CH_3$, $-C_2H_5$) than by one large alkyl group.

For polycyclic alcohols having the same formal substitution type, the elution time decreases with increasing size of the basic skeleton. The rate of this decrease depends on the composition of the mobile phase used. The effect of the mobile phase composition on the elution data for the compounds studied is discussed.

INTRODUCTION

Several thousand adamantane derivatives have been prepared at different laboratories. These compounds are important in basic research, and they also have practical applications in pharmacy, biochemistry, medicine, the chemistry of plastics and in the synthesis of special lubricants, etc.

The aim of the present work was to describe the liquid chromatographic behaviour of some polycyclic alcohols, using silica gel as stationary phase and different mobile phases based on *n*-heptane in combination with 2-propanol, chloroform and diethyl ether. The objectives may be summarized as follows: (i) to find the optimum conditions for the separation of some adamantane and diamantane alcohols by high-performance liquid chromatography (HPLC); (ii) to investigate the fundamental relationships between molecular structure and chromatographic behaviour of polycyclic alcohols in adsorption liquid chromatography; (iii) to utilize the data from the analytical study for separations using preparative scale liquid chromatography.

In adsorption liquid chromatography, the retention time of a compound on a column with a given geometrical arrangement and at a constant mobile phase flow-

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rate is determined by the type of adsorbent, the composition of the mobile phase and the constitution of the sample. The relationship between the chromatographic behaviour of a substance and its molecular structure represents one of the most important problems[1].

Two contributions of the sample character to the sample adsorption energy may be differentiated: (i) the type of functional groups present, *i.e.*, the "primary effect"; (ii) the arrangement of these groups, *i.e.*, the "secondary effect". With the steadily increasing separation efficiency of columns, it has become possible to separate compounds having very similar molecular structures.

EXPERIMENTAL

Apparatus

A Varian 8500 liquid chromatograph with a syringe pump was used, connected with a RI detector and A25 dual-channel strip-chart recorder (Varian, Palo Alto, CA, U.S.A.). Sample injection was performed with the stop-flow technique; 5- and 10-μl syringes (Hamilton, Bonaduz, Switzerland) were used. The column was a Micropak Si-10 (50 cm $\times$ 2 mm I.D.; Varian), packed with 10-μm silica gel LiChrosorb Si 60.

Retention data were calculated on an HP 9830A calculator connected with an HP 9866A thermal printer (Hewlett-Packard, Avondale, PA, U.S.A.). Graphical processing of data was carried out on the same calculator equipped with an HP 9862A plotter.

Reagents

Nearly all of the standard compounds used for measurements were prepared in our laboratory. Diamantan-3-ol and 1-hydroxymethyldiamantane were kindly provided by Professor M. A. McKervey, University College, Cork, Ireland. 2-Propanol, analytical grade (Lachema, Brno, Czechoslovakia), was used without further treatment. *n*-Heptane (Reakhim, Moscow, U.S.S.R.) and diethyl ether (Lachema) were dried over sodium before use, distilled and stored over Nalsit A4 molecular sieves (CHZJD, Bratislava, Czechoslovakia). Chloroform, analytical grade (Lachema), was shaken with a 20% solution of NaOH, then distilled water, dried over phosphorus pentoxide and distilled on a glass perforated-plate column with exclusion of moisture.

Mobile phase

The mobile phases were prepared by weight from the degassed components. The following mobile phases were used: *n*-heptane–2-propanol; *n*-heptane–diethyl ether; *n*-heptane–diethyl ether–2-propanol; and *n*-heptane–chloroform–2-propanol. The compositions are given in Table I.

Procedure

Retention data were measured at laboratory temperature (18–22°C). The flow-rate of the mobile phase was 30 ml/h. Before the measurements, the column was stabilized by washing with fresh mobile phase (flow-rate, 30 ml/h) for 12 h. Column activity was checked once before the beginning of a measurement, then several times during the analyses and again after the completion of the measurement, by injecting a solution of cyclohexanol in the mobile phase. The dead volume of the column was

TABLE I

MOBILE PHASE COMPOSITIONS (%)

No. 1	*n-Heptane*	*2-Propanol*
a	99	1
b	98	2
c	97	3
No. 2	*n-Heptane*	*Diethyl ether*
a	65	35
b	50	50
c	35	65
No. 3	*n-Heptane–diethyl ether (65:35)*	*2-Propanol*
a	99.9	0.1
b	99.5	0.5
c	99.0	1.0
No. 4	*n-Heptane–chloroform*	*2-Propanol*
a	99.5 (80:20)	0.5
b	99.5 (65:35)	0.5
c	99.5 (50:50)	0.5

determined by measuring the retention time of an unretained compound, *viz.*, iso-octane.

Retention data were measured on chromatograms obtained by injecting solutions of compounds in the mobile phase.

RESULTS AND DISCUSSION

Retention times t_R and capacity factors k' are given in Tables II–V.

It was found that three main factors affect the adsorption of adamantanols and diamantanols:

(1) the position of the OH group on the adamantane or diamantane skeleton
(2) the type of alkyl substitution
(3) the size of the basic skeleton

Effect of the OH group position

For adamantane compounds containing only one OH group, the position of this group has a predominant effect on the chromatographic behaviour. Compounds in which the OH group is attached to a tertiary carbon atom where it is easily accessible to the adsorption centres of the silica gel surface, *e.g.*, adamantan-1-ol and diamantan-4-ol (see Fig. 1), are characterized by the strongest interaction with the adsorbent and their elution times are the longest. Shorter elution times are observed for compounds in which the OH group is on a secondary carbon atom, *e.g.*, adamantan-2-ol and diamantan-3-ol. The fastest elution was found for diamantan-1-ol, where the interaction of the OH group with the silica gel adsorption centres is probably diminished by steric effects involving the *syn* axial hydrogen atoms on the carbon atoms in the vicinity of the hydroxyl group[2]. Chromatograms of the adamantanols, diamantanols and of cyclohexanol are shown in Fig. 2. Change of mobile phase

composition has a relatively greater effect on the elution time of cyclohexanol compared with the polycyclic alcohols (Tables II–V).

TABLE II

RETENTION DATA

Mobile phase: a% *n*-heptane–b% 2-propanol. C = Number of carbon atoms; t_R = Retention time (sec); k' = capacity factor.

Compound	C	$a = 99, b = 1$		$a = 98, b = 2$		$a = 97, b = 3$	
		t_R	k'	t_R	k'	t_R	k'
Cyclohexanol	6	1606	8.91	943	4.82	660	3.07
Adamantan-1-ol	10	1334	7.24	773	3.77	550	2.39
3-Methyladamantan-1-ol	11	1225	6.56	710	3.39	504	2.11
3,5-Dimethyladamantan-1-ol	12	1106	5.83	648	3.00	466	1.87
3,5,7-Trimethyladamantan-1-ol	13	996	5.15	590	2.64	428	1.64
3-Ethyladamantan-1-ol	12	1130	5.98	668	3.13	474	1.93
3-Ethyl-5-methyladamantan-1-ol	13	1013	5.25	607	2.75	434	1.68
3-Ethyl-5,7-dimethyladamantan-1-ol	14	924	4.70	580	2.58	406	1.50
3-Propyladamantan-1-ol	13	1058	5.53	635	2.92	463	1.86
3-Isopropyladamantan-1-ol	13	1068	5.59	624	2.85	446	1.76
3-Butyladamantan-1-ol	14	1002	5.19	602	2.72	431	1.66
2-Methyladamantan-1-ol	11	872	4.39	544	2.36	408	1.52
Adamantan-2-ol	10	948	4.85	588	2.63	444	1.74
1-Methyladamantan-2-ol	11	616	2.80	385	1.38	310	0.91
2-Methyladamantan-2-ol	11	666	3.11	420	1.59	336	1.07
2-Ethyladamantan-2-ol	12	468	1.89	310	0.91	262	0.61
2-Propyladamantan-2-ol	13	376	1.32	256	0.58	228	0.41
2-Butyladamantan-2-ol	14	358	1.21	234	0.44	214	0.32
2-Isobutyladamantan-2-ol	14	313	0.93	222	0.37	162	0.07
Diamantan-1-ol	14	610	2.76	418	1.58	324	1.00
Diamantan-3-ol	14	860	4.31	548	2.39	404	1.50
Diamantan-4-ol	14	1246	6.69	728	3.50	510	2.15
1-Hydroxymethylbicyclo[3,3,1]nonane	10	1007	5.21	612	2.78	450	1.78
1-Hydroxymethyladamantane	11	1114	5.87	630	2.89	455	1.81
2-Hydroxymethyladamantane	11	1290	6.96	766	3.73	536	2.31
3,5-Dimethyl-1-hydroxymethyladamantane	13	847	4.23	539	2.33	406	1.50
2-(Adamant-1-yl)propan-2-ol	13	516	2.19	358	1.21	300	0.85
1-Hydroxymethyldiamantane	15	876	4.41	527	2.25	406	1.50

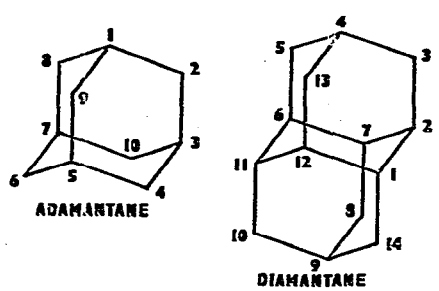


Fig. 1. Adamantane and diamantane.

TABLE III

RETENTION DATA

Mobile phase: a% n-heptane–b% diethyl ether.

Compound	*C*	$a = 65, b = 35$		$a = 50, b = 50$		$a = 35, b = 65$	
		t_R	k'	t_R	k'	t_R	k'
Cyclohexanol	6	1356	7.37	814	4.02	697	3.30
Adamantan-1-ol	10	1686	9.41	1094	5.76	842	4.20
3-Methyladamantan-1-ol	11	1524	8.41	1030	5.36	780	3.81
3,5-Dimethyladamantan-1-ol	12	1350	7.33	938	4.79	709	3.38
3,5,7-Trimethyladamantan-1-ol	13	1126	5.95	816	4.04	622	2.84
3-Ethyladamantan-1-ol	12	1326	7.19	791	3.88	618	2.81
3-Ethyl-5-methyladamantan-1-ol	13	1296	7.00	865	4.34	574	2.54
3-Ethyl-5,7-dimethyladamantan-1-ol	14	1126	5.95	739	3.56	490	2.02
3-Propyladamantan-1-ol	13	1326	7.19	841	4.19	684	3.22
3-Isopropyladamantan-1-ol	13	1398	7.63	827	4.10	671	3.14
3-Butyladamantan-1-ol	14	1302	7.04	858	4.30	670	3.13
2-Methyladamantan-1-ol	11	942	4.81	596	2.68	488	2.01
Adamantan-2-ol	10	894	4.52	586	2.61	467	1.88
1-Methyladamantan-2-ol	11	462	1.85	341	1.10	282	0.74
2-Methyladamantan-2-ol	11	570	2.52	418	1.58	334	1.06
2-Ethyladamantan-2-ol	12	346	1.13	278	0.72	240	0.48
2-Propyladamantan-2-ol	13	300	0.85	252	0.56	218	0.35
2-Butyladamantan-2-ol	14	270	0.67	228	0.41	202	0.24
2-Isobutyladamantan-2-ol	14	240	0.48	206	0.27	192	0.19
Diamantan-1-ol	14	648	3.00	458	1.83	370	1.28
Diamantan-3-ol	14	656	4.28	577	2.56	455	1.81
Diamantan-4-ol	14	1626	9.04	1055	5.51	840	4.19
1-Hydroxymethylbicyclo[3,3,1]nonane	10	786	3.85	500	2.09	406	1.50
1-Hydroxymethyladamantane	11	846	4.22	553	2.41	434	1.68
2-Hydroxymethyladamantane	11	1150	6.10	714	3.41	552	2.41
3,5-Dimethyl-1-hydroxymethyladamantane	13	690	3.26	577	2.56	360	1.22
2-(Adamant-1-yl)propan-2-ol	13	532	2.28	382	1.36	311	0.92
1-Hydroxymethyldiamantane	15	766	3.73	526	2.24	408	1.52

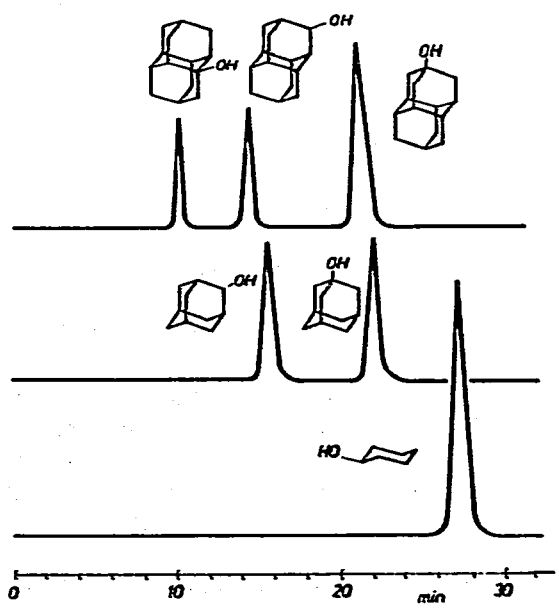


Fig. 2. Separation of diamantanols, adamantanols and cyclohexanol. Column, MicroPak Si-10; mobile phase, 99% n-heptane–1% 2-propanol; flow-rate, 30 ml/h.

TABLE IV

RETENTION DATA

Mobile phase: a% mixture of (65% n-heptane–35% diethyl ether)–b% 2-propanol.

Compound	*C*	*a* = 99.9, *b* = 0.1		*a* = 99.5, *b* = 0.5		*a* = 99.0, *b* = 1.0	
		t_R	k'	t_R	k'	t_R	k'
Cyclohexanol	6	1385	7.55	918	4.67	752	3.64
Adamantan-1-ol	10	1394	7.61	937	4.79	744	3.59
3-Methyladamantan-1-ol	11	1320	7.15	874	4.39	686	3.24
3,5-Dimethyladamantan-1-ol	12	1032	5.37	818	4.05	643	2.97
3,5,7-Trimethyladamantan-1-ol	13	886	4.47	683	3.21	606	2.74
3-Ethyladamantan-1-ol	12	1128	5.96	828	4.11	638	2.94
3-Ethyl-5-methyladamantan-1-ol	13	1020	5.30	780	3.81	594	2.67
3-Ethyl-5,7-dimethyladamantan-1-ol	14	880	4.43	630	2.89	564	2.48
3-Propyladamantan-1-ol	13	1080	5.67	774	3.78	600	2.70
3-Isopropyladamantan-1-ol	13	1092	5.74	766	3.73	598	2.69
3-Butyladamantan-1-ol	14	1073	5.62	742	3.58	588	2.63
2-Methyladamantan-1-ol	11	791	3.88	583	2.59	468	1.89
Adamantan-2-ol	10	784	3.84	574	2.54	478	1.95
1-Methyladamantan-2-ol	11	421	1.60	326	1.01	302	0.87
2-Methyladamantan-2-ol	11	518	2.20	406	1.50	346	1.13
2-Ethyladamantan-2-ol	12	325	1.01	274	0.69	254	0.57
2-Propyladamantan-2-ol	13	286	0.76	253	0.56	230	0.42
2-Butyladamantan-2-ol	14	252	0.56	228	0.41	216	0.33
2-Isobutyladamantan-2-ol	14	228	0.41	205	0.27	202	0.24
Diamantan-1-ol	14	608	2.76	444	1.74	371	1.29
Diamantan-3-ol	14	778	3.80	541	2.34	444	1.74
Diamantan-4-ol	14	1426	7.80	898	4.54	695	3.29
1-Hydroxymethylbicyclo[3,3,1]nonane	10	676	3.17	1150	6.10	420	1.59
1-Hydroxymethyladamantane	11	731	3.51	536	2.31	458	1.83
2-Hydroxymethyladamantane	11	948	4.85	674	3.16	588	2.63
3,5-Dimethyl-1-hydroxymethyladamantane	13	614	2.79	439	1.71	386	1.39
2-(Adamant-1-yl)propan-2-ol	13	469	1.90	360	1.22	322	0.99
1-Hydroxymethyldiamantane	15	690	3.26	503	2.10	422	1.61

Effect of alkyl substitution of adamantanols

Introduction of an alkyl group into adamantan-1-ol or -2-ol lowers the retention time relative to that of the parent molecule. Fig. 3 illustrates the dependence of log k' on the number of carbon atoms for 3-alkyladamantan-1-ols (both substituents on bridgehead positions) and for 2-alkyladamantan-2-ols (both substituents on one non-bridgehead position). In both cases, there is a linear relationship between the total number of carbon atoms in the molecule, the number of carbon atoms in the alkyl group and log k'. The differences in retention times ($\Delta\ t_R$) between the individual members of these homologous series are higher for 2-alkyladamantan-2-ols than for 3-alkyladamantan-1-ols, but even in the latter case the $\Delta\ t_R$ value is sufficient to permit efficient separation. Similarly, there is a linear dependence of log k' on the number of carbon atoms for polymethyladamantan-1-ols having methyl groups on tertiary carbon atoms and for ethylmethyladamantan-1-ols with one ethyl group in position 3 and methyl groups in positions 5 and 7 (Fig. 4). Fig. 5 illustrates the separation of the polymethyladamantanols.

When comparing the change in the capacity factor of adamantan-1-ol substi-

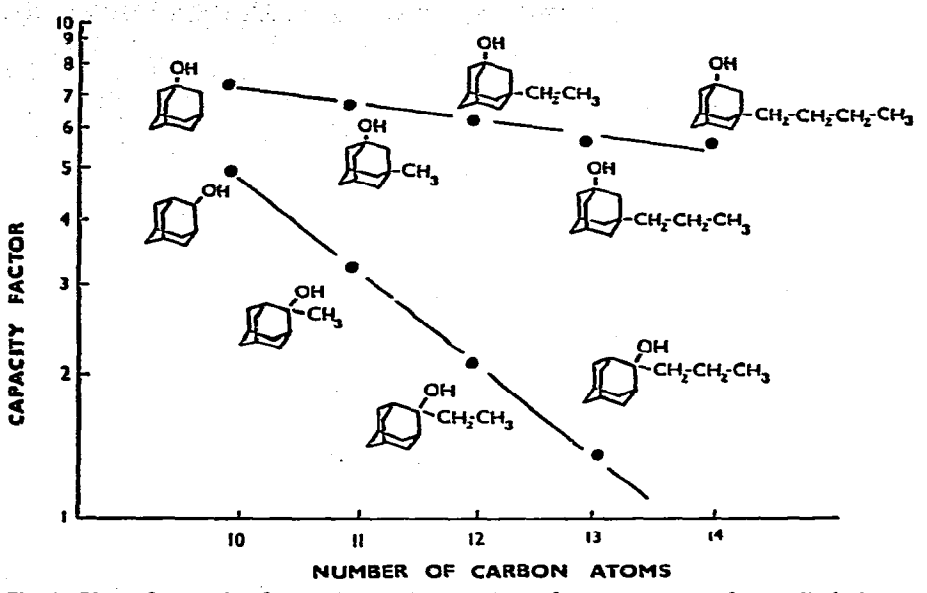


Fig. 3. Plot of capacity factor k' *vs.* the number of carbon atoms for 3-alkyladamantan-1-ols and 2-alkyladamantan-2-ols.

TABLE V

RETENTION DATA

Mobile phase: 99.5% (a% *n*-heptane–b% chloroform)–0.5% 2-propanol.

Compound	*C*	$a = 80, b = 20$		$a = 65, b = 35$		$a = 50, b = 50$	
		t_R	k'	t_R	k'	t_R	k'
Cyclohexanol	6	2004	11.37	1924	10.87	1772	9.94
Adamantan-1-ol	10	1560	8.63	1500	8.26	1410	7.70
3-Methyladamantan-1-ol	11	1378	7.50	1318	7.13	1264	6.80
3,5-Dimethyladamantan-1-ol	12	1248	6.70	1204	6.43	1141	6.04
3,5,7-Trimethyladamantan-1-ol	13	1150	6.10	1120	5.91	1054	5.50
3-Ethyladamantan-1-ol	12	1356	7.37	1284	6.93	1166	6.20
3-Ethyl-5-methyladamantan-1-ol	13	1298	7.01	1234	6.61	1030	5.36
3-Ethyl-5,7-dimethyladamantan-1-ol	14	1152	6.11	1098	5.78	960	4.93
3-Propyladamantan-1-ol	13	1195	6.38	1168	6.21	1068	5.59
3-Isopropyladamantan-1-ol	13	1202	6.42	1164	6.19	1038	5.41
3-Butyladamantan-1-ol	14	1146	6.07	1098	5.78	971	4.99
2-Methyladamantan-1-ol	11	1036	5.39	966	4.96	936	4.78
Adamantan-2-ol	10	1169	6.21	1084	5.69	1050	5.48
1-Methyladamantan-2-ol	11	638	2.94	546	2.37	576	2.56
2-Methyladamantan-2-ol	11	815	4.03	750	3.63	682	3.21
2-Ethyladamantan-2-ol	12	684	3.22	630	2.89	355	1.19
2-Propyladamantan-2-ol	13	655	3.04	606	2.74	329	1.03
2-Butyladamantan-2-ol	14	613	2.79	576	2.56	288	0.78
2-Isobutyladamantan-2-ol	14	582	2.59	544	2.36	262	0.61
Diamantan-1-ol	14	738	3.56	676	3.17	690	3.26
Diamantan-3-ol	14	1046	5.46	960	4.93	894	4.52
Diamantan-4-ol	14	1494	8.22	1350	7.33	1282	6.91
1-Hydroxymethylbicyclo[3.3.1]nonane	10	1410	7.70	1236	6.63	1032	5.37
1-Hydroxymethyladamantane	11	1387	7.56	1210	6.47	1069	5.60
2-Hydroxymethyladamantane	11	1685	9.40	1469	8.07	1298	7.01
3,5-Dimethyl-1-hydroxymethyladamantane	13	928	4.73	871	4.38	804	3.96
2-(Adamant-1-yl)propan-2-ol	13	686	3.24	672	3.15	612	2.78
1-Hydroxymethyldiamantane	15	1140	6.04	1036	5.39	886	4.47

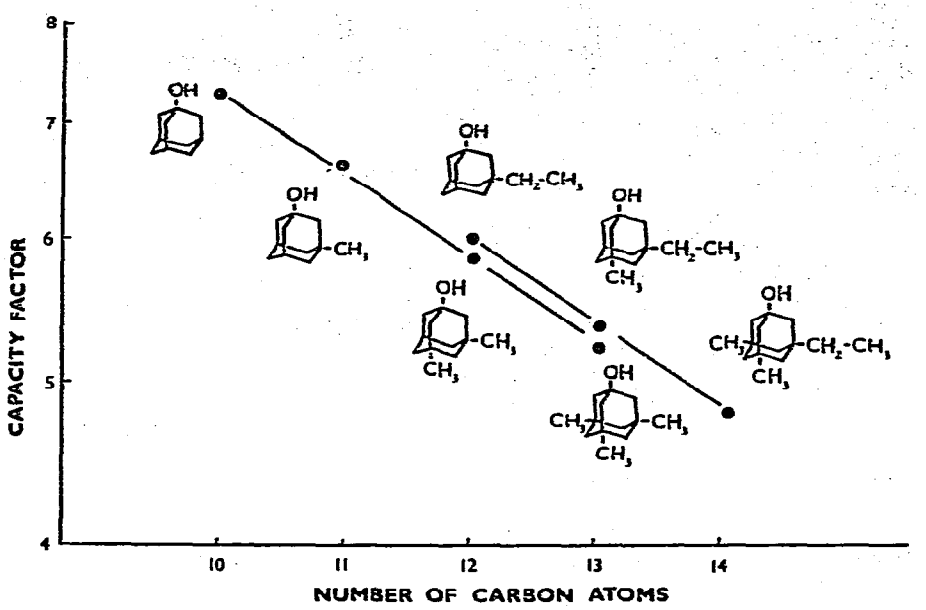


Fig. 4. Plot of capacity factor k' *vs.* the number of carbon atoms for polymethyladamantan-1-ols and ethylmethyladamantan-1-ols.

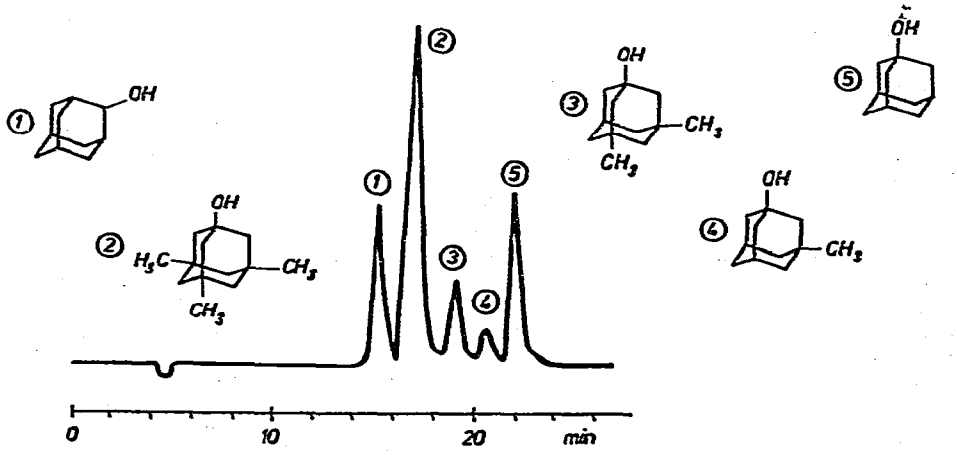


Fig. 5. Separation of adamantanols and polymethyladamantan-1-ols. Conditions as in Fig. 2.

tuted by several lower alkyls (*e.g.*, three methyls) with the change caused by substitution with a larger alkyl group giving the same overall number of carbon atoms (*e.g.*, propyl), it is evident that a greater change is achieved by introducing a higher number of lower alkyls. Fig. 6 shows two examples of this (polymethyladamantan-1-ols and 3-alkyladamantan-1-ols).

The largest change in retention times for substitution with one methyl group was found when this group is situated on the carbon atom adjacent to the carbon

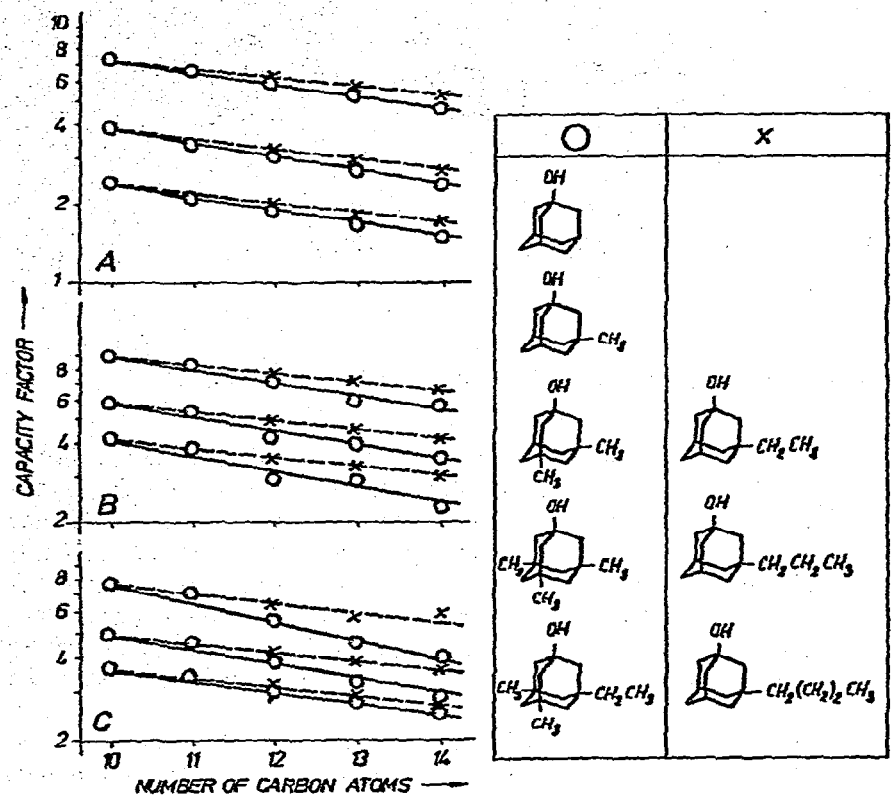
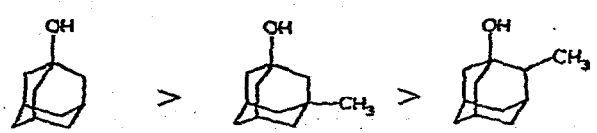


Fig. 6. Plots of log k' *versus* the number of carbon atoms for polymethyladamantan-1-ols and 3-alkyladamantan-1-ols. Mobile phases: A = *n*-heptane–2-propanol; B = *n*-heptane–diethyl ether; C = *n*-heptane–diethyl ether–2-propanol.

atom bearing the OH group. For alkyladamantan-1-ols, retention times decrease in the following order:



In the case of methyl substitution in adamantan-2-ol the situation is similar:

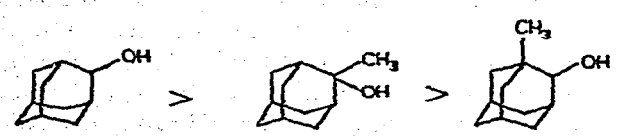


Fig. 7 summarizes the separations achieved with these adamantanol derivatives.

Comparison of the retention times of adamantanols having methyl or other alkyl substituents at the bridgehead (tertiary) positions with that of the parent alcohol reveals that successive replacement of bridgehead hydrogen atoms leads to gradual

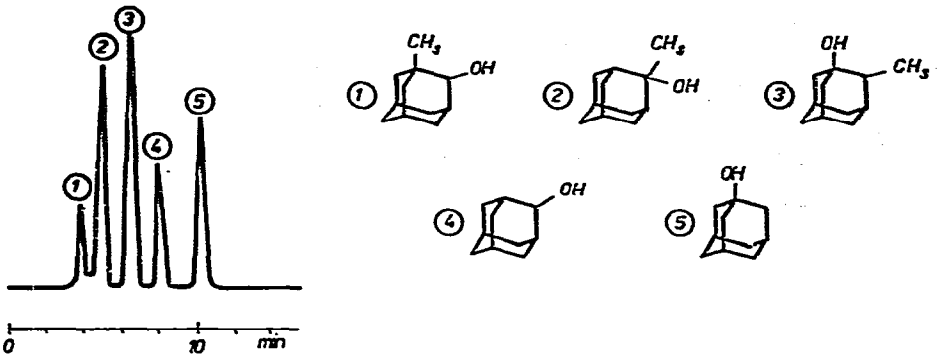


Fig. 7. Separation of adamantanols and methyladamantanols. Conditions as in Fig. 2.

reduction in retention times. This pattern of behaviour has also been observed in the gas chromatographic behaviour of polymethyladamantanols[3]. Increasing the length of the alkyl chain in 3-alkyladamantan-1-ols does not decrease the total molecular polarity to the same extent as does adding further bridgehead alkyl substituents. These effects may be associated with structural features of the adamantane skeleton. It follows from these observations that the increasing solubility of alkylated adamantan-1-ols in the mobile phase (interaction between solvent molecules and sample molecules in solution[1]) has a more significant effect on their chromatographic behaviour than the decreasing molecular polarity.

For methyl-substituted adamantan-1-ols, there is steric hindrance in the neighbourhood of the OH group if the methyl group is located at the 2 (vicinal) position. However, if the methyl group is at a tertiary carbon atom (positions 3, 5 or 7), there is practically no steric hindrance to the OH group. In the case of substituted adamantan-2-ols, there is steric hindrance at the OH group both for 2-substitution (geminal substitution) and 1-substitution (vicinal substitution). From the viewpoint of the chromatographic behaviour of the methyladamantan-2-ols, greater changes were found for the case of vicinal than for geminal substitution. Thus it can be concluded that steric hindrance has only a complementary effect on the change in k' with alkylated adamantanols.

Effect of the basic skeleton size

In the absence of additional steric effects, polycyclic alcohols substituted in a formally identical manner, *e.g.*, when the OH group is located on a tertiary carbon atom, exhibit retention times which decrease with increasing size of the basic skeleton of the molecule. The rate of this decrease is also dependent upon the composition of the mobile phase. In the case of cyclohexanol two different kinds of behaviour can be observed. When 2-propanol is present in the mobile phase the behaviour of cyclohexanol is similar to that of a polycyclic alcohol which has the OH group located on a tertiary carbon atom but without additional steric hindrance. Thus the cyclohexanol retention time is the longest, in agreement with the smaller size of the basic skeleton. On the other hand, in the absence of 2-propanol (for example in the *n*-heptane–diethyl ether system), the chromatographic behaviour of cyclohexanol is similar to that of the group of compounds in which the OH group is located at a secondary carbon

atom, the elution order being: diamantan-3-ol, adamantan-2-ol, cyclohexanol (see Fig. 8).

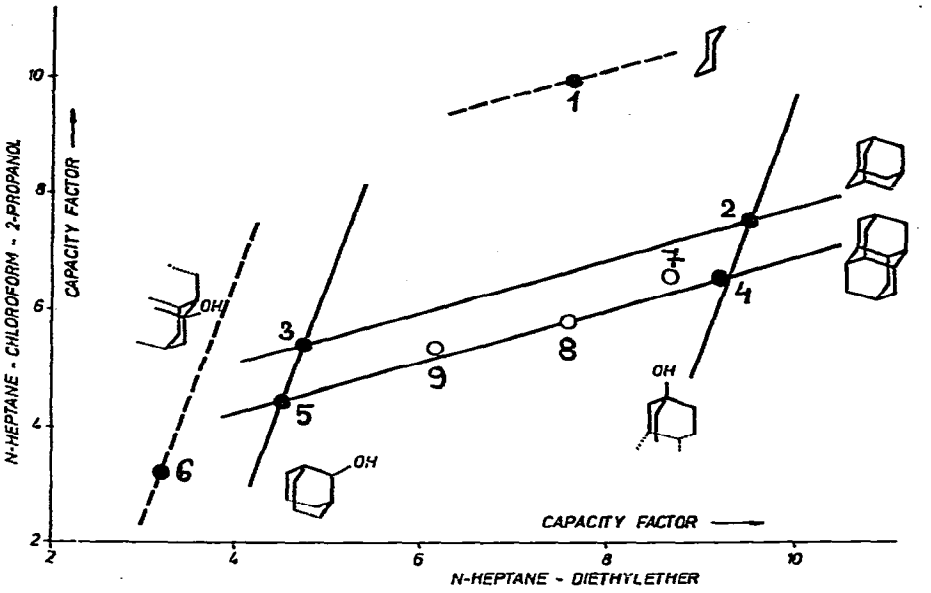


Fig. 8. Capacity factors of some adamantanols and diamantanols for two mobile phases. Compounds: 1 = cyclohexanol; 2 = adamantan-1-ol; 3 = adamantan-2-ol; 4 = diamantan-4-ol; 5 = diamantan-3-ol; 6 = diamantan-1-ol; 7 = 3-methyladamantan-1-ol; 8 = 3,5-dimethyladamantan-1-ol; 9 = 3,5,7-trimethyladamantan-1-ol.

Dependence of the capacity factor (k') on the mobile phase elution strength

When using two-component mobile phases, *i.e.*, *n*-heptane–2-propanol and *n*-heptane–diethyl ether, the change in the capacity factor k' with the change in elution strength of the mobile phase is determined by an approximate relation derived by Jandera and Churáček[4]

$$\log k' = A - n \log c \qquad (1)$$

where c is the concentration of the more polar component in the two-component mobile phase and n and A are constants.

In our case c corresponds to the concentration of 2-propanol. Good agreement has been found between this equation and the experimental results, even for a three-component mobile phase (*n*-heptane–diethyl ether–2-propanol with the *n*-heptane: diethyl ether ratio held constant). Fig. 9 illustrates the dependence of the k' value on the concentration of 2-propanol in *n*-heptane; Fig. 10 shows the same dependence for 2-alkyladamantan-2-ols on the 2-propanol concentration when using the three-component (*n*-heptane–diethyl ether–2-propanol) mobile phase. In the case of the *n*-heptane–chloroform–2-propanol mobile phase, a linear dependence of $\log k'$ on $\log c$ was found for most compounds, and this was the result with all the other mobile phases used.

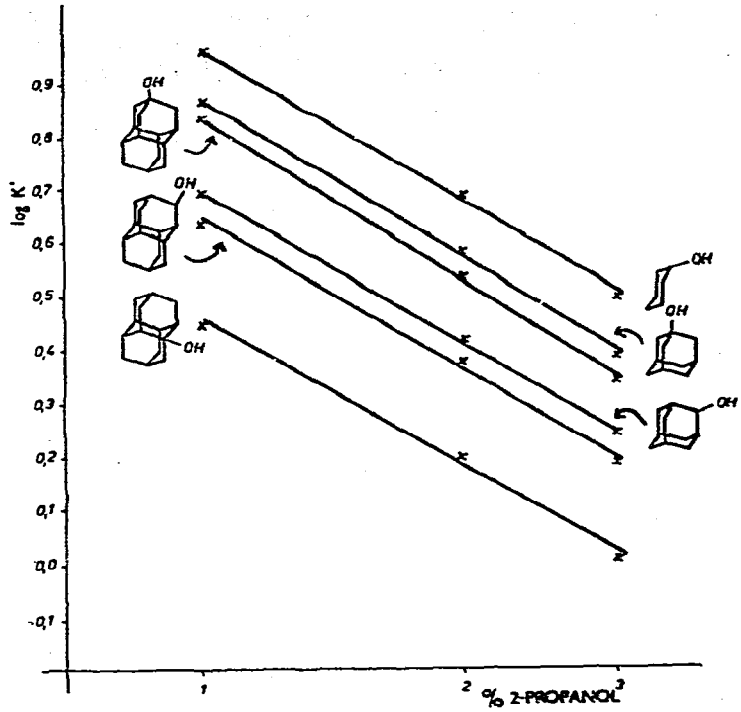


Fig. 9. Variation of the logarithm of capacity factors with the concentration of 2-propanol in the mobile phase (*n*-heptane–2-propanol) for adamantanols and diamantanols.

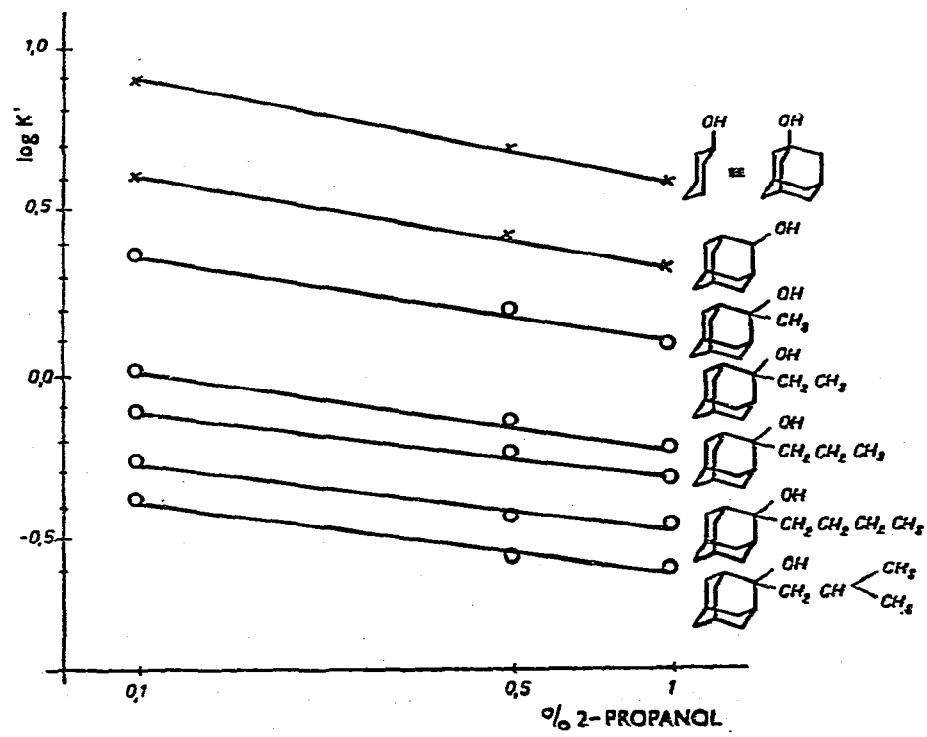


Fig. 10. Variation of the logarithm of capacity factors with the concentration of 2-propanol in the mobile phase (*n*-heptane–2-propanol) for 2-alkyladamantan-2-ols.

Effect of the mobile phase composition

The twelve mobile phases used in the present study may be divided into two basic groups according to their effect on the chromatographic behaviour of the compounds studied. The first group comprises nine systems containing 2-propanol and the second group includes mobile phases containing *n*-heptane and diethyl ether in various ratios. The difference found when using the two types of mobile phases is illustrated in Fig. 8, which gives k' values in the *n*-heptane–chloroform–2-propanol and *n*-heptane–diethyl ether systems.

Further small changes in the chromatographic behaviour of polycyclic alcohols may be achieved by changing the composition of the mobile phase used. The dependence of k' on the number of carbon atoms for alkyladamantan-1-ols is demonstrated in Fig. 6. When using the *n*-heptane-2-propanol mobile phase, the difference between the k' values for 3-alkyladamantan-1-ols (dashed line) and polymethyladamantan-1-ols (solid line) is insignificant and does not increase with decreasing elution strength. When using *n*-heptane–diethyl ether, the difference in k' values is larger and again it does not change greatly with the elution strength. However, in case of the *n*-heptane–diethyl ether–2-propanol system, the difference between the k' values for polymethyladamantan-1-ols and 3-alkyladamantan-1-ols increases with decreasing concentration of 2-propanol in the mobile phase.

Another mobile phase, containing only *n*-heptane–chloroform, has been tested. However, this system proved to be unsuitable in chromatographic analyses of polycyclic alcohols, as some of the compounds yielded broadened peaks, while others were not eluted from the column under these conditions.

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REFERENCES

1 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
2 D. E. Johnston, M. A. McKervey and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, (1972) 29.
3 J. Burkhard, J. Vais, L. Vodička and S. Landa, *J. Chromatogr.*, 42 (1969) 207.
4 P. Jandera and J. Churáček, *J. Chromatogr.*, 91 (1974) 207.