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REVERSED-PHASE CHROMATOGRAPHY OF KETO AND HYDROXY DERIVATIVES OF ADAMANTANE AND DIAMANTANE*

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SUMMARY

Chromatographic elution data for adamantane and diamantane derivatives, mostly diketones, hydroxyketones and dihydroxy derivatives, have been measured at 30, 50 and 70°C. Octadecyl-silica was used as the stationary phase, and methanol–water and acetonitrile–water as the mobile phases. For each mobile phase, three or four different concentration ratios of the relevant components were used.

From the viewpoint of the chromatographic behaviour of the studied compounds, the number of functional groups has the largest effect. When this number increases, the retention time of the compound in question decreases.

Interactions of difunctional compounds with octadecyl-silica are strongest when the two groups are adjacent. Retention time increases when the two groups get closer to each other.

Generally, retention time increases as the number of carbon atoms in the molecule increases. This is also valid for ring compounds, as well as for increasing number of rings in the molecule. Selectivity is influenced by changes of the mobile phase composition if acetonitrile or methanol are present. On the contrary, changes of the mobile phase concentrations influence the selectivity only a little. The dependence of $\log k'$ on the logarithm of the methanol or acetonitrile concentration in the mobile phase is linear for the most of the compounds studied. Temperature changes have little effect on the selectivity; the dependence of $\log k'$ on temperature is linear.

INTRODUCTION

High-performance liquid chromatographic (HPLC) data for monocyclic and polycyclic alcohols and ketones of the adamantane type on silica gel have been reported in previous papers^{1,2}. In adsorption liquid chromatography, the combination of silica gel and relatively non-polar mobile phases proved to be suitable for separating adamantane and diamantane derivatives containing one polar functional group. As the number of hydroxy and keto groups in the molecule increases, however, the corresponding retention times increase and the solubility of these compounds in the

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mobile phase decreases, making their detection by means of an RI detector rather difficult. This problem cannot be solved in a satisfactory manner even by using a mobile phase with a higher elution strength value.

In the present paper, the chromatographic behaviour of keto and hydroxy derivatives of adamantane and diamantane is described for octadecyl-silica as stationary phase and methanol-water and acetonitrile-water mixtures as mobile phases.

EXPERIMENTAL

Apparatus

A Varian 8500 liquid chromatograph with a syringe pump was used, connected to an RI detector and an A25 dual-channel strip-chart recorder (Varian, Palo Alto, CA, U.S.A.). Sample injection using the stop-flow technique was performed; a 10- μ l syringe (Hamilton, Bonaduz, Switzerland) was used. The column used was a MicroPak CH-10 (Varian; 25 cm \times 2.1 mm I.D.), packed with silica gel LiChrosorb Si-60 with chemically bonded octadecyl.

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

Reagents

Nearly all the standard compounds used for measurements were prepared in our laboratory. Diamantane-3,5-diol, diamantane-3,6-diol and diamantane-1,3-diol were kindly provided by Prof. M. A. McKervery from the University College, Cork, Ireland. Monocyclic ketones were kindly provided by the Department of Organic Technology, Prague Institute of Chemical Technology. Methanol, analytical grade (Lachema, Brno, Czechoslovakia) was used without further treatment. Acetonitrile (VEB Jenapharm Laborchemie, Apolda, G.D.R.) was distilled before use.

Mobile phase

The mobile phases were prepared from weighed degassed components. The compositions are listed in Table I.

TABLE I
MOBILE PHASE COMPOSITIONS

No. 1	CH ₃ OH (%)	H ₂ O (%)	No. 2	CH ₃ CN (%)	H ₂ O (%)
a	30	70	a	20	80
b	40	60	b	30	70
c	50	50	c	40	60
d	70	30			

Procedure

The column was thermostated and retention data were measured at three temperatures (30, 50 and 70°C). The flow-rate of the mobile phase was 60 ml/h. The

column was conditioned by washing with fresh mobile phase for 2–4 h (the total volume of mobile phase passed through the column before measurement was 250 ml). The dead volume of the column was determined by measuring the retention time of water.

Retention data were measured on chromatograms obtained by injecting solutions of compounds in methanol or acetonitrile. The retention data are listed in Tables II–VII.

TABLE II
RETENTION DATA
Mobile phase, methanol–water (30:70)

Compounds	Temperature ($^{\circ}\text{C}$)						$\log k'/10^{\circ}\text{C}$
	30		50		70		
	t_R (sec)	k'	t_R (sec)	k'	t_R (sec)	k'	
Adamantanone	171	3.07	143	2.41	127	2.01	0.0048
Adamantane-2,4-dione	75	0.78	77	0.82	64	0.51	0.0045
Adamantane-2,6-dione	66	0.57	63	0.49	59	0.40	0.0040
2-Thiaadamantane-4,8-dione	66	0.57	61	0.45	57	0.35	0.0055
Adamantane-1-ol-4-one	60	0.43	58	0.37	54	0.29	0.0040
Adamantane-4-ol-2-one	76	0.81	73	0.73	68	0.63	0.0028
Cyclohexanol	99	1.35	88	1.09	82	0.95	0.0038
Adamantan-1-ol	222	4.29	186	3.43	152	2.63	0.0053
Adamantan-2-ol	335	6.98	252	5.00	202	3.80	0.0065
Adamantane-1,2-diol	112	1.66	100	1.38	89	1.13	0.0043
Adamantane-1,3-diol	68	0.63	63	0.49	59	0.41	0.0045
Adamantane-2,6-diol	66	0.57	58	0.38	51	0.21	0.0108
Diamantane-1,4-diol	164	2.90	141	2.36	119	1.82	0.0050
Diamantane-1,6-diol	88	1.09	81	0.93	75	0.79	0.0035
Diamantane-1,7-diol	127	2.01	115	1.73	104	1.46	0.0033
Diamantane-1,9-diol	173	3.11	152	2.61	136	2.24	0.0035
Diamantane-4,9-diol	80	0.89	74	0.75	67	0.60	0.0043
4-Oxahomoadamantan-5-one	105	1.50	95	1.27	87	1.07	0.0038
Adamantane-2 ^a ,4 ^a -diol	123	1.94	108	1.58	97	1.31	0.0043
Adamantane-2 ^a ,4 ^e -diol	89	1.13	80	0.91	74	0.77	0.0040
Adamantane-2 ^e ,4 ^e -diol	77	0.82	70	0.67			

RESULTS AND DISCUSSION

The effect of the number of hydroxy and keto groups in the molecule

When comparing chromatographic behaviour of monocyclic and polycyclic alcohols and ketones of the adamantane type in the case of reversed phases (using methanol–water and acetonitrile–water mixtures as mobile phases) with their behaviour on silica gel^{1,2}, alumina, or other stationary phases³ (using relatively non-polar mobile phases), the expected reversal in chromatographic behaviour is not observed in all cases. When using silica gel, the retention time (t_R) increases with increasing number of polar functional groups, t_R for alcohols being higher than t_R for ketones. In the case of reversed-phase chromatography, t_R decreases with increasing number

TABLE III
RETENTION DATA
Mobile phase, methanol-water (40:60)

Compounds	Temperature (°C)						log k' / 10°C
	30		50		70		
	t_R (sec)	k'	t_R (sec)	k'	t_R (sec)	k'	
Cyclohexanone	95	1.27					
Adamantanone	150	2.57	123	1.94	108	1.56	0.0055
Adamantane-2,4-dione	68	0.62	63	0.50	59	0.41	0.0045
Adamantane-2,6-dione	62	0.48	60	0.43	56	0.34	0.0035
2-Thiaadamantane-4,8-dione	60	0.43	56	0.34	54	0.29	0.0043
Adamantan-1-ol-4-one	59	0.41	70	0.66	54	0.29	0.0035
Adamantan-4-ol-2-one	70	0.66	65	0.56	63	0.50	0.0030
Cyclohexanol	86	1.06	77	0.83	72	0.71	0.0043
Adamantan-1-ol	181	3.31	143	2.41	131	2.11	0.0050
Adamantan-2-ol	246	4.86	197	3.70	158	2.77	0.0063
Adamantane-1,2-diol	97	1.31	87	1.07	77	0.84	0.0050
Adamantane-1,3-diol	65	0.54	60	0.43	57	0.35	0.0048
Diamantane-1,4-diol	140	2.34	117	1.74	100	1.38	0.0058
Diamantane-1,6-diol	77	0.83	73	0.74	70	0.66	0.0025
Diamantane-1,7-diol	107	1.54	100	1.37	86	1.06	0.0033
Diamantane-1,9-diol	138	2.29	119	1.83	104	1.46	0.0048
Diamantane-3,6-diol	105	1.50	92	1.18	84	0.99	0.0045
Diamantane-4,9-diol	75	0.78	68	0.63	63	0.50	0.0048
4-Oxahomoadamantan-5-one	90	1.14	81	0.94	75	0.79	0.0040
Adamantane-2 ^a ,4 ^a -diol	102	1.43	95	1.27	85	1.02	0.0025
Adamantane-2 ^a ,4 ^e -diol	77	0.82	73	0.73	66	0.58	0.0038
Adamantane-2 ^e ,4 ^e -diol	68	0.61	65	0.56	61	0.46	0.0030

of functional groups. Generally, retention times of adamantanoid substances substituted with hydroxy or keto groups depend mainly on the position of the group and on the mobile phase used, rather than on the character of the group.

Functional group arrangement

Generally speaking, retention times of difunctional compounds are greater if the groups are nearer each other. In case of substitution on secondary carbon atoms, the retention time of adamantane-2,4-dione is greater than that of adamantane-2,6-dione; similarly, all adamantane-2,4-diol stereoisomers are eluted after adamantane-2,6-diol. The effect of the mutual arrangement of OH groups in the molecule is significant enough to enable even a separation of all three adamantane-2,4-diol stereoisomers using both methanol (Fig. 1) and acetonitrile in the mobile phase. All adamantanediols with OH groups on secondary carbon atoms are eluted in the following order:

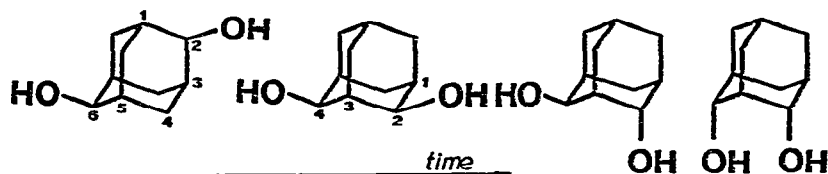


TABLE IV

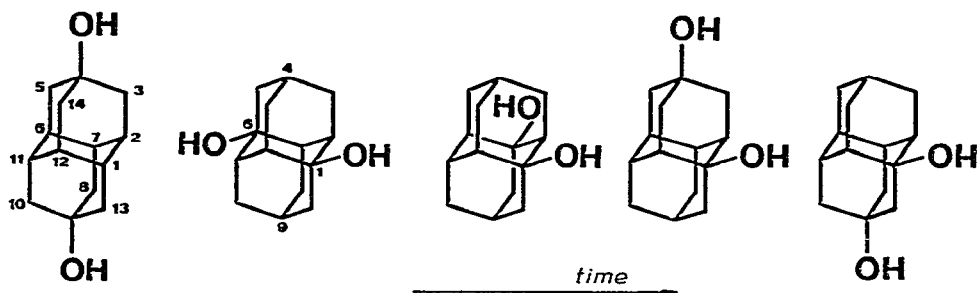
RETENTION DATA

Mobile phase, methanol-water (50:50)

Compounds	Temperature ($^{\circ}\text{C}$)						$\log k'/10^{\circ}\text{C}$
	30		50		70		
	t_R (sec)	k'	t_R (sec)	k'	t_R (sec)	k'	
Adamantanone	92	1.20	83	0.98	75	0.79	0.0045
Bicyclo[3,3,1]nonane-2,6-dione	74	0.75	70	0.66	49	0.16	0.0028
Adamantane-2,4-dione	57	0.36	54	0.29	52	0.24	0.0043
Adamantane-2,6-dione	53	0.27	51	0.22	49	0.17	0.0050
2-Thiaadamantane-4,8-dione	51	0.21	49	0.16	47	0.13	0.0058
Adamantan-1-ol-4-one	51	0.22	50	0.18	48	0.14	0.0050
Adamantan-4-ol-2-one	57	0.35	56	0.32	54	0.29	0.0020
Cyclohexanol	73	0.74	59	0.41	57	0.35	0.0040
Adamantan-1-ol	110	1.63	96	1.29	84	1.01	0.0053
Adamantan-2-ol	138	2.29	115	1.73	95	1.27	0.0065
Adamantane-1,2-diol	71	0.68	65	0.55	60	0.44	0.0048
Adamantane-1,3-diol	54	0.29	52	0.24	50	0.20	0.0040
Adamantane-2,6-diol	53	0.25	51	0.21	49	0.16	0.0050
Diamantane-1,4-diol	88	1.10	79	0.89	72	0.71	0.0048
Diamantane-1,6-diol	62	0.46	59	0.41	88	0.37	0.0025
Diamantane-1,7-diol	77	0.82	71	0.70	68	0.62	0.0030
Diamantane-1,9-diol	88	1.09	81	0.93	75	0.79	0.0035
Diamantane-3,6-diol	74	0.76	69	0.64	62	0.48	0.0050
Diamantane-4,9-diol	59	0.41	57	0.36	54	0.29	0.0040
4-Oxahomoadamantan-5-one	66	0.57	65	0.54	61	0.45	0.0040
Adamantane-2 ^a ,4 ^a -diol	75	0.78	70	0.66	67	0.59	0.0030
Adamantane-2 ^a ,4 ^c -diol	60	0.43	58	0.37	56	0.32	0.0040

The two adamantane-1,4-diol stereoisomers may be separated in an analogous manner (Fig. 2). The relevant retention times are not listed in the tables because of small amounts of the samples used.

Dihydroxydiamantane derivatives with OH groups on tertiary carbon atoms are eluted in the following order:



Diamantane-3,6-diol, which has one group on a secondary carbon atom, is eluted between diamantane-1,6-diol and diamantane-1,7-diol. Diamantane-3,5-diol, which

TABLE V

RETENTION DATA

Mobile phase, acetonitrile-water (20:80)

Compounds	Temperature (°C)						log k' / 10°C
	30		50		70		
	t_R (sec)	k'	t_R (sec)	k'	t_R (sec)	k'	
Cyclohexanone	430	2.77	377	2.31	329	1.89	0.0040
Adamantanone	2006	16.60	1440	11.63	1056	8.26	0.0075
Protoadamantan-4-one	1924	15.88	1272	10.16	947	7.31	0.0085
Bicyclo[3,3,1]nonane-2,6-dione	185	0.62	178	0.56	172	0.51	0.0020
Adamantane-2,4-dione	289	1.54	270	1.37	251	1.20	0.0028
Adamantane-2,6-dione	217	0.90	196	0.72	183	0.61	0.0043
2-Thiaadamantane-4,8-dione	278	1.44	245	1.15	218	0.91	0.0050
Adamantan-1-ol-2-one	327	1.87	299	1.62	278	1.44	0.0028
Adamantan-1-ol-4-one	174	0.53	167	0.47	160	0.41	0.0028
Adamantan-2-ol-6-one	178	0.56	169	0.48	161	0.42	0.0033
Adamantan-4-ol-2-one	246	1.16	218	0.91	201	0.76	0.0045
Diamantan-1-ol-3-one	795	5.97	649	4.69	540	3.74	0.0053
Tricyclo[4,4,0,0 ^{2,9}]decan-9-ol-5-one	200	0.76	203	0.78	188	0.65	0.0018
Cyclohexanol	450	2.95	391	2.43	343	2.01	0.0043
Adamantan-1-ol	1836	15.11	1371	11.03	1004	7.81	0.0073
Adamantan-2-ol	2910	24.53	2115	17.55	1498	12.14	0.0078
Adamantane-1,2-diol	347	2.04	318	1.78	292	1.56	0.0030
Adamantane-2 ^a ,4 ^a -diol	533	3.68	449	2.94	373	2.27	0.0053
Adamantane-2 ^a ,4 ^c -diol	251	1.20	228	1.00	206	0.81	0.0043
Adamantane-2 ^c ,4 ^c -diol	195	0.71	187	0.64			
Diamantane-1,4-diol	547	3.80	483	3.24	421	2.69	0.0038
Diamantane-1,7-diol	432	2.79	388	2.41	354	2.11	0.0033
Diamantane-1,9-diol	528	3.63	458	3.02	400	2.51	0.0040
Diamantane-3,5-diol	2496	20.89	1762	14.45	1280	10.23	0.0078
Adamantanonoxim	1178	9.33	1074	8.42	797	5.99	0.0048
4-Oxahomoadamantan-5-one	687	4.95	576	4.05	455	2.99	0.0053
Cyclopentanone	258	1.26	236	1.07	220	0.93	0.0033
Cyclooctanone	1307	10.47	902	6.92	758	5.65	0.0043

has both functional groups on secondary carbon atoms on one side of the molecule, has a retention time several times greater than those of other dihydroxydiamantane derivatives in acetonitrile-water, being eluted between adamantan-1-ol and adamantan-2-ol. This fact can possibly be accounted for by the formation of an intramolecular hydrogen bond, resulting in another six-membered ring⁴ and a decreased interaction with the mobile phase in case of the diaxial 3,5-stereoisomer (I).

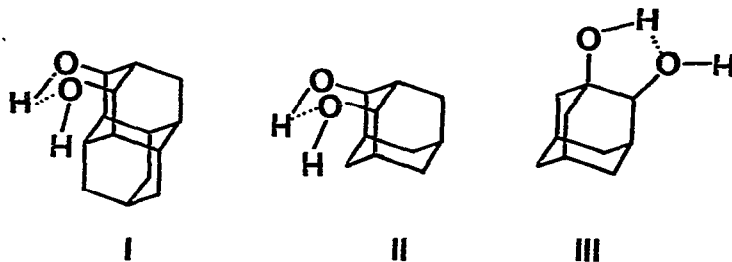


TABLE VI
RETENTION DATA

Mobile phase, acetonitrile-water (30:70)

Compounds	Temperature (°C)						log k' / 10°C
	30		50		70		
	t_R (sec)	k'	t_R (sec)	k'	t_R (sec)	k'	
Cyclohexanone	274	1.68	256	1.51	233	1.29	0.0030
Adamantanone	876	7.59	689	5.75	546	4.35	0.0060
Protoadamantan-4-one	840	7.24	641	5.29	511	4.01	0.0065
Bicyclo[3,3,1]nonane-2,6-dione	150	0.47	144	0.41	138	0.35	0.0030
Adamantane-2,4-dione	202	0.98	186	0.82	174	0.71	0.0035
Adamantane-2,6-dione	166	0.62	154	0.51	146	0.43	0.0040
2-Thia-adamantane-4,8-dione	191	0.87	173	0.69	159	0.56	0.0048
Adamantan-1-ol-2-one	217	1.13	202	0.98	197	0.93	0.0020
Adamantan-1-ol-4-one	139	0.36	134	0.32	130	0.28	0.0030
Adamantan-2-ol-6-one	142	0.39	137	0.34	131	0.29	0.0033
Adamantan-4-ol-2-one	168	0.65	160	0.56	151	0.48	0.0033
Diamantan-1-ol-3-one	389	2.82	335	2.29	292	1.86	0.0045
Tricyclo[4,4,0,0 ^{2,9}]decan-9-ol-5-one	155	0.52	152	0.49	149	0.46	0.0013
Cyclohexanol	279	1.74	255	1.50	233	1.28	0.0033
Adamantan-1-ol	791	6.76	637	5.25	509	3.99	0.0058
Adamantan-2-ol	1195	10.72	894	7.76	672	5.59	0.0070
Adamantane-1,2-diol	220	1.18	210	1.06	198	0.94	0.0025
Adamantane-2 ^a ,4 ^a -diol	301	1.95	269	1.64	243	1.38	0.0038
Adamantane-2 ^a ,4 ^e -diol	174	0.71	161	0.58	153	0.50	0.0038
Diamantane-1,4-diol	275	1.69	257	1.52	236	1.31	0.0028
Diamantane-1,6-diol	267	1.62	247	1.42	229	1.25	0.0028
Diamantane-1,7-diol	240	1.35	224	1.20	210	1.06	0.0028
Diamantane-1,9-diol	292	1.86	264	1.59	240	1.35	0.0035
Diamantane-3,5-diol	1056	9.35	792	6.76	595	4.83	0.0072
Adamantanoxim	576	4.65	496	3.86	406	2.98	0.0050
4-Oxahomoadamantan-5-one	364	2.57	317	2.11	275	1.70	0.0045
Cyclopentanone	202	0.98	189	0.85	179	0.75	0.0028
Cyclooctanone	614	5.02	521	4.11	422	3.14	0.0050

The same hydrogen bond may be formed by adamantane-2^a,4^a-diol (II), with a retention time also rather different from those of the other stereoisomers. A retention time only slightly lower than for (II) is observed for adamantane-1,2-diol (III), where the formation of a strained five-membered ring might be possible.

Effect of the basic skeleton size

Retention times increase with increasing number of carbon atoms in the molecule. The observed influence appears strongly for an increasing number of rings *i.e.* cyclohexanone, adamantanone and diamantanone, or cyclohexanol, adamantanol and diamantanol, and especially for an increasing number of carbon atoms in the ring, *i.e.* cyclopentanone, cyclohexanone and cyclooctanone. (The orientation measurement of monofunctional derivatives of diamantane showed the bad solubility and long retention times of these compounds. Therefore, more detailed studies were not performed.)

TABLE VII
RETENTION DATA

Mobile phase, acetonitrile–water (40:60)

Compounds	Temperature (°C)						log k' / 10°C
	30		50		70		
	t_R (sec)	k'	t_R (sec)	k'	t_R (sec)	k'	
Cyclohexanone	214	1.10	200	0.96	189	0.85	0.0028
Adamantanone	460	3.51	401	2.93	332	2.25	0.0050
Protoadamantan-4-one	447	3.38	384	2.76	317	2.11	0.0053
Bicyclo[3,3,1]nonane-2,6-dione	139	0.36	132	0.29	127	0.24	0.0045
Adamantane-2,4-dione	163	0.59	151	0.48	142	0.39	0.0043
Adamantane-2,6-dione	142	0.39	138	0.35	134	0.31	0.0028
2-Thiaadamantane-4,8-dione	155	0.52	146	0.43	138	0.35	0.0043
Adamantan-1-ol-2-one	174	0.71	170	0.67	163	0.59	0.0020
Adamantan-1-ol-4-one	128	0.26	125	0.22	122	0.19	0.0030
Adamantan-2-ol-6-one	130	0.28	126	0.24	122	0.19	0.0038
Adamantan-4-ol-2-one	143	0.40	139	0.36	133	0.31	0.0028
Diamantan-1-ol-3-one	238	1.33	216	1.12	198	0.94	0.0113
Tricyclo[4,4,0,0 ^{2,9}]decan-9-ol-5-one	137	0.35	136	0.33	134	0.32	0.0010
Cyclohexanol	210	1.06	194	0.91	184	0.81	0.0028
Adamantan-1-ol	429	3.21	366	2.59	305	1.99	0.0053
Adamantan-2-ol	560	4.49	462	3.53	372	2.65	0.0058
Adamantane-1,2-diol	177	0.74	168	0.65	160	0.57	0.0028
Adamantane-2 ^a ,4 ^a -diol	217	1.12	199	0.95	185	0.82	0.0035
Adamantane-2 ^e ,4 ^e -diol	143	0.40	137	0.35	132	0.29	0.0033
Adamantane-2 ^c ,4 ^c -diol	131	0.28	126	0.24	123	0.21	0.0035
Adamantane-2,6-diol	119	0.16	119	0.16	117	0.15	0.0013
Diamantane-1,4-diol	217	1.12	183	0.79	172	0.69	0.0028
Diamantane-1,6-diol	187	0.83	180	0.76	171	0.68	0.0023
Diamantane-1,7-diol	174	0.71	163	0.60	155	0.52	0.0033
Diamantane-1,9-diol	206	1.02	187	0.83	172	0.69	0.0043
Diamantane-3,5-diol	550	4.39	430	3.22	342	2.35	0.0068
Adamantanoxim	349	2.42	300	1.94	252	1.47	0.0053
4-Oxahomoadamantan-5-one	245	1.40	222	1.18	202	0.98	0.0040
Cyclopentanone	181	0.77	168	0.65	161	0.58	0.0033
Cyclooctanone	417	3.09	352	2.45	299	1.93	0.0050

During the measurements on silica the retention times of polycyclic alcohols substituted in a formally identical manner (e.g. adamantan-1-ol and diamantan-4-ol or adamantan-2-ol and diamantan-3-ol) were very close¹. On the reversed phases the retention times of the compounds formally equally substituted are rather different because of the different number of carbon atoms. So, the retention time of the diamantane-3,5-diol mentioned above is essentially longer than t_R of the adamantane-2,4-diols; also, diamantan-4-ol and diamantan-3-ol eluted substantially later than adamantan-1-ol and adamantan-2-ol, respectively.

Even 2-thiaadamantane-4,8-dione has nearly the same retention time as adamantane-2,6-dione in the mobile phase containing methanol. In the mobile phase containing acetonitrile, this heterocyclic derivative is eluted later. The difference in retention times caused by the different structure of protoadamantanone (IV) and

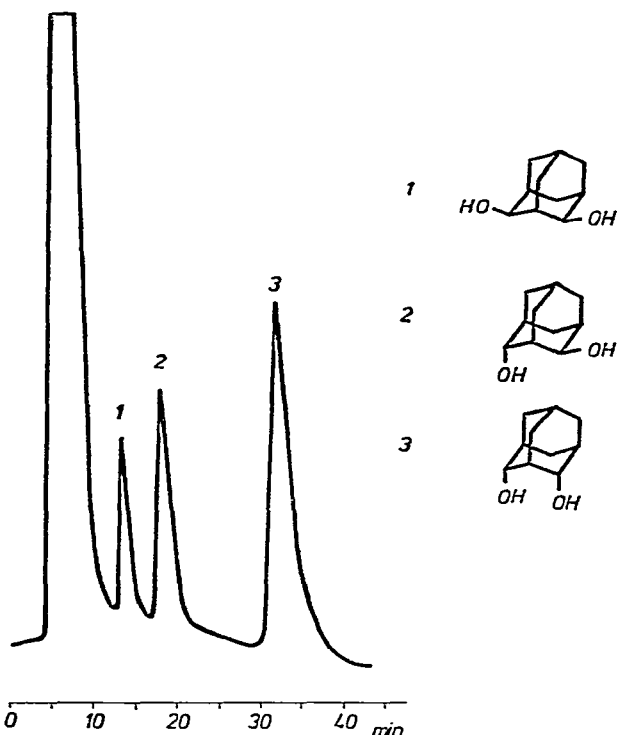


Fig. 1. Separation of the three adamantane-2,4-diol stereoisomers. Column, MicroPak CH-10; mobile phase, methanol-water (20:80); flow-rate, 10 ml/h; temperature, 30°C.

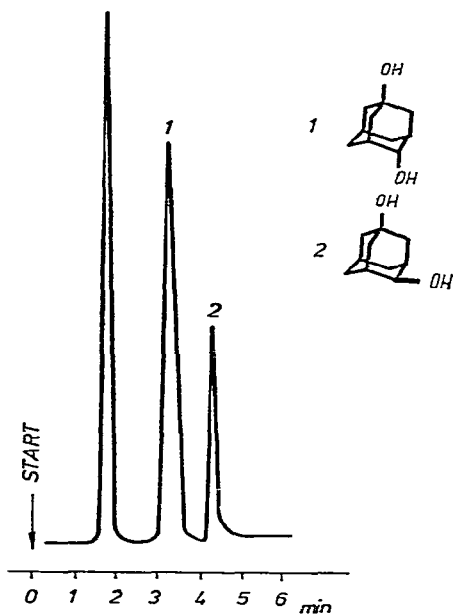
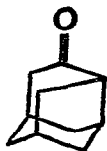


Fig. 2. Separation of the two adamantane-1,4-diol stereoisomers. Column, MicroPak CH-10; mobile phase, methanol-water (30:70); flow-rate, 10 ml/h; temperature, 30°C.

adamantanone (the same number of carbon atoms) appears greatest in the mobile phase with the lowest concentration of acetonitrile at the highest temperature.



IV

The effect of mobile phase composition

An equation derived by Jandera and Churáček⁵ describes the dependence of the capacity factor k' on the concentration of acetonitrile in the mobile phase:

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

where c is the concentration of acetonitrile in the mobile phase, and n and A are constants (Figs. 3 and 4).

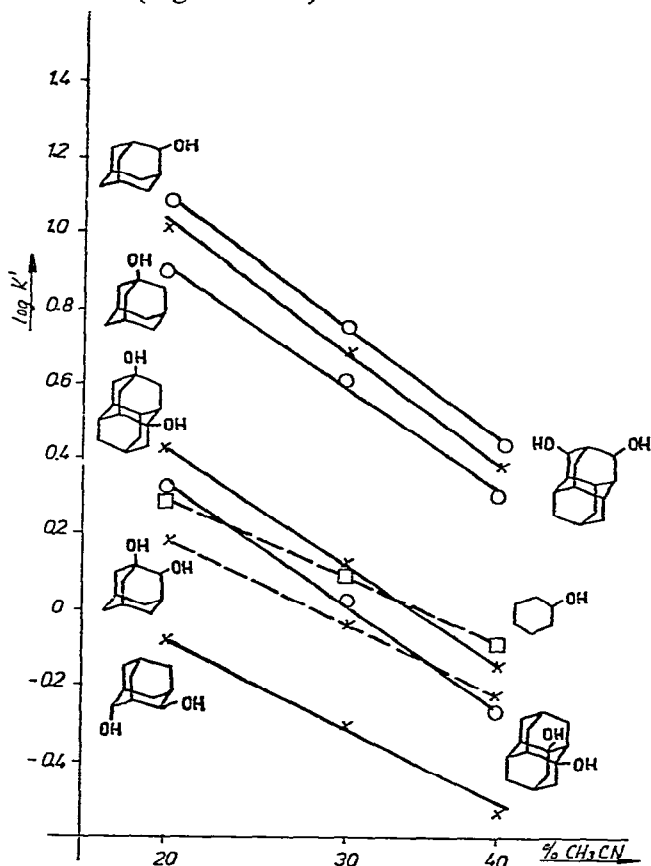


Fig. 3. Variation of the $\log k'$ with the concentration of acetonitrile in the mobile phase (water-acetonitrile).

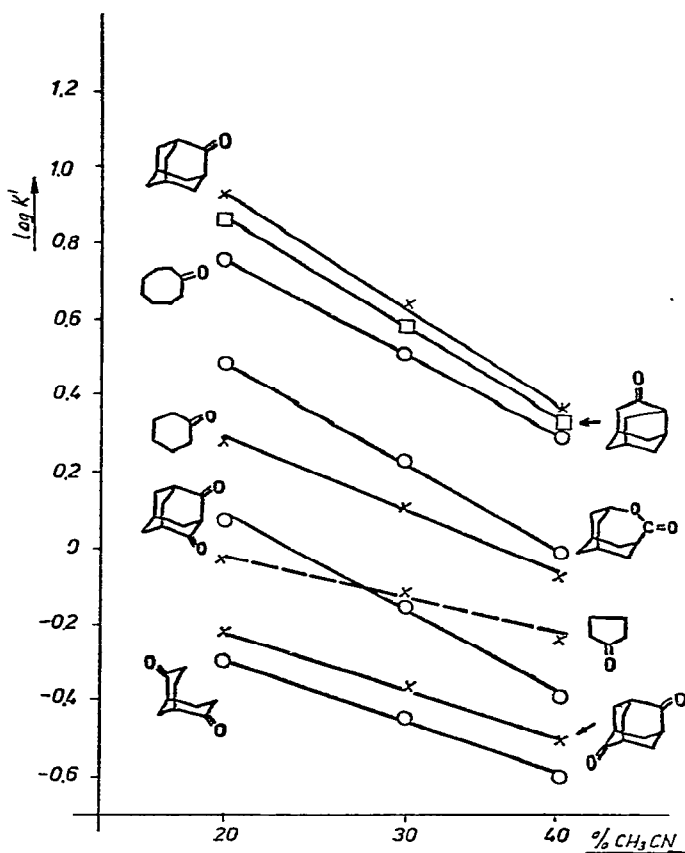


Fig. 4. Variation $\log k'$ with the concentration of acetonitrile in the mobile phase (water-acetonitrile).

Fig. 5 shows the dependence of $\log k'$ of some compounds on methanol concentration in the mobile phase. In the 40–70% range of methanol content, this dependence is linear and eqn. 1 holds true. The behaviour of the compounds investigated begins to change at 40% methanol, the change being approximately the same for all compounds. However, the selectivity of the separation of individual types of compound, as well as of isomeric derivatives, is not much influenced by changes in methanol concentration.

The dependence of retention times on water concentration is more pronounced for the acetonitrile mobile phase than for the methanol phase. A 10% change in water content in the mobile phase results in a more substantial change in $\log k'$ values of the compounds measured when using the acetonitrile-water mixture. The most significant differences were found for adamantanone, protoadamantanone, both adamantanols, and diamantane-3,5-diol, *i.e.* compounds with the highest retention times in the given system.

The mobile phases used are compared in Fig. 6. In both cases, the mobile phase contains 40% of the organic solvent (*i.e.* acetonitrile or methanol) in water. Straight lines representing the selected systems are used for plotting the capacity

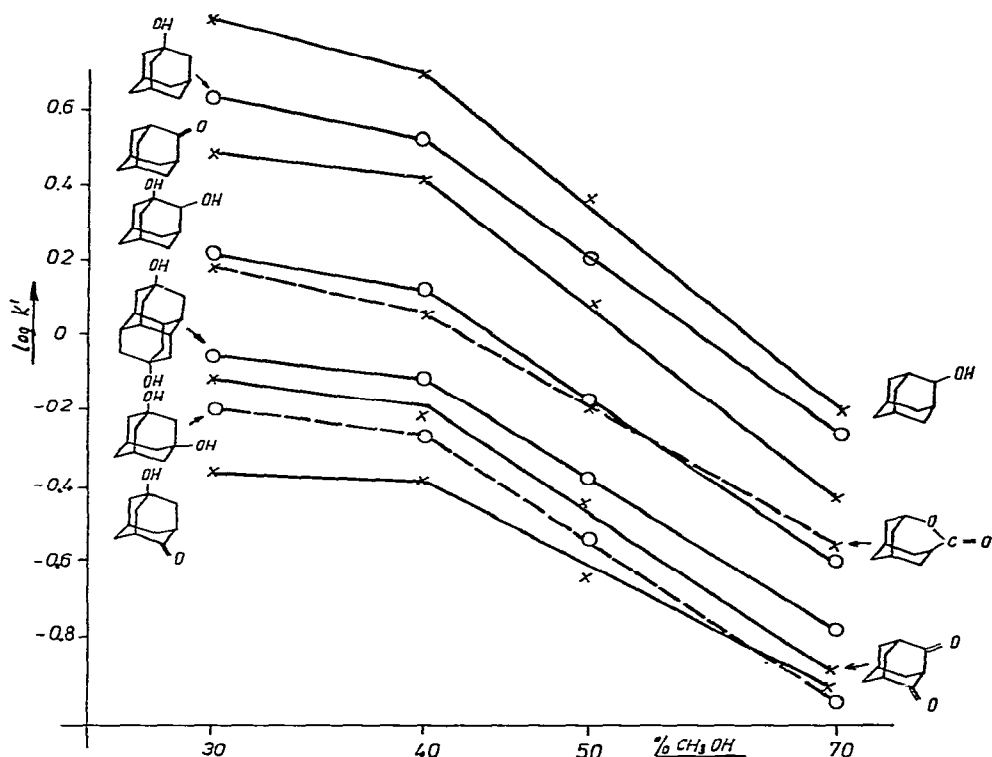


Fig. 5. Variation of the $\log k'$ with the concentration of methanol in the mobile phase (water-methanol).

factor values for the compounds chosen. The following conclusions can be drawn:

(1) When methanol replaces acetonitrile, retention times of alcohols increase; this increase is more substantial for molecules with more OH groups and for bigger molecules.

(2) When methanol replaces acetonitrile, retention times of ketones decrease. The elution order adamantan-1-ol, adamantanone, and adamantan-2-ol is changed to adamantanone, adamantan-1-ol and adamantan-2-ol in methanol.

(3) The selectivity of separation of the adamantan-1-ol-adamantan-2-ol pair is *ca.* 1.3–1.4, and is independent of mobile phase composition and temperature.

(4) Retention time differences for compounds substituted on identical secondary carbon atoms by various combinations of keto and hydroxy groups decrease. Thus compounds with nearly the same t_R values in methanol at 30°C are eluted in the order adamantane-2,6-diol, adamantane-2-ol-6-one, and finally adamantane-2,6-dione when acetonitrile is used.

(5) The use of the acetonitrile mobile phase is advisable for separations of ditopic adamantane derivatives.

(6) The selectivity of diamantanediol separations is either the same (1,4/1,9 dihydroxy derivatives) or better (1,6/1,4 and 1,6/1,9 dihydroxy derivatives) in methanol than in acetonitrile.

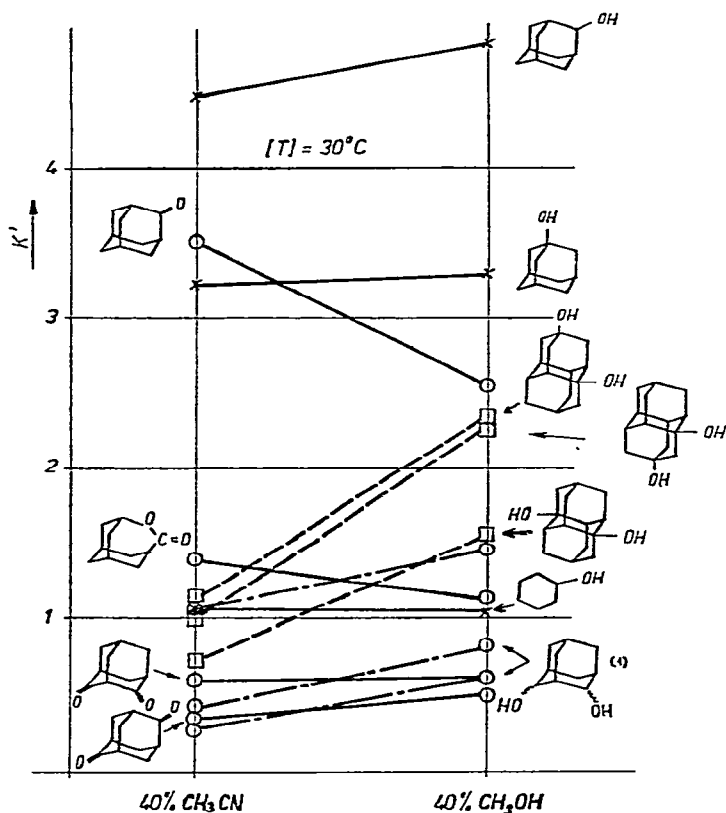


Fig. 6. Comparison of the capacity factors of some compounds, measured in two different mobile phases.

Temperature effects

All measurements in both systems investigated were performed at three temperatures, viz. 30, 50, and 70°C . The change of k' or $\log k'$ with temperature was studied. Values calculated from retention data, related to a 10°C temperature change, are summarized in Tables II–VII for the corresponding concentrations and compositions of mobile phases.

Capacity factors of the compounds studied are rather independent of temperature. In acetonitrile–water the temperature does not affect the selectivity or the separation efficiency. In case of the methanol mobile phase, there are some small changes improving the separation of several compounds (mostly of low solubility), the solubility being increased at higher temperatures (separation of diamantane-1,4-diol and diamantane-1,9-diol).

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