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

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#### **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 nheptane 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<sub>3</sub> group. The influence of the position of -COOCH<sub>3</sub> 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<sub>3</sub> 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<sup>1</sup>, ketones<sup>2</sup>, and halogene derivatives<sup>3</sup>, with silica gel as the stationary phase, or of diketones, hydroxyketones and dihydroxy derivatives, with reversed-phase systems<sup>4</sup>.

#### **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- $\mu$ l 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- $\mu$ m 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
:	99.7	0.3
	99.5	0.5
Io. 2.	n-Heptane	Diethyl ether
	97	3
)	95	5
	90	10
lo. 3	n-Heptane-	2-Propanol
	diethyl ether	•
	(97: <b>3</b> )	
	99.95	0.05
)	99.9	0.1
	99.8	0.2
No. 4	n-Heptane-	2-Propanol
	chloroform	•
	(80:20)	
l.	99.8	0.2

## Procedure

Retention data were determined at laboratory temperature ( $20 \pm 1$ °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.

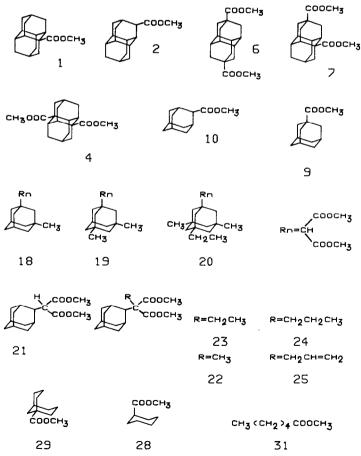


Fig. 1. The structures of some methyl esters included in this investigation.

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.

Methyl diamantane-1-carboxylate	No.	Compound	C	a = 97,	b=3	a = 95,	b = 5	a = 90,	0I = q
Methyl diamantane-1-carboxylate         16         300         2.01         221         1.22         169           Methyl diamantane-1-carboxylate         16         338         2.04         227         1.28         175           Dimethyl diamantane-1-defaerboxylate         18         2.04         227         1.28         175           Dimethyl diamantane-1-defaerboxylate         18         2.04         2.01         1069         9.73         479           Dimethyl diamantane-1-defaerboxylate         18         2.04         2.02         1069         9.73         479           Dimethyl diamantane-1-defaerboxylate         18         2.34         2.25         1190         1095         511           Methyl admantane-1-carboxylate         12         366         2.07         233         1.34         175           Methyl admantane-1-carboxylate         12         36         2.07         233         1.34         175           Methyl admantyllormiate         13         3.0         2.42         2.0         1.54         18           Methyl [1-G-methyl)adamantyllormiate         13         3.0         2.42         2.0         1.44         18           Methyl [1-G-amethyl)adamantylloromate         13         3				<sup>[</sup> R	K'	IR	K	, tr	κ,
Methyl diamantane-3-carboxylate         16         343         2.04         227         1.28         175           Methyl diamantane-3-carboxylate         16         3.88         2.06         261         1.62         188           Dimethyl diamantane-1-dedicarboxylate         18         2104         20.12         1069         9.73         479           Dimethyl diamantane-1-dedicarboxylate         18         310         36.2         2067         200         783           Dimethyl diamantane-1-dedicarboxylate         18         234         2.25         1190         10.95         511           Methyl adamantane-1-dedicarboxylate         12         36         2.07         203         783           Methyl adamantane-1-dedicarboxylate         12         36         2.07         233         1.34         175           Methyl II-Q-methyladamantyllormiate         13         340         2.4         2.0         1.51         189           Methyl II-Q-methyladamantyllormiate         13         34         2.5         2.0         1.5         1.8         18           Methyl II-Q-methyladamantyllormiate         15         3.4         2.5         2.0         1.5         1.6         1.8         1.5         1.6	-	Methyl diamantane-1-carboxylate	16	300	2.01	221	1.22	691	0.70
Methyl diamantane-4-ærboxylate         16         358         2.60         261         162         188           Dimethyl diamantane-4-ærboxylate         18         1915         18.22         959         8.63         429           Dimethyl diamantane-1,-dicarboxylate         18         2104         20.12         1069         9.73           Dimethyl diamantane-1,-dicarboxylate         18         246         22.5         1190         0.095           Dimethyl diamantane-1,-dicarboxylate         18         246         2.55         1190         0.095           Methyl damantane-1,-dicarboxylate         12         362         2.65         1.67         191           Methyl damantane-1,-dicarboxylate         12         362         2.65         1.67         191           Methyl damantane-1, dicarboxylate         13         34         2.42         2.66         1.67         191           Methyl (1-3-methyl)adamantyl]formiate         13         34         2.42         2.6         1.67         191           Methyl (1-3-methyl)adamantyl]proporate         13         34         2.2         2.5         1.4         1.8         118           Methyl (2-damantyl)proporate         14         30         2.2         2.5	7		16	303	2.04	727	1.28	175	9.76
Dimethyl diamantane-1, d-dicarboxylate         18         1915         18.2         95         8.63         4.99           Dimethyl diamantane-1, d-dicarboxylate         18         20.12         1069         9.73         4.99           Dimethyl diamantane-1, d-dicarboxylate         18         2         2.52         1783         6.90         8.53           Dimethyl diamantane-1, d-dicarboxylate         18         2         2.53         1190         10.95         511           Methyl damantane-1, d-dicarboxylate         12         362         2.67         2.63         183         1.94           Methyl damantane-1, d-dicarboxylate         12         36         2.07         2.33         1.54         175           Methyl [1-3-methyl)adamantyl]formiate         13         34         2.4         2.53         1.91           Methyl [1-3-demantyl]propionate         13         390         2.93         2.71         1.72         185           Methyl [1-3-damantyl]propionate         14         3.35         2.36         2.47         1.48         187           Methyl [1-3-damantyl]propionate         15         3.94         2.3         2.7         1.25         188           Methyl [1-3-damantyl]propionate         16         <	3		91	358	2.60	791	1.62	188	0.88
Dimethyl diamantane-1,7-dicarboxylate         18         2104         20.12         1669         9.73         479           Dimethyl diamantane-1,7-dicarboxylate         18         -         -         -         2097         0.005         583           Dimethyl diamantane-1,4-dicarboxylate         18         -         -         -         2097         0.005         581           Methyl adamantane-1,5-dicarboxylate         12         36         2.63         2.66         1.67         191           Methyl adamantane-1,3-dicarboxylate         12         36         2.63         2.66         1.67         191           Methyl adamantyllormiate         14         -         -         1732         1.67         191           Methyl [1-Ch-methyladamantyllormiate         13         340         2.42         2.90         1.51         187           Methyl [1-Ch-methyladamantyllormiate         13         390         2.92         271         1.48         187           Methyl [2-Ch-adamantyllormiate         14         30         2.92         271         1.18         187           Methyl [2-Ch-adamantylloroporate         14         30         2.92         271         1.18         114           Methyl [2-Ch-a	4	Dimethyl diamantane-1,6-dicarboxylate	18	1915	18.22	959	8.63	429	3.30
Dimethyl diamantane-4,9-dicarboxylate         18         3912         38.28         1783         16.90         685           Dimethyl diamantane-1,-dicarboxylate         18         -         -         2097         2005         783           Dimethyl diamantane-1,-dicarboxylate         12         362         2.63         266         1.67         191           Methyl adamantane-1,-dicarboxylate         12         362         2.63         266         1.67         191           Methyl adamantane-1,-dicarboxylate         14         -         -         2.07         233         1.34         175           Methyl [1-C-methyladamantyl]formiate         13         340         2.42         250         1.51         187           Methyl [1-C-methyladamantyl]formiate         13         340         2.42         250         1.51         187           Methyl [1-C-methyladamantyl]propionate         15         346         2.52         271         1.72         188           Methyl [1-C-damantyl]propionate         14         335         2.36         247         1.48         181           Dimethyl [1-C-damantyl]malonate         16         145         2.52         2.71         1.72         186           Dimethyl [1-C-da	S	Dimethyl diamantane-1,7-dicarboxylate	18	2104	20.12	1069	9.73	479	3.81
Dimethyl diamantane-1,4-dicarboxylate         18         -         -         2097         20.05         783           Dimethyl diamantane-1,4-dicarboxylate         18         24         2.25         1190         10.05         511           Methyl adamantane-1,4-dicarboxylate         12         366         2.07         233         1.34         175           Dimethyl adamantane-1,3-dicarboxylate         13         340         2.07         233         1.34         175           Methyl [1-(3-methyl)adamantyl]formiate         13         340         2.42         250         1.51         187           Methyl [1-(2-methyl)adamantyl]formiate         13         390         2.92         271         1.48         187           Methyl [1-(2-damantyl)]propionate         15         354         2.55         257         1.88         187           Methyl [2-(2-adamantyl]propionate         15         354         2.55         257         1.88         187           Methyl [2-(3-adamantyl]propionate         16         145         300         2.01         228         1.20         1.88         100           Dimethyl [1-(3-adamantyl]propionate         16         145         300         2.01         228         1.20         1.20<	9	Dimethyl diamantane-4,9-dicarboxylate	18	3912	38.28	1783	16.90	695	2.97
Dimethyl diamantane-1,5-dicarboxylate         18         2346         22.55         190         10.95         511           Methyl adamantane-1,5-dicarboxylate         12         362         2.63         266         1.67         191           Methyl adamantane-1,3-dicarboxylate         12         362         2.63         266         1.67         191           Methyl adamantane-1,3-dicarboxylate         13         340         2.42         250         1.51         187           Methyl [1-(2-methyl)adamantyl]formiate         13         390         2.92         271         1.72         16.39         736           Methyl [2-(3-damantyl)formiate         13         390         2.92         271         1.73         188         187           Methyl [2-(3-damantyl)formiate         14         300         2.93         271         1.73         188         187           Methyl [2-(3-damantyl)formiate         14         300         2.91         2.74         188         181           Methyl [2-(3-damantyl)formiate         14         300         2.91         2.74         188         181           Dimethyl [1-(3-damantyl)formiate         15         12.86         1.73         16         36         26         38 </td <td>7</td> <td>Dimethyl diamantane-1,4-dicarboxylate</td> <td>18</td> <td>I</td> <td>1</td> <td>2097</td> <td>20.05</td> <td>783</td> <td>98.9</td>	7	Dimethyl diamantane-1,4-dicarboxylate	18	I	1	2097	20.05	783	98.9
Methyl adamantane-1-carboxylate         12         362         2.63         266         1.67         191           Methyl adamantane-1-carboxylate         12         306         2.07         233         1.34         175           Dimethyl adamantane-1,3-dicarboxylate         13         340         2.42         250         1.51         187           Methyl [1-(3-methyl)adamantyl]formiate         13         340         2.42         250         1.51         187           Methyl [1-(2-methyl)adamantyl]formiate         13         390         2.92         271         1.58         187           Methyl [4-(2-adamantyl]]propionate         14         300         2.01         228         1.26         188         180           Methyl [4-(3-adamantyl]]propionate         14         300         2.01         228         1.29         168         180         1.46         180         1.86         1.80	œ		18	2346	22.55	1190	10.95	511	4.13
Methyl adamantane-2-carboxylate         12         306         2.07         233         1.34         175           Dimethyl adamantane-1,3-dicarboxylate         14         —         —         1732         16.39         736           Methyl [1-(3-methyl)adamantyl]formiate         13         349         2.92         271         172         195           Methyl [1-(2-methyl)adamantyl]formiate         13         390         2.92         271         1.72         195           Methyl [2-(2-adamantyl)]potionate         15         354         2.55         257         1.88         187           Methyl [2-(2-adamantyl)]propionate         14         335         2.36         249         1.48         181           Methyl [2-(2-adamantyl)]propionate         14         335         2.36         249         1.48         187           Dimethyl [2-(2-adamantyl)]propionate         16         1369         12.70         753         6.56         386           Dimethyl [1-(3-enthyl)adamantyl]malonate         15         186         11.43         690         5.93         355           Dimethyl [1-(3-edamantyl,ethyl)malonate         16         955         8.89         560         465         319           Dimethyl (2-adamantyl,eth	6		12	362	2.63	790	1.67	161	0.92
Dimethyl adamantane-1,3-dicarboxylate         14         -         -         1732         16.39         736           Methyl [1-(3-methy)ladamantyl]formiate         13         340         2.42         250         1.51         187           Methyl [1-(2-methy)ladamantyl]formiate         13         395         2.92         271         1.72         195           Methyl [4-(2-adamantyl)]porpionate         14         335         2.36         249         1.46         180           Methyl [2-(2-adamantyl)]porpionate         14         335         2.36         249         1.46         180           Methyl [2-(3-adamantyl)]porpionate         14         30         2.92         271         1.72         180           Dimethyl [1-(3-methyl)]adamantyl]malonate         16         136         12.70         753         6.56         386           Dimethyl [1-(3-ethyl-5.7-dimethyl)]adamantyl]malonate         15         128         11.43         690         5.93         355           Dimethyl [1-(3-damantyl)]malonate         16         456         457         3.99         269           Dimethyl [2-damantyl,methyl]malonate         16         456         457         3.99         269           Dimethyl [2-damantyl,methyl]malonate         <	10		12	306	2.07	233	1.34	175	97.0
Methyl [1-(3-methyl)adamantyl]formiate         13         340         2.42         250         1.51         187           Methyl [1-(3-methyl)adamantyl]formiate         13         335         2.36         247         1.48         181           Methyl [2-(2-adamantyl)portoinate         15         335         2.36         249         1.46         180           Methyl [2-(2-adamantyl)portoinate         14         300         2.01         228         1.29         168           Methyl [2-(2-adamantyl)propionate         14         300         2.01         228         1.29         168           Dimethyl [2-(1-adamantyl)propionate         16         1456         13.61         795         6.98         410           Dimethyl [2-(1-adamantyl)propionate         17         1369         1.270         1.28         1.46         180           Dimethyl [1-(3-ethyl-37-dimethyl)adamantylmalonate         17         136         1.27         1.06         9.58         410           Dimethyl (2-adamantyl-ethyl)malonate         16         955         8.58         560         4.63         316           Dimethyl (2-adamantyl-ethyl)malonate         16         962         8.66         366         3.73         417           Dimethyl (	Ξ		4	t	ł	1732	16.39	736	6.39
Methyl [1-(2-methyl)adamantyl]formiate         13         335         2.36         247         1.48         181           Methyl (2-adamantyl)acetate         15         354         2.25         271         1.72         195           Methyl (2-(2-adamantyl)propionate         14         335         2.36         249         1.48         181           Methyl (2-(1-adamantyl)propionate         14         306         2.01         228         1.29         168           Dimethyl (2-(1-adamantyl)propionate         16         1456         13.61         795         6.98         410           Dimethyl (1-(3-cthyl-2-damantyl)malonate         17         1369         12.70         753         6.56         386           Dimethyl (2-adamantyl-methyl)malonate         15         1866         17.73         1014         9.18         486           Dimethyl (2-adamantyl-methyl)malonate         16         955         8.58         560         4.63         319           Dimethyl (2-adamantyl-methyl)malonate         16         955         8.58         560         4.63         316           Dimethyl (2-adamantyl-methyl)malonate         16         955         8.58         560         4.63         316           Dimethyl (2-adamantyl-	12		13	340	2.42	250	1.51	187	0.88
Methyl (2-adamantyl)acetate         13         390         2.92         271         1.72         195           Methyl (2-adamantyl)butanoate         15         354         2.55         277         1.58         187           Methyl [2-(2-adamantyl)propionate         14         305         2.01         228         1.29         168           Methyl [2-(1-adamantyl)propionate         16         1456         1361         795         6.98         410           Dimethyl [1-(3-cthyl-5,7-dimethyl)adamantylmalonate         17         1369         12.70         753         6.56         386           Dimethyl [1-(3-cthyl-5,7-dimethyl)adamantylmalonate         15         1866         17.73         1014         9.18         486           Dimethyl [1-(3-cthyl-5,7-dimethyl)malonate         15         1866         17.73         1014         9.18         486           Dimethyl [2-adamantyl,cthyl)malonate         16         955         8.58         560         4.63         319           Dimethyl [2-damantyl,propyl)malonate         16         962         8.66         457         3.59         269           Dimethyl [2-damantyl,methyl)malonate         16         962         8.66         4.63         316           Dimethyl [1-damantyl,	13		13	335	2.36	247	1.48	181	0.81
Methyl [4-(2-adamantyl)]butanoate         15         354         2.55         257         1.58         187           Methyl [2-(2-adamantyl)]butanoate         14         335         2.36         249         1.46         180           Methyl [2-(2-adamantyl)]propionate         14         300         2.01         228         1.29         168           Dimethyl [1-(3-eduhyl)]adamantyl]malonate         17         1369         12.70         753         6.56         386           Dimethyl [1-(3-eduhyl)]Aclamantyl]malonate         15         186         17.73         1014         9.18         486           Dimethyl (2-adamantyl,methyl)malonate         16         955         8.58         560         4.63         319           Dimethyl (2-adamantyl,methyl)malonate         17         763         6.66         457         3.59         269           Dimethyl (2-adamantyl,methyl)malonate         18         730         6.31         441         3.43         264           Dimethyl (2-adamantyl,methyl)malonate         18         730         6.36         4.63         316           Dimethyl (2-adamantyl,acthyl)malonate         16         962         8.66         4.63         316           Dimethyl (2-adamantyl,acthyl)malonate <t< td=""><td>14</td><td>Methyl (2-adamantyl)acetate</td><td>13</td><td>330</td><td>2.92</td><td>271</td><td>1.72</td><td>195</td><td>96.0</td></t<>	14	Methyl (2-adamantyl)acetate	13	330	2.92	271	1.72	195	96.0
Methyl [2-(2-adamantyl)]propionate         14         335         2.36         249         1.46         180           Methyl [2-(1-adamantyl)]propionate         14         300         2.01         228         1.29         168           Dimethyl [1-(3-methyl)adamantyl]malonate         17         1369         12.70         753         6.56         386           Dimethyl [1-(3-ethyl)adamantyl]malonate         15         1866         17.73         1014         9.18         486           Dimethyl (2-adamantyl)malonate         16         955         8.58         560         4.63         319           Dimethyl (2-adamantyl,methyl)malonate         17         763         6.66         457         3.59         269           Dimethyl (2-adamantyl,methyl)malonate         18         73         6.84         416         3.18         253           Dimethyl (2-adamantyl,methyl)malonate         18         73         6.66         457         3.59         264           Dimethyl (2-adamantyl,methyl)malonate         18         73         6.31         441         3.18         253           Dimethyl (2-adamantyl,methyl)malonate         16         962         8.66         4.68         316           Dimethyl (2-adamantyl,methyl)malonate <td>15</td> <td>Methyl [4-(2-adamantyl)]butanoate</td> <td>15</td> <td>354</td> <td>2.55</td> <td>257</td> <td>1.58</td> <td>187</td> <td>0.87</td>	15	Methyl [4-(2-adamantyl)]butanoate	15	354	2.55	257	1.58	187	0.87
Methyl [2-(1-adamantyl)]propionate       14       300       2.01       228       1.29       168         Dimethyl [1-(3-methyl)]adamantyl]malonate       17       1369       12.70       753       6.56       386         Dimethyl [1-(3-cthyl-5,7-dimethyl)]adamantyl]malonate       19       12.38       11.43       690       5.93       355         Dimethyl [1-(3-cthyl-5,7-dimethyl)]adamantyl]malonate       15       1866       17.73       1014       9.18       486         Dimethyl (2-adamantyl)malonate       16       955       8.58       560       4.63       319         Dimethyl (2-adamantyl,chyl)malonate       18       784       416       3.18       253         Dimethyl (2-adamantyl,chyl)malonate       18       784       416       3.18       253         Dimethyl (2-adamantyl,chyl)malonate       16       96.6       457       3.59       269         Dimethyl (2-adamantyl,methyl)malonate       16       96.2       3.66       4.63       316         Dimethyl (2-adamantyl,methyl)malonate       16       96.2       3.66       4.68       316         Dimethyl (2-adamantyl,methyl)malonate       17       1.47       1.73       1.94         Methyl bicyclof(3.3.1]nonanoate       8 <t< td=""><td>91</td><td>Methyl [2-(2-adamantyl)]propionate</td><td>14</td><td>335</td><td>2.36</td><td>249</td><td>1.46</td><td>180</td><td>0.81</td></t<>	91	Methyl [2-(2-adamantyl)]propionate	14	335	2.36	249	1.46	180	0.81
Dimethyl [1-(3-methyl)adamantyl]malonate       16       1456       13.61       795       6.98       410         Dimethyl [1-(3-chyl-3,7-dimethyl)adamantyl]malonate       17       1369       12.70       753       6.56       386         Dimethyl [1-(3-cthyl-5,7-dimethyl)adamantyl]malonate       15       1866       17.73       1014       9.18       486         Dimethyl (2-adamantyl,methyl)malonate       16       955       8.58       560       4.63       319         Dimethyl (2-adamantyl,cthyl)malonate       17       763       6.66       457       3.59       269         Dimethyl (2-adamantyl,cthyl)malonate       18       681       5.84       416       3.18       253         Dimethyl (2-adamantyl,acthyl)malonate       16       962       8.66       457       3.59       264         Dimethyl (2-adamantyl)cthylmalonate       16       962       8.66       456       456       3.18       254         Dimethyl (2-adamantyl)cthylmalonate       16       962       8.66       456       3.66       4.68       316         Dimethyl (2-adamantyl)cthylmalonate       8       380       2.82       272       1.73       196         Methyl bicyclofaxylcarboxylate       8       36	11	Methyl [2-(1-adamantyl)]propionate	14	300	2.01	228	1.29	168	9.0
Dimethyl [1-(3,5-dimethyl)adamantyl]malonate       17       1369       12.70       753       6.56       386         Dimethyl [1-(3-ethyl-5,7-dimethyl)adamantyl]malonate       15       1866       17.73       1014       9.18       486         Dimethyl (2-adamantyl)malonate       16       955       8.58       560       463       319         Dimethyl (2-adamantyl,methyl)malonate       17       763       6.66       457       3.59       269         Dimethyl (2-adamantyl,propyl)malonate       18       681       5.84       416       3.18       253         Dimethyl (2-adamantyl,propyl)malonate       18       6.66       457       3.59       269         Dimethyl (2-adamantyl,methyl)malonate       16       962       8.66       457       3.18       254         Dimethyl (1-adamantyl)ethylmalonate       16       962       8.66       456       4.68       316         Dimethyl (2-damantyl)ethylmalonate       8       3.84       8.29       7.33       417         Methyl cyclofexylcarboxylate       8       3.86       4.68       1.65       1.73       1.74       199         Methyl bicyclo[3.3.1]nonanoate       7       377       2.78       1.73       1.74       199 </td <td>81</td> <td>Dimethyl [1-(3-methyl)adamantyl]malonate</td> <td>91</td> <td>1456</td> <td>13.61</td> <td>795</td> <td>86.9</td> <td>410</td> <td>3.12</td>	81	Dimethyl [1-(3-methyl)adamantyl]malonate	91	1456	13.61	795	86.9	410	3.12
Dimethyl [1-(3-ethyl-5,7-dimethyl)adamantyl]malonate       19       1238       11.43       690       5.93       355         Dimethyl (2-adamantyl)malonate       15       1866       17.73       1014       9.18       486         Dimethyl (2-adamantyl,methyl)malonate       17       763       6.66       457       3.59       269         Dimethyl (2-adamantyl,ethyl)malonate       18       681       5.84       416       3.18       253         Dimethyl (2-adamantyl,propyl)malonate       18       730       6.31       441       3.43       264         Dimethyl (2-adamantyl,methyl)malonate       16       962       8.66       366       4.68       316         Dimethyl (2-dadmantyl)ethylmalonate       17       1478       13.84       829       7.33       417         Methyl cyclolexylcarboxylate       8       366       264       1.73       196         Methyl bicyclof3.3. Ilonanoate       5       -       -       2318       22.28       1095         Methyl hexanoate       7       377       2.78       174       199         Methyl heptanoate       8       352       253       163       190	19	Dimethyl [1-(3,5-dimethyl)adamantyl]malonate	17	1369	12.70	753	6.56	386	2.87
Dimethyl (2-adamantyl)malonate         15         1866         17.73         1014         9.18         486           Dimethyl (2-adamantyl,methyl)malonate         16         955         8.58         560         4.63         319           Dimethyl (2-adamantyl,ethyl)malonate         17         763         6.66         457         3.59         269           Dimethyl (2-adamantyl,propyl)malonate         18         681         5.84         416         3.18         253           Dimethyl (2-adamantyl,propyl)malonate         16         962         8.66         366         4.68         316           Dimethyl (1-adamantyl)ethylmalonate         16         962         8.66         366         4.68         316           Methyl cyclofexylcarboxylate         8         386         2.82         272         1.73         196           Methyl bicyclof3. Jlonanoate         5         -         -         2.318         22.28         1095           Methyl hexanoate         7         377         2.78         1.74         199           Methyl heptanoate         8         352         2.53         262         1.63         190	8	Dimethyl [1-(3-ethyl-5,7-dimethyl)adamantyl]malonate	19	1238	11.43	069	5.93	355	2.56
Dimethyl (2-adamantyl,methyl)malonate         16         955         8.58         560         4.63         319           Dimethyl (2-adamantyl,ethyl)malonate         17         763         6.66         457         3.59         269           Dimethyl (2-adamantyl,propyl)malonate         18         6.81         5.84         416         3.18         253           Dimethyl (2-adamantyl,2-propenyl)malonate         16         962         8.66         366         4.68         316           Dimethyl (1-adamantyl,methyl)malonate         17         1478         13.84         829         7.33         417           Methyl cycloficxylcarboxylate         8         380         2.82         272         177         196           Methyl bicyclofi.3.1 Ilonanoate         5         -         -         2.318         1.55         187           Dimethyl malonate         7         377         2.78         2.73         1.74         199           Methyl hexanoate         8         352         2.53         262         1.63         190           Methyl heptanoate         8         352         2.53         2.62         1.63         190	21	Dimethyl (2-adamantyl)malonate	15	1866	17.73	1014	81.6	486	3.88
Dimethyl (2-adamantyl,ethyl)malonate       17       763       6.66       457       3.59       269         Dimethyl (2-adamantyl,propyl)malonate       18       681       5.84       416       3.18       253         Dimethyl (2-adamantyl,propyl)malonate       18       730       6.31       441       3.43       264         Dimethyl (1-adamantyl,methyl)malonate       16       962       8.66       366       4.68       316         Dimethyl [2-(2-adamantyl)ethyl]malonate       17       1478       13.84       829       7.33       417         Methyl cyclohexylcarboxylate       8       380       2.82       272       1.73       196         Methyl bicyclo[3.3.1]nonanoate       5       -       -       2318       22.28       1095         Methyl hexanoate       7       377       2.78       273       1.74       199         Methyl heptanoate       8       352       2.53       262       1.63       190	77	Dimethyl (2-adamantyl,methyl)malonate	91	955	8.58	<b>9</b> 9	4.63	319	2.20
Dimethyl (2-adamantyl, propyl)malonate       18       681       5.84       416       3.18       253         Dimethyl (2-adamantyl, 2-propenyl)malonate       18       730       6.31       441       3.43       264         Dimethyl (1-adamantyl, methyl)malonate       16       962       8.66       366       4.68       316         Dimethyl [2-(2-adamantyl)ethyl]malonate       17       1478       13.84       829       7.33       417         Methyl cyclohexylcarboxylate       8       380       2.82       272       1.73       196         Methyl bicyclo[3.3.1]nonanoate       5       -       -       2318       22.28       1095         Methyl hexanoate       7       377       2.78       273       1.74       199         Methyl heptanoate       8       352       2.53       262       1.63       190	23		17	763	99.9	457	3.59	569	1.70
Dimethyl (2-adamantyl,2-propenyl)malonate       18       730       6.31       441       3.43       264         Dimethyl (1-adamantyl,methyl)malonate       16       962       8.66       366       4.68       316         Dimethyl [2-(2-adamantyl)ethyl)malonate       17       1478       13.84       829       7.33       417         Methyl cyclohexylcarboxylate       8       380       2.82       272       1.73       196         Methyl bicyclo[3.3.1]nonanoate       11       345       2.46       254       1.55       187         Dimethyl malonate       5       -       -       2318       22.28       1095         Methyl hexanoate       8       352       2.53       262       1.63       190	7	Dimethyl (2-adamantyl, propyl) malonate	18	681	5.84	416	3.18	253	<u></u>
Dimethyl (1-adamantyl,methyl)malonate       16       962       8.66       366       4.68       316         Dimethyl [2-(2-adamantyl)ethyl]malonate       17       1478       13.84       829       7.33       417         Methyl cyclohexylcarboxylate       8       380       2.82       272       1.73       196         Methyl bicyclo[3.3.1]nonanoate       11       345       2.46       254       1.55       187         Dimethyl malonate       5       -       -       2318       22.28       1095         Methyl hexanoate       8       352       2.53       262       1.63       190	25	Dimethyl (2-adamantyl, 2-propenyl) malonate	81	730	6.31	<u>4</u>	3.43	26 49	1.65
Dimethyl [2-(2-adamantyl)ethyl]malonate       17       1478       13.84       829       7.33       417         Methyl cyclohexylcarboxylate       8       380       2.82       272       1.73       196         Methyl bicyclo[3.3.1]nonanoate       11       345       2.46       254       1.55       187         Dimethyl malonate       5       -       -       2318       22.28       1095         Methyl hexanoate       8       352       2.53       262       1.63       190	76	Dimethyl (1-adamantyl,methyl)malonate	16	362	99.8	399	4.68	316	2.17
Methyl cyclohexylcarboxylate         8         380         2.82         272         1.73         196           Methyl bicyclo[3.3.1]nonanoate         11         345         2.46         254         1.55         187           Dimethyl malonate         5         -         -         2318         22.28         1095           Methyl hexanoate         7         377         2.78         273         1.74         199           Methyl heptanoate         8         352         2.53         262         1.63         190	27	Dimethyl [2-(2-adamantyl)ethyl]malonate	17	1478	13.84	828	7.33	417	3.19
Methyl bicyclo[3.3.1]nonanoate       11       345       2.46       254       1.55       187         Dimethyl malonate       5       -       -       2318       22.28       1095         Methyl hexanoate       7       377       2.78       273       1.74       199         Methyl heptanoate       8       352       2.53       262       1.63       190	78	Methyl cyclohexylcarboxylate	<b>∞</b>	380	2.82	272	1.73	196	96.0
Dimethyl malonate         5         -         -         2318         22.28         1095           Methyl hexanoate         7         377         2.78         273         1.74         199           Methyl heptanoate         8         352         2.53         262         1.63         190	53	Methyl bicyclo[3.3.1]nonanoate	Ξ	345	2.46	254	1.55	187	0.88
Methyl hexanoate         7         377         2.73         1.74         199           Methyl heptanoate         8         352         2.53         262         1.63         190	30	Dimethyl malonate	\$	I	l	2318	22.28	1095	66.6
e 8 352 2.53 262 1.63 190	31	Methyl hexanoate	7	377	2.78	273	1.74	<u>86</u>	1.00
	32	Methyl heptanoate	œ	352	2.53	262	1.63	<u>8</u>	0.91

FABLE III

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

No.	Compound	C	a = 99	99.9, b = 0.1	a = 99	99.8, b = 0.2	a = 99	99.7, b = 0.3	a = 9	99.5, b = 0.5
			I'R	K'	l'R	k'	l'R	K'	íR	**
_	Methyl diamantane-1-carboxylate	16	271	1.72	176	0.77	152	0.53	126	0.27
7	Methyl diamantane-3-carboxylate	16	566	1.67	173	0.73	151	0.52	126	0.27
æ	Methyl diamantane-4-carboxylate	91	317	2.18	961	0.97	163	20.0	134	0.35
4	Dimethyl diamantane-1,6-dicarboxylate	18	1	1	762	6.65	337	2.38	506	1.07
5	Dimethyl diamantane-1,7-dicarboxylate	18	1	1	772	6.75	200	4.02	230	1.31
9	Dimethyl diamantane-4,9-dicarboxylate	18	1	I	1061	99.6	615	5.17	302	2.03
7	Dimethyl diamantane-1,4-dicarboxylate	18	I	I	1127	10.32	<b>3</b>	5.48	311	2.13
∞	Dimethyl diamantane-1,5-dicarboxylate	18	ı	ı	784	6.87	497	3.99	226	1.27
6	Methyl adamantane-1-carboxylate	12	338	2.40	214	1.14	169	69.0	139	0.39
10	Methyl adamantane-2-carboxylate	12	280	1.81	190	0.90	154	0.55	131	0.32
=	Dimethyl adamantane-1,3-dicarboxylate	7	I	1	1068	9.72	<b>₹</b>	5.43	317	2.18
12	Methyl [1-(3-methyl)adamantyl]formiate	13	313	2.14	700	1.01	<u>2</u>	9.65	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	89.0	135	0.35
91	Methyl [2-(2-adamantyl)]propionate	14	317	2.18	194	0.95	168	69.0	134	0.35
17	Methyl [2-(1-adamantyl)]propionate	14	291	1.92	185	98.0	158	0.59	131	0.32
<b>8</b>	Dimethyl [1-(3-methyl)adamantyl]malonate	91	1	1	491	3.93	319	2.20	504	1.05
19	Dimethyl [1-(3,5-dimethyl)adamantyl]malonate	17	1	I	464	3.66	315	2.17	198	0.99
70	Dimethyl [1-(3-ethyl-5,7-dimethyl)adamantyl]malonate	19	ı	I	433	3.34	301	2.02	18	0.91
21	Dimethyl (2-adamantyl)malonate	15	ı	1	734	6.37	521	4.23	240	1.41
22	Dimethyl (2-adamantyl,methyl)malonate	91	ı	I	372	2.74	265	1.66	179	08.0
23	Dimethyl (2-adamantyl, ethyl) malonate	17	859	5.61	313	2.14	237	1.38	162	0.63
<b>74</b>	Dimethyl (2-adamantyl,propyl)malonate	18	575	4.77	287	1.89	211	1.12	15	0.55
25	Dimethyl (2-adamantyl, 2-propenyl) malonate	18	611	5.13	290	1.92	212	1.13	158	0.59
76	Dimethyl (1-adamantyl, methyl) malonate	91	1	1	383	2.84	768	1.69	178	0.79
27	Dimethyl [2-(2-adamantyl)ethyl]malonate	17	ł	I	515	4.17	325	2.26	209	1.10
78	Methyl cyclohexylcarboxylate	∞	<del>2</del> 4	2.45	218	1.19	182	0.83	145	0.46
53	Methyl bicyclo[3.3.1]nonanoate	=	320	2.22	<b>504</b>	1.05	174	0.75	139	0.39
30	Dimethyl malonate	S	1	I	2113	20.22	1292	11.97	089	5.83
31	Methyl hexanoate	7	I	1	216	1.17	170	0.71	<del>4</del>	0.45
32	Methyl heptanoate	∞	297	1.98	506	1.07	167	99.0	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 = 99.9	99.95, b = 0.05	= v	99.9, b = 0.1	66 = p	99.8, b = 0.2
				l <sub>R</sub>	k'	ľR	k'	t <sub>R</sub>	k'
-	Methyl diamantane-1-carboxylate		16	212	1.13	179	080	151	0.51
7	Methyl diamantane-3-carboxylate		16	212	1.13	179	0.80	150	0.50
33	Methyl diamantane-4-carboxylate		16	245	1.46	199	1.00	191	0.62
4	Dimethyl diamantane-1,6-dicarboxylate		18	906	8.03	554	4.57	334	2.35
5	Dimethyl diamantane-1,7-dicarboxylate		18	1015	9.19	624	5.27	369	2.70
9	Dimethyl diamantane-4,9-dicarboxylate		18	1750	16.57	934	8.37	209	4.11
7			18	1948	18.55	1014	9.18	533	4.35
œ	Dimethyl diamantane-1,5-dicarboxylate		18	1128	10.33	979	5.28	368	2.69
6	Methyl adamantane-1-carboxylate		12	262	1.63	706	1.07	169	69:0
10	Methyl adamantane-2-carboxylate		12	230	1.31	189	0.00	155	0.56
11	Dimethyl adamantane-1,3-dicarboxylate		4	1684	15.90	911	8.15	510	4.12
12	Methyl [1-(3-methyl)adamantyl]formiate		13	243	1.42	197	86.0	162	0.62
13	Methyl [1-(2-methyl)adamantyl]formiate		13	240	1.41	194	0.95	191	0.61
14	Methyl (2-adamantyl)acetate		13	263	<del>2</del> .1	506	1.10	167	89.0
15	Methyl [4-(2-adamantyl)]butanoate		15	246	1.47	195	96.0	160	0.61
16	Methyl [2-(2-adamantyl)]propionate		4	238	1.39	191	0.92	157	0.58
17	Methyl [2-(1-adamantyl)]propionate		7	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	44	3.46	289	1.90
70	Dimethyl [1-(3-ethyl-5,7-dimethyl)adamantyl]malonate		61	859	5.61	412	4.04	268	1.70
21	Dimethyl (2-adamantyl)malonate		15	971	8.75	260	4.62	326	2.58
77	Dimethyl (2-adamantyl, methyl) malonate		91	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
74	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	589	1.90	<b>50</b>	1.05
92	Dimethyl (1-adamantyl,methyl)malonate		16	543	4.45	352	2.53	243	4.1
27	Dimethyl [2-(2-adamantyl)ethyl]malonate		17	691	6.72	476	3.78	305	2.07
8	Methyl cyclohexylcarboxylate		∞	273	1.74	217	1.17	170	0.71
53	Methyl bicyclo[3.3.1]nonanoate		=	251	1.52	204	1.05	162	0.63
30	Dimethyl malonate		5	1	1	1328	12.34	<b>7</b> 6	29.9
31	Methyl hexanoate		7	569	1.70	218	1.19	174	0.75
32	Methyl heptanoate		œ	257	1.58	207	1.08	168	69:0

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
0	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
١7	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<sub>3</sub> groups;
- (2) the position of the -COOCH<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> group

In the group of monotopic diamantoic derivatives, the position of the functional group has a dominant effect on chromatographic behaviour<sup>1,3</sup>. As in the case of adamantanols<sup>1</sup>, diamantanols<sup>2</sup> and halogen derivatives<sup>3</sup> of adamantane and diamantane, compounds with a -COOCH<sub>3</sub> 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:

$$\mathbb{R} = \mathbb{R} \leq \mathbb{R} \leq \mathbb{R} \leq \mathbb{R} \leq \mathbb{R} \leq \mathbb{R}$$

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<sup>1</sup> and ketones<sup>2</sup>, the retention times of compounds having the -COOCH<sub>3</sub> 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.

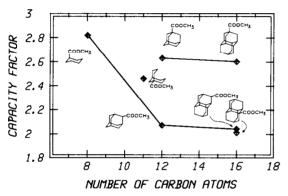


Fig. 2. Plot of capacity factor k' vs. the number of carbon atoms. Mobile phase: n-heptane-diethyl ether (97:3, w/w).

# 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<sub>3</sub> 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.

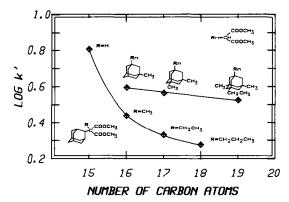


Fig. 3. Plot of  $\log k'$  vs. the number of carbon atoms. Mobile phase: n-heptane-2-propanol (99.8:0.2, w/w).

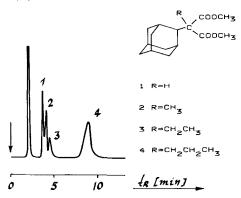


Fig. 4. Separation of dimethyl [1-(alkyl)adamantyl]malonates. Column ( $250 \times 4$  mm I.D.) packed with 7.5- $\mu$ m silica gel; mobile phase, n-heptane-2-propanol (99.7:0.3, w/w). Flow-rate 30 ml/h.

# 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<sup>1</sup> and ketones<sup>2</sup>, 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<sup>5</sup>:

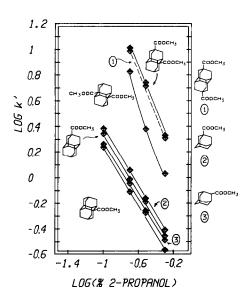


Fig. 5. Variation of the logarithm of the capacity factor with the concentration of 2-propanol in the mobile phase n-heptane-2-propanol.

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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