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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF METHYL ESTERS OF DIAMANTANE AND ADAMANTANE CARBOXYLIC ACIDS

J. KŘÍŽ*, L. VODIČKA and J. BURDA
Laboratory of Synthetic Fuels, Institute of Chemical Technology, Suchbátarova 5, 166 28 Prague 6 (Czechoslovakia)

SUMMARY

Chromatographic elution data for methyl and dimethyl esters of adamantane and diamantane derivatives of carboxylic and dicarboxylic acids have been determined using silica gel as the stationary phase. Eleven mobile phases containing *n*-heptane and/or diethyl ether, 2-propanol and chloroform were used in different concentrations.

Among all the compounds tested, esters having two functional groups have a longer retention time than esters having only one $-COOCH_3$ group. The influence of the position of $-COOCH_3$ groups on the chromatographic behaviour is discussed. For esters having the same formal substitution type, the elution time decreases with increasing size of the basic skeleton. The introduction of an alkyl group into the adamantane nucleus results in a decrease in the retention time of the relevant ester, while the introduction of an alkyl group between the adamantane skeleton and the $-COOCH_3$ group results in an increase in retention time. The effects of mobile phase composition on elution data for the compounds studied are discussed.

INTRODUCTION

Among the several thousand adamantane and diamantane derivatives prepared up to now, the esters play an important role both in basic research and in practical applications (*e.g.* pharmacy, biochemistry, medicine and the synthesis of special lubricants). Dimethyl esters of adamantane and diamantane dicarboxylic acids serve as the starting material for the synthesis of plastics with special properties, *e.g.* high thermal, oxidizing and radiation stability.

This study is part of a project dealing with the chromatographic analysis of diamantoic compounds. Previous reports have dealt with the high-performance liquid chromatographic (HPLC) characteristic of alcohols[1], ketones[2], and halogene derivatives[3], with silica gel as the stationary phase, or of diketones, hydroxyketones and dihydroxy derivatives, with reversed-phase systems[4].

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EXPERIMENTAL

Apparatus

A Varian 8500 liquid chromatograph with a syringe pump, connected to refractive-index detector and an A25 dual-channel strip-chart recorder, was used (Varian, Palo Alto, CA, U.S.A.). Sample injection by the stop-flow technique was performed; a 5-μl syringe (Hamilton, Bonaduz, Switzerland) was used. A stainless-steel column (250 × 4 mm I.D.; manufactured in our laboratory) was filled by the slurry-packing technique with 7.5-μm irregularly-shaped silica gel (Silasorb; Lachema, Brno, Czechoslovakia).

Reagents

Almost all of the standard compounds used for measurements were prepared in our laboratory. 2-Propanol (analytical grade; Lachema, Brno, Czechoslovakia) was used without further treatment. *n*-Heptane (Reakchim, Moscow, U.S.S.R.) and diethyl ether (Lachema) were dried over sodium before use and distilled in glass. Chloroform (analytical grade; Lachema) was shaken with a 20% solution of sodium hydroxide and then with distilled water, dried over phosphorus pentoxide, and distilled through a glass perforated-plate column with exclusion of moisture.

Mobile phases

The mobile phases were mixed 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.

TABLE I

MOBILE PHASE COMPOSITIONS (wt.%)

No. 1	*n-Heptane*	*2-Propanol*
a	99.9	0.1
b	99.8	0.2
c	99.7	0.3
d	99.5	0.5
No. 2.	*n-Heptane*	*Diethyl ether*
a	97	3
b	95	5
c	90	10
No. 3	*n-Heptane–diethyl ether (97:3)*	*2-Propanol*
a	99.95	0.05
b	99.9	0.1
c	99.8	0.2
No. 4	*n-Heptane–chloroform (80:20)*	*2-Propanol*
a	99.8	0.2

Procedure

Retention data were determined at laboratory temperature (20 ± 1°C). The flow-rate of the mobile phase was 30 ml/h. The column was stabilized prior to measurement by washing with fresh mobile phase (flow-rate 90 ml/h) for 10 h. Column activity was checked before starting the measurements, then several times during the analyses, and again after completion of the measurements by injecting a solution of diamantane-1,6-dicarboxylic acid dimethyl ester in benzene. The dead-volume of the column was determined by measuring the retention time of an unretained compound, *i.e.* isooctane. Retention data were determined on chromatograms obtained by injecting solutions of the compounds in benzene.

RESULTS AND DISCUSSION

The values of retention times (t_R) and capacity factors (k') are given in Tables II–V. The formulae of some of the compounds are shown in Fig. 1.

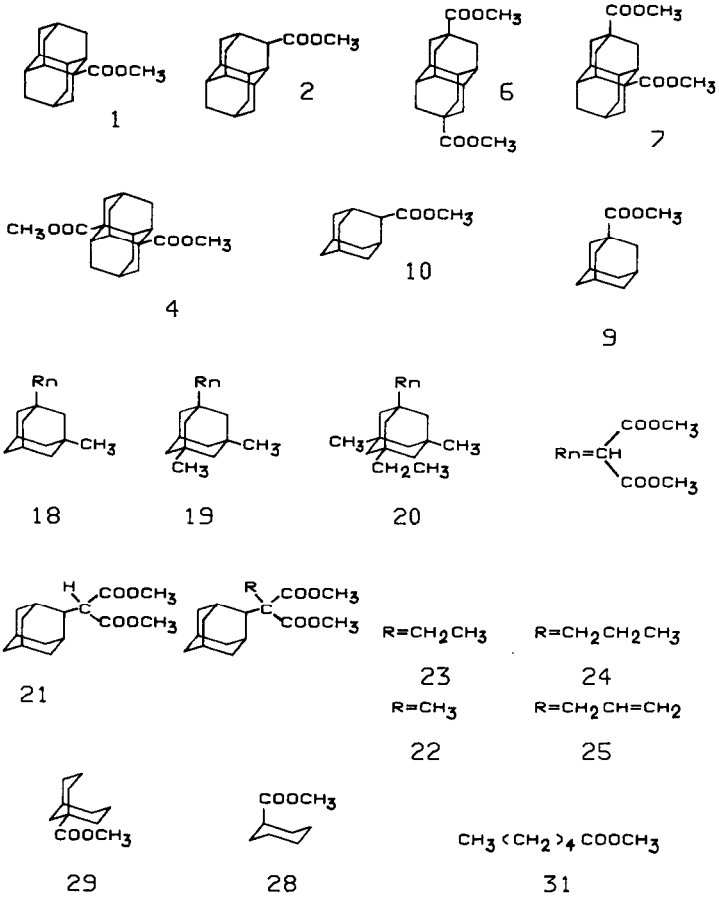


Fig. 1. The structures of some methyl esters included in this investigation.

TABLE II

RETENTION DATA

Mobile phases (%): a = *n*-heptane, b = diethyl ether; C = no. of carbon atoms; t_R = retention time (s); k' = capacity factor.

No.	*Compound*	*C*	*a = 97, b = 3*		*a = 95, b = 5*		*a = 90, b = 10*	
			t_R	k'	t_R	k'	t_R	k'
1	Methyl diamantane-1-carboxylate	16	300	2.01	221	1.22	169	0.70
2	Methyl diamantane-3-carboxylate	16	303	2.04	227	1.28	175	0.76
3	Methyl diamantane-4-carboxylate	16	358	2.60	261	1.62	188	0.88
4	Dimethyl diamantane-1,6-dicarboxylate	18	1915	18.22	959	8.63	429	3.30
5	Dimethyl diamantane-1,7-dicarboxylate	18	2104	20.12	1069	9.73	479	3.81
6	Dimethyl diamantane-4,9-dicarboxylate	18	3912	38.28	1783	16.90	695	5.97
7	Dimethyl diamantane-1,4-dicarboxylate	18	–	–	2097	20.05	783	6.86
8	Dimethyl diamantane-1,5-dicarboxylate	18	2346	22.55	1190	10.95	511	4.13
9	Methyl adamantane-1-carboxylate	12	362	2.63	266	1.67	191	0.92
10	Methyl adamantane-2-carboxylate	12	306	2.07	233	1.34	175	0.76
11	Dimethyl adamantane-1,3-dicarboxylate	14	–	–	1732	16.39	736	6.39
12	Methyl [1-(3-methyl)adamantyl]formiate	13	340	2.42	250	1.51	187	0.88
13	Methyl [1-(2-methyl)adamantyl]formiate	13	335	2.36	247	1.48	181	0.81
14	Methyl (2-adamantyl)acetate	13	390	2.92	271	1.72	195	0.96
15	Methyl [4-(2-adamantyl)]butanoate	15	354	2.55	257	1.58	187	0.87
16	Methyl [2-(2-adamantyl)]propionate	14	335	2.36	249	1.46	180	0.81
17	Methyl [2-(1-adamantyl)]propionate	14	300	2.01	228	1.29	168	0.69
18	Dimethyl [1-(3-methyl)adamantyl]malonate	16	1456	13.61	795	6.98	410	3.12
19	Dimethyl [1-(3,5-dimethyl)adamantyl]malonate	17	1369	12.70	753	6.56	386	2.87
20	Dimethyl [1-(3-ethyl-5,7-dimethyl)adamantyl]malonate	19	1238	11.43	690	5.93	355	2.56
21	Dimethyl (2-adamantyl)malonate	15	1866	17.73	1014	9.18	486	3.88
22	Dimethyl (2-adamantyl,methyl)malonate	16	955	8.58	560	4.63	319	2.20
23	Dimethyl (2-adamantyl,ethyl)malonate	17	763	6.66	457	3.59	269	1.70
24	Dimethyl (2-adamantyl,propyl)malonate	18	681	5.84	416	3.18	253	1.54
25	Dimethyl (2-adamantyl,2-propenyl)malonate	18	730	6.31	441	3.43	264	1.65
26	Dimethyl (1-adamantyl,methyl)malonate	16	962	8.66	366	4.68	316	2.17
27	Dimethyl [2-(2-adamantyl)ethyl]malonate	17	1478	13.84	829	7.33	417	3.19
28	Methyl cyclohexylcarboxylate	8	380	2.82	272	1.73	196	0.96
29	Methyl bicyclo[3.3.1]nonanoate	11	345	2.46	254	1.55	187	0.88
30	Dimethyl malonate	5	–	–	2318	22.28	1095	9.99
31	Methyl hexanoate	7	377	2.78	273	1.74	199	1.00
32	Methyl heptanoate	8	352	2.53	262	1.63	190	0.91

TABLE III

RETENTION DATA

Mobile phases (%): a = *n*-heptane, b = 2-propanol.

No.	*Compound*	*C*	*a = 99.9, b = 0.1*		*a = 99.8, b = 0.2*		*a = 99.7, b = 0.3*		*a = 99.5, b = 0.5*	
			t_R	k'	t_R	k'	t_R	k'	t_R	k'
1	Methyl diamantane-1-carboxylate	16	271	1.72	176	0.77	152	0.53	126	0.27
2	Methyl diamantane-3-carboxylate	16	266	1.67	173	0.73	151	0.52	126	0.27
3	Methyl diamantane-4-carboxylate	16	317	2.18	196	0.97	163	0.64	134	0.35
4	Dimethyl diamantane-1,6-dicarboxylate	18	–	–	762	6.65	337	2.38	206	1.07
5	Dimethyl diamantane-1,7-dicarboxylate	18	–	–	772	6.75	500	4.02	230	1.31
6	Dimethyl diamantane-4,9-dicarboxylate	18	–	–	1061	9.66	615	5.17	302	2.03
7	Dimethyl diamantane-1,4-dicarboxylate	18	–	–	1127	10.32	646	5.48	311	2.13
8	Dimethyl diamantane-1,5-dicarboxylate	18	–	–	784	6.87	497	3.99	226	1.27
9	Methyl adamantane-1-carboxylate	12	338	2.40	214	1.14	169	0.69	139	0.39
10	Methyl adamantane-2-carboxylate	12	280	1.81	190	0.90	154	0.55	131	0.32
11	Dimethyl adamantane-1,3-dicarboxylate	14	–	–	1068	9.72	640	5.43	317	2.18
12	Methyl [1-(3-methyl)adamantyl]formiate	13	313	2.14	200	1.01	164	0.65	137	0.37
13	Methyl [1-(2-methyl)adamantyl]formiate	13	312	2.13	202	1.02	163	0.63	135	0.36
14	Methyl (2-adamantyl)acetate	13	334	2.36	208	1.09	170	0.71	139	0.39
15	Methyl [4-(2-adamantyl)]butanoate	15	307	2.08	200	1.01	167	0.68	135	0.35
16	Methyl [2-(2-adamantyl)]propionate	14	317	2.18	194	0.95	168	0.69	134	0.35
17	Methyl [2-(1-adamantyl)]propionate	14	291	1.92	185	0.86	158	0.59	131	0.32
18	Dimethyl [1-(3-methyl)adamantyl]malonate	16	–	–	491	3.93	319	2.20	204	1.05
19	Dimethyl [1-(3,5-dimethyl)adamantyl]malonate	17	–	–	464	3.66	315	2.17	198	0.99
20	Dimethyl [1-(3-ethyl-5,7-dimethyl)adamantyl]malonate	19	–	–	433	3.34	301	2.02	190	0.91
21	Dimethyl (2-adamantyl)malonate	15	–	–	734	6.37	521	4.23	240	1.41
22	Dimethyl (2-adamantyl,methyl)malonate	16	–	–	372	2.74	265	1.66	179	0.80
23	Dimethyl (2-adamantyl,ethyl)malonate	17	658	5.61	313	2.14	237	1.38	162	0.63
24	Dimethyl (2-adamantyl,propyl)malonate	18	575	4.77	287	1.89	211	1.12	154	0.55
25	Dimethyl (2-adamantyl,2-propenyl)malonate	18	611	5.13	290	1.92	212	1.13	158	0.59
26	Dimethyl (1-adamantyl,methyl)malonate	16	–	–	383	2.84	268	1.69	178	0.79
27	Dimethyl [2-(2-adamantyl)ethyl]malonate	17	–	–	515	4.17	325	2.26	209	1.10
28	Methyl cyclohexylcarboxylate	8	344	2.45	218	1.19	182	0.83	145	0.46
29	Methyl bicyclo[3.3.1]nonanoate	11	320	2.22	204	1.05	174	0.75	139	0.39
30	Dimethyl malonate	5	–	–	2113	20.22	1292	11.97	680	5.83
31	Methyl hexanoate	7	–	–	216	1.17	170	0.71	144	0.45
32	Methyl heptanoate	8	297	1.98	206	1.07	167	0.68	139	0.39

TABLE IV

RETENTION DATA

Mobile phases (%): a = mixture of 97% *n*-heptane and 3% diethyl ether, b = 2-propanol.

No.	*Compound*	*C*	*a = 99.95, b = 0.05*		*a = 99.9, b = 0.1*		*a = 99.8, b = 0.2*	
			t_R	k'	t_R	k'	t_R	k'
1	Methyl diamantane-1-carboxylate	16	212	1.13	179	0.80	151	0.51
2	Methyl diamantane-3-carboxylate	16	212	1.13	179	0.80	150	0.50
3	Methyl diamantane-4-carboxylate	16	245	1.46	199	1.00	161	0.62
4	Dimethyl diamantane-1,6-dicarboxylate	18	900	8.03	554	4.57	334	2.35
5	Dimethyl diamantane-1,7-dicarboxylate	18	1015	9.19	624	5.27	369	2.70
6	Dimethyl diamantane-4,9-dicarboxylate	18	1750	16.57	934	8.37	509	4.11
7	Dimethyl diamantane-1,4-dicarboxylate	18	1948	18.55	1014	9.18	533	4.35
8	Dimethyl diamantane-1,5-dicarboxylate	18	1128	10.33	626	5.28	368	2.69
9	Methyl adamantane-1-carboxylate	12	262	1.63	206	1.07	169	0.69
10	Methyl adamantane-2-carboxylate	12	230	1.31	189	0.90	155	0.56
11	Dimethyl adamantane-1,3-dicarboxylate	14	1684	15.90	911	8.15	510	4.12
12	Methyl [1-(3-methyl)adamantyl]formiate	13	243	1.42	197	0.98	162	0.62
13	Methyl [1-(2-methyl)adamantyl]formiate	13	240	1.41	194	0.95	161	0.61
14	Methyl (2-adamantyl)acetate	13	263	1.64	209	1.10	167	0.68
15	Methyl [4-(2-adamantyl)]butanoate	15	246	1.47	195	0.96	160	0.61
16	Methyl [2-(2-adamantyl)]propionate	14	238	1.39	191	0.92	157	0.58
17	Methyl [2-(1-adamantyl)]propionate	14	223	1.23	181	0.82	151	0.52
18	Dimethyl [1-(3-methyl)adamantyl]malonate	16	808	7.11	472	3.74	298	1.99
19	Dimethyl [1-(3,5-dimethyl)adamantyl]malonate	17	718	6.20	445	3.46	289	1.90
20	Dimethyl [1-(3-ethyl-5,7-dimethyl)adamantyl]malonate	19	658	5.61	412	4.04	268	1.70
21	Dimethyl (2-adamantyl)malonate	15	971	8.75	560	4.62	356	2.58
22	Dimethyl (2-adamantyl,methyl)malonate	16	530	4.33	346	2.47	242	1.43
23	Dimethyl (2-adamantyl,ethyl)malonate	17	431	3.33	295	1.96	214	1.15
24	Dimethyl (2-adamantyl,propyl)malonate	18	394	2.95	272	1.73	199	1.00
25	Dimethyl (2-adamantyl,2-propenyl)malonate	18	408	3.10	289	1.90	204	1.05
26	Dimethyl (1-adamantyl,methyl)malonate	16	543	4.45	352	2.53	243	1.44
27	Dimethyl [2-(2-adamantyl)ethyl]malonate	17	769	6.72	476	3.78	305	2.07
28	Methyl cyclohexylcarboxylate	8	273	1.74	217	1.17	170	0.71
29	Methyl bicyclo[3.3.1]nonanoate	11	251	1.52	204	1.05	162	0.63
30	Dimethyl malonate	5	–	–	1328	12.34	764	6.67
31	Methyl hexanoate	7	269	1.70	218	1.19	174	0.75
32	Methyl heptanoate	8	257	1.58	207	1.08	168	0.69

TABLE V

RETENTION DATA

Mobile phase: 99.8% mixture of (80% *n*-heptane–20% chloroform) and 0.2% 2-propanol.

No.	*Compound*	*C*	t_R	*k'*
1	Methyl diamantane-1-carboxylate	16	162	0.63
2	Methyl diamantane-3-carboxylate	16	158	0.59
3	Methyl diamantane-4-carboxylate	16	176	0.77
4	Dimethyl diamantane-1,6-dicarboxylate	18	410	3.11
5	Dimethyl diamantane-1,7-dicarboxylate	18	443	3.45
6	Dimethyl diamantane-4,9-dicarboxylate	18	738	7.41
7	Dimethyl diamantane-1,4-dicarboxylate	18	779	6.83
8	Dimethyl diamantane-1,5-dicarboxylate	18	445	3.47
9	Methyl adamantane-1-carboxylate	12	178	0.78
10	Methyl adamantane-2-carboxylate	12	163	0.64
11	Dimethyl adamantane-1,3-dicarboxylate	14	730	6.33
12	Methyl [1-(3-methyl)adamantyl]formiate	13	169	0.70
13	Methyl [1-(2-methyl)adamantyl]formiate	13	168	0.69
14	Methyl (2-adamantyl)acetate	13	170	0.71
15	Methyl [4-(2-adamantyl)]butanoate	15	165	0.66
16	Methyl [2-(2-adamantyl)]propionate	14	164	0.65
17	Methyl [2-(1-adamantyl)]propionate	14	160	0.60
18	Dimethyl [1-(3-methyl)adamantyl]malonate	16	328	2.29
19	Dimethyl [1-(3,5-dimethyl)adamantyl]malonate	17	308	2.09
20	Dimethyl [1-(3-ethyl-5,7-dimethyl)adamantyl]malonate	19	275	1.76
21	Dimethyl (2-adamantyl)malonate	15	381	2.83
22	Dimethyl (2-adamantyl,methyl)malonate	16	256	1.57
23	Dimethyl (2-adamantyl,ethyl)malonate	17	227	1.28
24	Dimethyl (2-adamantyl,propyl)malonate	18	208	1.08
25	Dimethyl (2-adamantyl,2-propenyl)malonate	18	209	1.10
26	Dimethyl (1-adamantyl,methyl)malonate	16	268	1.69
27	Dimethyl [2-(2-adamantyl)ethyl]malonate	17	318	2.19
28	Methyl cyclohexylcarboxylate	8	183	0.84
29	Methyl bicyclo[3.3.1]nonanoate	11	174	0.75
30	Dimethyl malonate	5	1154	10.58
31	Methyl hexanoate	7	174	0.75
32	Methyl heptanoate	8	166	0.67

It was found that four main factors affect adsorption of the investigated esters and diesters:

(1) the number of $-COOCH_3$ groups;

(2) the position of the $-COOCH_3$ group on the adamantane and diamantane skeleton;

(3) the size of the basic skeleton;

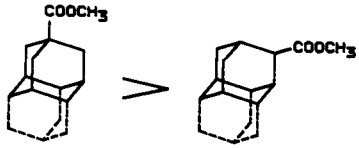
(4) the substitution of the alkyl group.

Effect of the number of $-COOCH_3$ groups

Under all conditions, and with the 32 esters measured, it was found that all diesters have longer retention times than any of the monoesters.

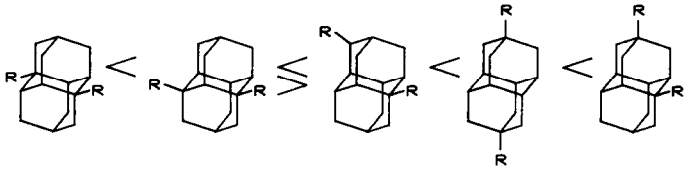
Effect of position of $-COOCH_3$ group

In the group of monotopic diamantoic derivatives, the position of the functional group has a dominant effect on chromatographic behaviour[1,3]. As in the case of adamantanols[1], diamantanols[2] and halogen derivatives[3] of adamantane and diamantane, compounds with a $-COOCH_3$ group attached to a tertiary carbon atom, where it is easily accessible to adsorption on silica, have the longest retention times. Methyl adamantane-1-carboxylate has a longer retention time than the 2-isomer.



Of the three isomeric methyl adamantane carboxylates, methyl diamantane-4-carboxylate has the longest retention time. Elution times of methyl diamantane-1-carboxylate (substituent located on medial tertiary carbon atom) and methyl diadamantane-3-carboxylate are shorter and do not differ to such an extent. Their relative elution order is influenced further by the composition of the mobile phase.

For dimethyl diamantane dicarboxylates, the retention times increase in the following order:

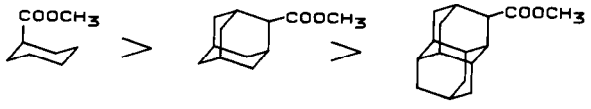


where R = $COOCH_3$.

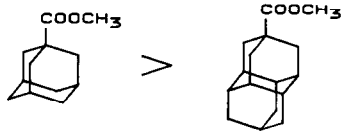
The elution order of 1,7- and 1,5-derivatives is also further influenced by the composition of the mobile phase. This effect will be discussed later.

Effect of the basic skeleton size

In the absence of additional steric effects, methyl esters of adamantane and diamantane, substituted in a formally identical manner, exhibit retention times which decrease with increasing size of the basic skeleton of the molecule. As in the case of adamantoic alcohols[1] and ketones[2], the retention times of compounds having the $-COOCH_3$ group attached to the secondary carbon atom, decrease in the following order: methyl cyclohexylcarboxylate, methyl adamantane-2-carboxylate and methyl diamantane-3-carboxylate.



The same effect was observed for esters when the functional group is attached to tertiary carbon atoms:



The chromatographic behaviour of methyl bicyclo[3.3.1]nonanoate is exceptional. Its retention time is shorter than that of methyl adamantane-1-carboxylate and methyl diadamantane-4-carboxylate. The dependence of k' on the number of carbon atoms is shown in Fig. 2; the composition of the mobile phase used was 97% *n*-heptane and 3% 2-propanol.

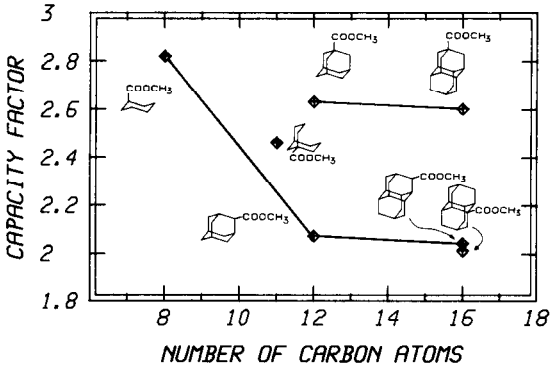
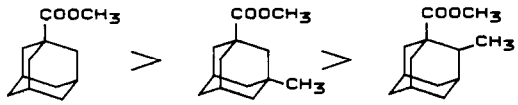


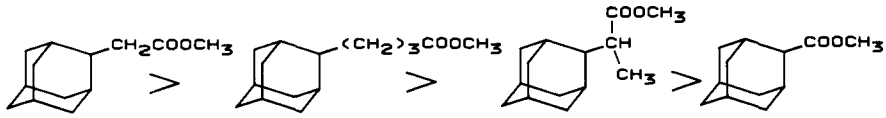
Fig. 2. Plot of capacity factor k' *vs.* the number of carbon atoms. Mobile phase: *n*-heptane–diethyl ether (97:3, w/w).

Effect of alkyl substitution

Under all the conditions examined, the introduction of an alkyl group into position 2 or 3 of methyl adamantane-1-carboxylate, lowers the retention time to that of the parent molecule:



The elution order of methyl [1-(3-methyl)adamantane] formiate and methyl [1-(2-methyl)adamantane] formiate is influenced further by the composition of the mobile phase. On the other hand, the introduction of an alkyl group between the adamantane skeleton and $-COOCH_3$ group increases the retention time. The retention order of some of these compounds is as follows:



The linear dependence of log k' on the number of carbon atoms observed for three alkyl derivatives of dimethyl adamantyl-1-malonate is shown in Fig. 3. Fig. 3 also shows the influence of log k' on the alkyl introduction for the homologous series of dimethyl (2-adamantyl, alkyl) malonates. The chromatogram of the dimethyl[1-(alkyl)adamantyl] malonates is shown in Fig. 4.

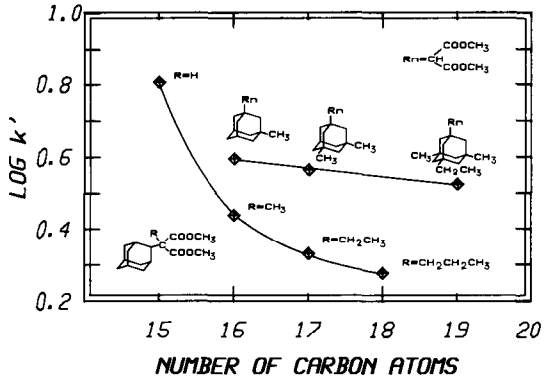


Fig. 3. Plot of log k' *vs.* the number of carbon atoms. Mobile phase: *n*-heptane–2-propanol (99.8:0.2, w/w).

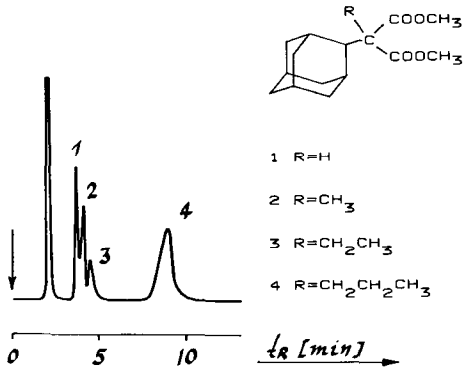
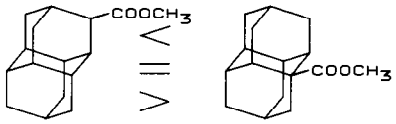


Fig. 4. Separation of dimethyl [1-(alkyl)adamantyl]malonates. Column (250 × 4 mm I.D.) packed with 7.5-μm silica gel; mobile phase, *n*-heptane–2-propanol (99.7:0.3, w/w). Flow-rate 30 ml/h.

Effect of mobile phase composition

Diethyl ether and 2-propanol have a reverse influence on the chromatographic behaviour of methyl diamantane-1-carboxylate and methyl diamantane-3-carboxylate. The addition of 2-propanol to the mobile phase increases the retention time of the 1-derivative in comparison with the 3-derivative. The addition of diethyl ether, however, brings about a change in the elution order of both isomers. When a mobile

phase containing all these components is used, *i.e.* *n*-heptane, 2-propanol and diethyl ether, the elution times of both compounds are equal.



Mobile phase:
n-heptane–2-propanol
n-heptane–2-propanol–diethyl ether
n-Heptane–diethyl ether

The same influence was found for the composition of the mobile phase on the chromatographic behaviour of the pair of dimethyl diamantane dicarboxylates substituted in positions 1,5-and 1,7-, respectively. In fact, these compounds differ from the original pair of monoesters by the addition of another group to the tertiary medial carbon atom.

The elution order of different dimethyl esters of dicarboxylic acids for three mobile phases containing 0.2% 2-propanol reveals no essential changes. The change of elution order occurs for dimethyl(2-adamantyl)malonate and dimethyl diamantan-1,6-dicarboxylate. While elution order is identical for the mobile phases *n*-heptane–2-propanol and *n*-heptane–chloroform–2-propanol, when *n*-heptane–diethyl ether–2-propanol is used as the mobile phase, the elution order is exactly the reverse.

Dependence of capacity factor on mobile phase elution strength

As in the case of alcohols[1] and ketones[2], a linear dependence of log k' on the logarithm of the concentration of the more polar component of the mobile phase exists for monomethyl esters, as described by the Jandera equation[5]:

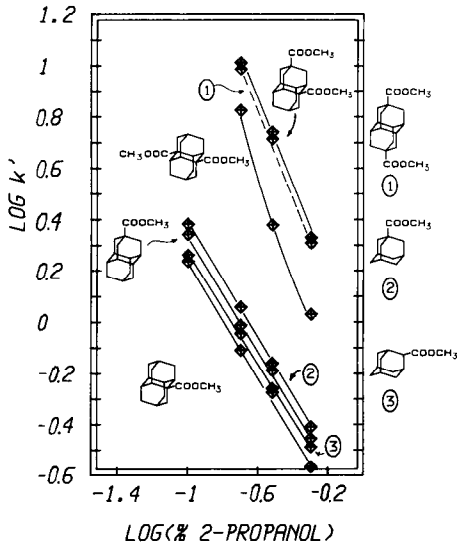


Fig. 5. Variation of the logarithm of the capacity factor with the concentration of 2-propanol in the mobile phase *n*-heptane–2-propanol.

where c is the concentration of the more polar component in a two-component mobile phase, and n and A are constants. Fig. 5 illustrates the dependence of the log k' value on the log of concentration of 2-propanol in n-heptane. The straight lines of the methyl carboxylates are virtually parallel. A deviation from the linear relationship was observed for dimethyl dicarboxylates, the lines expressing the dependence being steeper. The same conclusion can be drawn for other mobile phases from measurements of the dependencies mentioned.

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