Journal of Chromatography, 370 (1986) 49–61
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 976

FUSED-SILICA CAPILLARY GAS CHROMATOGRAPHY–MASS SPECTROMETRY OF SOME DICARBOXYLIC ACIDS PRESENT IN CONDENSATION-TYPE POLYMERS

II*. BIS(TRIMETHYLSILYL) ESTERS

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(Received July 10th, 1986)

SUMMARY

Isothermal retention indices of some dicarboxylic acid bis(trimethylsilyl) esters at four temperatures of a non-polar capillary column with a cross-linked polymethylsiloxane stationary phase are presented. The separation of particular esters is discussed and the chromatographic behaviour of bis(trimethylsilyl) esters is compared with that of dimethyl esters. The characteristic features of electron impact and methane and isobutane chemical ionization mass spectra and their usefulness for the identification of the trimethylsilyl derivatives are discussed.

INTRODUCTION

In contrast with the use of methyl esters as convenient derivatives for the gas chromatography (GC) of carboxylic acids in condensation-type polymers after degradation of the polymer chain and derivatization of the liberated acids[1], trimethylsilyl (TMS) esters have been used in only a limited number of applications[2–5]. On the other hand, the silylation of aliphatic carboxylic acids is widely used in biochemical analyses[6], and TMS derivatives being chromatographed on non-polar capillary columns[7–9]. The isothermal[7] and methylene unit (MU)[8,9] retention indices for saturated and unsaturated aliphatic bis(TMS) esters have been published.

The reason for the wide use of TMS derivatives ensues not only from the versatility of the silylation reaction but also from the convenient character of the mass spectra of TMS esters. The presence of the ion $(M-15)^+$ in the electron impact

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* For Part I, see ref. 13.

(EI) mass spectrum of TMS derivatives enables the relative molecular mass of a compound to be determined without employing soft ionization methods[10–12].

This paper deals with the chromatographic behaviour of 23 dicarboxylic acid bis(TMS) esters in terms of retention indices with respect to the chemical structure of the particular compound. The dominant and characteristic ions in the EI and chemical ionization (CI) mass spectra are discussed with respect to their use for reliable identification.

EXPERIMENTAL

The TMS esters were prepared by silylation of individual acids with a 20-fold molar excess of BSTFA (Pierce, Rockford, IL, U.S.A.) in screw-capped vials with PTFE-lined silicone-rubber septa. The vials were heated in an aluminium block at 60°C for 30 min. The silylation of aromatic acids required a longer reaction time.

Gas chromatography

The GC experiments were performed on a Model 3700 gas chromatograph with a flame ionization detector (Varian Aerograph, Palo Alto, CA, U.S.A.) fitted with a 25 m × 0.20 mm I.D. Ultra 1 fused-silica capillary column (Hewlett-Packard, Palo Alto, CA, U.S.A.), with a film thickness of the polymethylsiloxane cross-linked stationary phase of 0.32 μm. The splitting ratio was 1:140 and the linear velocity of the carrier gas (nitrogen) was *ca.* 17 cm/s. To ensure that the column capacity was not exceeded, not more than 10 ng of each component were introduced into the column. The retention times were measured with an Autolab System IV (Spectra-Physics, Mountain View, CA, U.S.A.) with an accuracy of 0.1 s. The Kováts retention indices were calculated from the data obtained from the GC analyses where all the necessary components, *i.e.*, methane, *n*-alkanes and the studied TMS esters, were injected simultaneously. In this way a high reproducibility, even after operation of the capillary column for 1 year, was achieved. The standard deviations of the retention indices given in Table I are *ca.* 0.3 index unit.

Gas chromatography–mass spectrometry

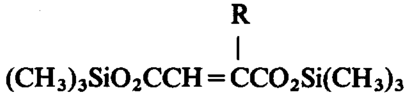
Mass spectrometric data were obtained on a Varian-MAT 44S GC–MS system coupled to a Model 3700 gas chromatograph via an open split interface. The introduction of compounds into the mass spectrometer was performed through the same polarity Ultra 1 column (25 m × 0.32 mm I.D.), film thickness 0.52 μm, to verify the elution order of coeluting solutes. The quadrupole mass spectrometer was operated at an ion source pressure (helium carrier gas flow) of 10^{-3} Pa with an ionization energy of 70 eV (EI) and 210 eV (CI) and an ion source temperature of 160–170°C. The pressure of the CI reaction gas, methane or isobutane, in the CI ion box was 25 Pa. All EI and CI mass spectra were taken at the maximum of the overloaded chromatographic peak to ensure an approximately constant pressure of the measured compound vapour in the ion source during scanning.

RESULTS AND DISCUSSION

The studied TMS esters were divided into four classes according to the chemical structure of the parent acid: aliphatic saturated (S), aliphatic unsaturated (U), aromatic (A) and alicyclic dicarboxylic acid bis(trimethylsilyl) esters:

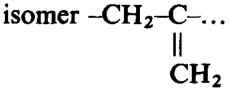
$(CH_3)_3SiO_2C(CH_2)_nCO_2Si(CH_3)_3$

(S2) $n = 0$
(S3) $n = 1$
(S4) $n = 2$
⋮ ⋮
(S12) $n = 10$

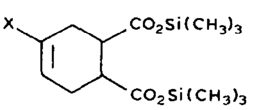


$$(CH_3)_3SiO_2CCH{=}\overset{\displaystyle R}{\overset{|}{C}}CO_2Si(CH_3)_3$$

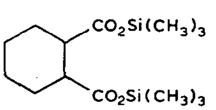
(U4Z) R=H (*Z*)
(U4E) R=H (*E*)
(U5Z) R=CH_3 (*Z*)
(U5E) R=CH_3 (*E*)
(U5I) isomer



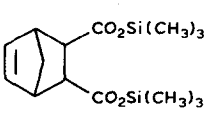
$$-CH_2-\underset{\displaystyle CH_2}{\underset{\|}{C}}-\ldots$$



(THF) X=H
(MTHF) X=CH_3
(CTHF) X=Cl



(HHF)



(NAD)

Compounds A12, A13 and A14 are TMS phthalate, isophthalate and terephthalate, respectively.

Gas chromatography

The Kováts retention indices of the TMS esters, the capacity factors and the retention index dependence on temperature, dI/dT, are given in Table I.

As is apparent from the methylene retention index increments (Table II), the TMS esters of linear saturated alkanedioic acids do not form such an ideal homologous series as the *n*-alkanes and the values of methylene increments alternate strongly round the theoretical value 100 for the lowest homologues.

The homologous series of aliphatic saturated TMS esters can be efficiently separated by temperature-programmed analysis, 120°C for 2 min followed by an increase of 10°C/min up to 260°C, which ensures the separation of compounds with retention indices in the range 1000–2300 (Fig. 1).

The retention indices of aliphatic saturated TMS diesters are temperature dependent with negative values of dI/dT (*ca.* −0.22 for the studied compounds), which contrasts with the temperature-independent retention indices of long-chain aliphatic dimethylesters[13].

The introduction of a TMS group into the molecule of aliphatic unsaturated acids affected the chromatographic behaviour of these derivatives in comparison with the behaviour of dimethyl esters. TMS maleinate (U4Z) elutes before and TMS fumarate (U4E) elutes after the saturated analogue TMS succinate (S4). The values of ΔI for planar isomers, U4Z, U4E and U5Z, U5E, are *ca.* 50 index units (Table II)

TABLE I

KOVÁTS RETENTION INDICES, CAPACITY FACTORS AND d*I*/d*T* VALUES FOR DICARBOXYLIC ACID BIS(TRIMETHYLSILYL) ESTERS ON A NON-POLAR POLYMETHYLSILOXANE STATIONARY PHASE AT COLUMN TEMPERATURES OF 125, 150, 175 AND 200°C

TMS ester	*125°C*			*150°C*		
	I	*k'*	*dI/dT*	*I*	*k'*	*dI/dT*
S2	1105.0	1.64	−0.37	1095.4	0.73	−0.32
S3	1189.3	2.60	−0.24	1183.4	1.11	−0.22
S4	1302.1	4.78	−0.24	1296.3	1.89	−0.22
S5	1394.2	7.83	−0.26	1387.6	2.90	−0.24
S6	1498.6	13.59	−0.25	1492.2	4.70	−0.24
S7	1599.2	23.51	−0.27	1592.6	7.50	−0.24
S8	1695.1	38.56	−0.23	1689.5	11.71	−0.22
S9	–	–	–	–	–	–
S10	–	–	–	–	–	–
S11	–	–	–	–	–	–
U4Z	1288.2	4.38	−0.16	1284.6	1.80	−0.12
U4E	1341.8	5.86	−0.32	1333.4	2.26	−0.32
U5Z	1338.0	5.74	−0.15	1334.2	2.27	−0.13
U5E	1394.9	7.80	−0.33	1386.5	2.90	−0.33
U5I	1331.0	5.55	−0.19	1326.3	2.19	−0.19
THF	–	–	–	1594.7	7.63	+0.14
MTHF	–	–	–	1646.2	9.63	+0.07
CTHF	–	–	–	1746.5	15.38	+0.16
HHF	–	–	–	1602.9	7.89	+0.14
NAD	–	–	–	1655.4	10.09	+0.24
A12	–	–	–	1675.2	11.06	+0.10
A13	–	–	–	1744..8	15.30	–
A14	–	–	–	1784.0	18.19	+0.12

and the values ΔI for chain branching are similar for the *cis*-isomer pair U4Z, U5Z and the *trans*-isomer pair U4E, U5E.

Within the range 140–200°C the elution order of TMS fumarate (U4E), citraconate (U5Z) and itaconate (U5I) varies and for their complete separation a column with a more polar stationary phase should be used. The retention indices of *trans*-isomers show temperature dependence whereas with the *cis*-isomers this dependence is less apparent.

The elution order of aromatic TMS esters is TMS phthalate (A12), isophthalate (A13) and terephthalate (A14), with a high ΔI value between the particular isomers, which enables them to be separated on a relatively low-efficient packed column.

The temperature dependence of the retention indices of aromatic acid TMS diesters is relatively small in comparison with those of dimethyl esters, which have been shown to be strongly temperature dependent[13]. Owing to the different signs of d*I*/d*T* with aliphatic saturated (S) and aromatic (A) TMS esters, the coelution of TMS phthalate (A12) with TMS suberate (S8) at 193°C and TMS terephthalate with TMS azelate (S9) at 167°C occurs.The separation of alicyclic TMS esters on a non-

175°C			*200°C*		
I	*k'*	*dI/dT*	*I*	*k'*	*dI/dT*
1088.5	0.38	−0.30	1080.7	0.22	−0.26
1178.2	0.55	−0.22	1173.0	0.30	−0.20
1290.8	0.88	−0.22	1285.5	0.46	−0.22
1381.3	1.28	−0.23	1375.9	0.64	−0.22
1486.7	1.96	−0.22	1481.2	0.92	−0.21
1587.1	2.95	−0.22	1581.8	1.32	−0.20
1684.0	4.37	−0.20	1679.0	1.87	−0.20
1785.0	6.56	−0.20	1780.3	2.68	−0.20
1884.1	9.76	−0.21	1879.0	3.79	−0.20
1982.9	14.50	−0.20	1978.0	5.37	−0.19
1281.7	0.85	−0.10	1279.4	0.45	−0.09
1325.3	1.01	−0.32	1317.7	0.51	−0.32
1330.6	1.04	−0.12	1327.6	0.53	−0.11
1378.2	1.25	−0.33	1369.9	0.62	−0.33
1321.7	1.00	−0.19	1317.6	0.51	−0.19
1598.8	3.01	+0.14	1602.1	1.41	+0.14
1648.5	3.79	+0.10	1651.4	1.69	+0.12
1750.8	5.70	+0.22	1757.0	2.47	+0.26
1606.9	3.20	+0.17	1611.7	1.47	+0.21
1661.9	3.98	+0.26	1669.0	1.81	+0.28
1678.0	4.25	+0.12	1681.6	1.89	+0.15
1745.4	5.58	–	1745.1	2.37	–
1787.8	6.66	+0.13	1790.8	2.78	+0.13

polar capillary column is more favourable than the separation of the corresponding dimethyl esters because of the higher ΔI values for particular TMS esters. Moreover, the separation is performed with higher capacity factors and, therefore, at higher number of effective plates (Fig. 2).

As is obvious from the presented and published data[13], the chromatographic behaviour of the bis(TMS) esters and dimethylesters of dicarboxylic acids on a non-polar capillary column differs significantly. The introduction of the TMS group strongly affects the molecular structure of the compounds, which can be observed indirectly as a decrease in dI/dT with all the types of TMS esters studied relatively to the corresponding dimethyl esters. Further, the elution order of some solutes changes, *e.g.*, the elution of aromatic acid TMS esters on a non-polar capillary column follows the elution of higher *n*-alkyl esters[14]. The values of ΔI for the isomeric pairs fumarate–maleate and isophthalate–terephthalate increase and the separation of critical pair tetrahydrophthalate (THF)–hexahydrophthalate (HHF) is also possible (Fig. 2).

The ΔI values for two solutes for the bis(TMS) ester and dimethyl ester of the

TABLE II

RETENTION INDEX INCREMENTS FOR THE CH_2 GROUP IN THE HOMOLOGOUS SERIES OF ALIPHATIC SATURATED BIS(TMS) ESTERS, FOR CHAIN AND CYCLE BRANCHING, FOR PAIRS OF ISOMERS OF BIS(TMS) ESTERS OF DICARBOXYLIC ACIDS ON A NON-POLAR POLYMETHYLSILOXANE FUSED-SILICA CAPILLARY COLUMN AT 125, 150, 175 AND 200°C

TMS esters	*125°C*	*150°C*	*175°C*	*200°C*
S3–S2	84.3	88.0	89.7	92.3
S4–S3	112.8	112.9	112.6	112.5
S5–S4	92.1	91.3	90.5	90.4
S6–S5	104.4	104.6	105.4	105.3
S7–S6	100.6	100.4	100.4	100.6
S8–S7	95.9	96.9	96.9	97.4
S9–S8	–	–	101.0	101.1
S10–S9	–	–	99.1	98.7
S11–S10	–	–	98.8	99.0
U4E–U4Z	53.6	48.8	43.6	38.3
U5E–U5Z	56.9	52.3	47.6	42.3
U5Z–U4Z	49.8	49.6	48.9	48.2
U5E–U4E	53.1	53.1	52.9	52.2
THF–HHF	–	8.2	8.1	9.6
THF–MTHF	–	51.5	49.7	49.3
A13–A12	–	69.6	67.4	63.5
A14–A12	–	108.8	109.8	109.2
A14–A13	–	39.2	42.4	45.7

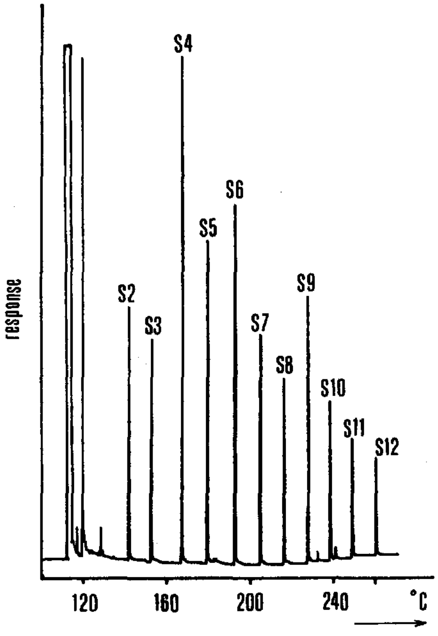


Fig. 1. Chromatogram of the separation of linear saturated dicarboxylic acid bis(trimethylsilyl) esters by temperature-programming (120°C for 2 min, increased at 10°C/min to 260°C) on an Ultra 1 non-polar fused-silica capillary column (25 m × 0.20 mm I.D.; 0.32 μm film thickness). S2 = bis(TMS) oxalate, S3 = bis(TMS) malonate, S4 = bis(TMS) succinate, ..., S12 = bis(TMS) dodecanedioate.

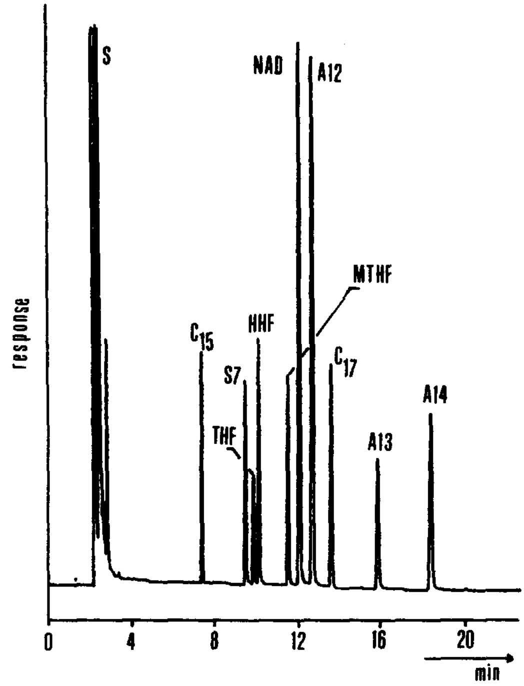


Fig. 2. Isothermal separation of bis(trimethylsilyl) esters of aromatic dicarboxylic acids (A12 = phthalate; A13 = isophthalate; A14 = terephthalate), aliphatic TMS ester (S7 = pimelate) and alicyclic bis(TMS) esters (THF = tetrahydrophthalate, HHF = hexahydrophthalate, MTHF = 4-methyltetrahydrophthalate, NAD = nadicate) at 183°C on an Ultra 1 non-polar fused-silica capillary column (25 m × 0.20 mm I.D.; 0.32 μm film thickness) in the region of C_{16}–C_{18} alkanes elution. S = BSTFA and its reaction products.

same acid on the same column at the same temperature (Table III) show that the increase in retention between these two derivatives, which ranges from 103.3 to 174.5 index units per ester group, is influenced by the type and the structure of the carboxylic acid. This retention index difference for two solutes can be used as a second identification parameter when two derivatization procedures, methylation and silylation, are used in the GC analysis of carboxylic acids in condensates.

Mass spectrometry

In contrast with dimethyl esters, the EI mass spectra of TMS esters show a very limited number of dominant ions. The main fragments at *m/z* 73, 75 and 147 indicate the presence of the TMS group in the molecule of the studied compound but do not state much about the character of the underivatized parent molecule. On the other hand, the EI mass spectra of TMS esters consist of a large number of low-intensity ions and it is possible to use them in the discussion of the identity of the derivatives.

In the upper of the part EI mass spectra of aliphatic saturated (S) TMS esters (Table IV), the characteristic fragment of TMS derivatives $(M-15)^+$ of medium intensity is present, enabling the relative molecular mass of the ester to be determined.

TABLE III

RETENTION INDEX INCREMENTS FOR TWO SOLUTES, DICARBOXYLIC ACID BIS(TRIMETHYLSILYL) ESTERS AND DIMETHYL ESTERS ON A NON-POLAR POLYMETHYLSILOXANE FUSED-SILICA CAPILLARY COLUMN AT 125, 150, 175 AND 200°C

Ester	*125°C*	*150°C*	*175°C*	*200°C*
S3	305.3	301.9	–	–
S4	306.9	302.6	–	–
S5	294.5	288.8	–	–
S6	293.2	288.4	284.9	–
S7	291.2	285.5	280.4	–
S8	284.8	279.9	274.7	269.7
S9	–	–	273.9	268.7
S10	–	–	271.2	265.5
S11	–	–	269.3	264.0
U4Z	308.9	306.3	–	–
U4E	349.0	340.5	–	–
U5Z	281.6	278.8	–	–
U5E	310.3	301.8	–	–
U5I	272.0	269.5	–	–
THF	233.0	229.5	226.1	221.1
MTHF	–	216.9	212.8	209.2
CTHF	–	216.4	211.2	206.6
HHF	–	236.6	232.3	227.7
NAD	236.8	232.7	228.1	224.1
A12	263.3	257.3	251.2	244.4
A13	–	264.5	256.9	246.3
A14	–	313.9	307.3	298.7

TABLE IV

DOMINANT AND CHARACTERISTIC IONS IN THE EI MASS SPECTRA OF DICARBOXYLIC ACID BIS(TRIMETHYLSILYL) ESTERS FOR m/z $\geqslant$ 50 WITH THEIR RELATIVE INTENSITIES AT AN ION SOURCE TEMPERATURE OF 170°C, MOLECULAR FORMULA AND RELATIVE MOLECULAR MASS OF THE ESTER

Ester	*Ions (m/z)*
S3, M = 248, $C_9H_{20}O_4Si_2$	59(6), 72(8), 73(84), 74(9), 75(27), 117(2), 147(100), 148(16), 149(8), 233(10)
S4, M = 262, $C_{10}H_{22}O_4Si_2$	55(27), 56(21), 57(5), 59(6), 61(6), 72(8), 73(100), 74(14), 75(46), 77(6), 116(3), 117(2), 129(5), 147(93), 148(14), 149(8), 172(3), 173(2), 247(4)
S5, M = 276, $C_{11}H_{24}O_4Si_2$	55(77), 59(5), 61(7), 72(12), 73(100), 74(12), 75(51), 76(4), 97(15), 116(11), 117(6), 129(11), 147(81), 148(14), 149(9), 158(18), 159(5), 204(6), 233(5), 261(23)
S6, M = 290, $C_{12}H_{26}O_4Si_2$	55(57), 56(7), 59(5), 61(8), 67(5), 69(6), 72(5), 73(100), 74(11), 75(82), 76(5), 77(8), 83(19), 111(54), 117(10), 129(7), 141(20), 147(24), 149(4), 159(8), 172(11), 217(3), 275(11)
S7, M = 304, $C_{13}H_{28}O_4Si_2$	55(52), 56(4), 59(5), 61(9), 69(35), 72(8), 73(100), 74(14), 75(89), 76(6), 77(5), 79(8), 81(10), 83(7), 97(13), 116(6), 117(11), 125(23), 129(9), 147(17), 149(5), 155(26), 173(12), 204(3), 217(4), 289(11)

TABLE IV (*continued*)

Ester	*Ions (m/z)*
S8, M = 318, $C_{14}H_{30}O_4Si_2$	55(62), 56(6), 59(5), 61(11), 67(8), 69(15), 72(7), 73(100), 74(14), 75(96), 76(7), 77(8), 79(4), 83(15), 93(9), 95(10), 97(9), 111(4), 117(13), 129(13), 138(7), 139(10), 147(10), 149(10), 169(13), 187(14), 204(5), 217(5), 303(16)
S9, M = 332, $C_{15}H_{32}O_4Si_2$	55(61), 56(5), 59(5), 61(9), 67(12), 69(8), 72(8), 73(100), 74(13), 75(91), 76(6), 77(5), 79(7), 81(8), 83(11), 93(5), 95(8), 97(8), 107(6), 111(6), 117(16), 129(15), 147(10), 149(13), 152(11), 201(15), 204(7), 217(5), 317(17)
S10, M = 346, $C_{16}H_{34}O_4Si_2$	55(49), 56(6), 57(6), 59(4), 61(8), 67(7), 69(19), 72(7), 73(100), 74(13), 75(91), 76(6), 77(5), 79(7), 81(9), 83(6), 93(7), 95(5), 97(10), 107(5), 116(5), 117(17), 125(5), 129(17), 138(4), 147(9), 149(11), 204(8), 215(14), 331(20)
S11, M = 360, $C_{17}H_{36}O_4Si_2$	55(44), 56(4), 57(8), 59(5), 61(7), 67(10), 69(24), 72(6), 73(100), 74(12), 75(83), 76(7), 77(7), 79(6), 81(8), 83(10), 93(7), 95(6), 97(8), 98(5), 107(3), 111(3), 116(5), 117(18), 129(15), 139(5), 147(8), 149(10), 152(4), 204(12), 217(11), 229(17), 345(20)
S12, M = 374, $C_{18}H_{38}O_4Si_2$	55(42), 56(5), 57(7), 59(5), 61(7), 67(11), 69(19), 72(7), 73(100), 74(11), 75(85), 76(6), 77(7), 81(11), 83(15), 93(8), 95(7), 97(8), 98(6), 111(4), 116(4), 117(22), 129(19), 147(8), 149(12), 204(19), 217(15), 243(15), 359(28)
U4Z, M = 260, $C_{10}H_{20}O_4Si_2$	54(4), 55(3), 58(4), 59(6), 61(2), 66(5), 72(3), 73(89), 74(8), 75(22), 83(4), 115(6), 126(2), 133(4), 143(3), 147(100), 148(17), 149(9), 170(3), 215(2), 245(21), 246(5)
U4E, M = 260, $C_{10}H_{20}O_4Si_2$	53(6), 54(3), 55(3), 58(5), 59(12), 61(5), 73(74), 74(7), 75(34), 83(6), 84(4), 115(8), 133(6), 143(15), 144(2), 147(31), 148(5), 149(5), 155(3), 157(2), 217(3), 245(100), 246(22), 247(10)
U5E, M = 274, $C_{11}H_{22}O_4Si_2$	59(4), 61(3), 67(11), 73(100), 74(8), 75(24), 83(2), 97(6), 112(2), 122(4), 133(3), 141(2), 147(38), 148(6), 149(5), 157(2), 169(2), 184(37), 185(6), 259(35), 260(9), 261(4)
U5I, M = 274, $C_{11}H_{22}O_4Si_2$	58(3), 59(6), 61(3), 67(6), 68(6), 72(5), 73(100), 74(8), 75(20), 83(3), 97(3), 98(2), 117(2), 122(2), 131(2), 133(5), 147(78), 148(14), 149(8), 215(6), 230(5), 259(12), 260(3)
THF, M = 314, $C_{14}H_{26}O_4Si_2$	59(4), 73(100), 74(9), 75(17), 77(5), 78(16), 79(8), 103(2), 107(2), 117(6), 118(2), 133(2), 147(28), 148(4), 149(3), 152(11), 153(2), 181(1), 196(7), 224(8), 225(2), 299(8), 300(2), parent 0.52
MTHF, M = 328, $C_{15}H_{28}O_4Si_2$	59(4), 61(2), 72(3), 73(100), 74(9), 75(19), 77(5), 91(5), 92(47), 93(19), 103(2), 117(6), 147(21), 148(3), 149(3), 166(8), 210(9), 211(2), 238(3), 313(5), parent 0.93
CTHF, M = 348, $C_{14}H_{25}ClO_4Si_2$	59(3), 61(2), 72(3), 73(100), 74(9), 75(19), 77(6), 78(36), 79(5), 93(2), 103(2), 112(2), 117(5), 118(2), 133(1), 147(26), 148(4), 149(2), 186(3), 188(1), 230(3), 232(1), 258(3), 260(1), 333(4), 335(1), parent 0.60
HHF, M = 316, $C_{14}H_{28}O_4Si_2$	53(4), 54(3), 55(8), 59(4), 61(3), 67(3), 72(4), 73(100), 74(9), 75(25), 79(5), 80(6), 81(31), 82(7), 108(2), 109(5), 110(4), 117(6), 133(3), 147(51), 148(9), 149(6), 154(4), 183(6), 198(9), 204(2), 217(2), 226(10), 227(3), 243(2), 257(2), 272(3), 301(12), 302(3), parent 1.58
NAD, M = 326, $C_{15}H_{26}O_4Si_2$	55(3), 59(3), 61(2), 65(6), 66(46), 67(3), 72(4), 73(100), 74(9), 75(21), 83(1), 91(8), 92(3), 99(2), 115(5), 118(4), 119(17), 120(3), 133(2), 147(24), 148(4), 149(3), 171(25), 172(3), 193(4), 208(4), 209(20), 210(4), 236(12), 237(2), 245(23), 246(5), 261(6), 311(1), parent 0.70
A12, M = 310, $C_{14}H_{22}O_4Si_2$	59(3), 61(1), 72(3), 73(80), 74(8), 75(9), 76(8), 77(4), 89(2), 91(3), 103(2), 104(2), 105(5), 119(3), 126(2), 131(2), 133(3), 135(2), 140(7), 147(100), 148(17), 149(9), 163(3), 193(2), 220(4), 221(7), 295(15), 296(4), parent 2.86
A13, M = 310, $C_{14}H_{22}O_4Si_2$	59(3), 61(2), 65(2), 72(3), 73(100), 74(10), 75(23), 76(29), 77(5), 89(5), 90(2), 91(4), 103(25), 104(17), 105(4), 118(3), 119(4), 121(2), 126(3), 133(4), 135(6), 140(17), 141(2), 147(4), 149(2), 177(6), 178(2), 193(3), 205(12), 206(2), 207(8), 221(13), 222(2), 251(3), 279(14), 280(2), 295(74), 296(17), 309(2), parent 7.51
A14, M = 310, $C_{14}H_{22}O_4Si_2$	59(3), 61(2), 72(2), 73(56), 74(6), 75(23), 76(31), 77(4), 89(7), 90(2), 91(3), 103(63), 104(30), 105(4), 118(4), 119(2), 126(3), 133(3), 134(3), 135(7), 140(19), 147(1), 149(2), 177(3), 178(6), 192(2), 193(5), 221(30), 222(5), 223(2), 251(17), 252(4), 294(2), 295(100), 296(25), 297(10), parent 7.74

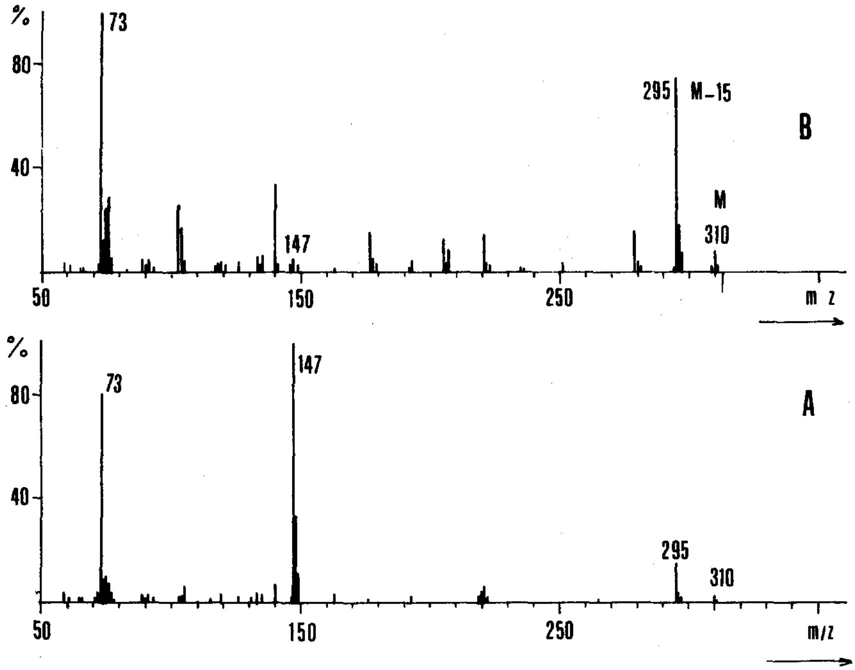


Fig. 3. Influence of the *ortho* effect on the molecular ion fragmentation on differences between the mass spectra of substituted isomers. The relative intensities of the ions at *m/z* 147 and 295 in the EI mass spectrum of bis(TMS) phthalate (A) are reversed in the mass spectrum of the *meta* isomer, bis(TMS) isophthalate (B).

The other ions present, $(M-131)^+$ and $(M-179)^+$ (S5–S8), resemble the ions $(M-73)^+$ and $(M-63)^+$ found in the EI mass spectra of aliphatic saturated dimethyl esters. In the lower part of the spectrum ions are apparent at *m/z* 55, 59, 61, 72, 74, 76, 77 and 117 and with the long-chain homologues ions are present at *m/z* 79, 81, 83, 95, 97, 129, 204 and 217.

The ions $(M-15)^+$ in the EI mass spectra of aliphatic unsaturated (U) TMS esters have medium intensity. Owing to a convenient planar *cis* configuration[11] of TMS maleate, the ion at *m/z* 147, originating from the ion $(M-15)^+$, thus constitutes the base peak of the spectrum.

The influence of the *ortho* position on the formation of the ion at *m/z* 147 from the ion $(M-15)^+$ is apparent in the EI mass spectra of isomeric TMS phthalate esters. The structure of the *ortho* isomer of TMS phthalate enables the facile elimination of the ion at *m/z* 147 that forms the base peak of the spectrum. With TMS isophthalate (A13) and terephthalate (A14) the ion at *m/z* 147 is of low intensity. This phenomenon supports the opinion[15] that the ion $(M-15)^+$ with *cis* and *ortho* isomers seems to have the form of a cyclic silyloxonium ion and the elimination of the ion at *m/z* 147 with two silicone atoms is possible. In TMS isophthalate and terephthalate, where the rigid molecular structure does not permit the formation of a cyclic ion, the ion at *m/z* 147 is of low intensity and the ion $(M-15)^+$ forms the dominant peak of the spectrum (Fig. 3).

In addition to the common ions at m/z 73, 75 and 147 and $(M-15)^+$ ions, the ions $(M-118)^{+\cdot}$ and $(M-90)^{+\cdot}$ are also present in the EI mass spectra of alicyclic 1,2-bis(TMS) esters. These ions may be considered as analogous to the ions $(M-60)^{+\cdot}$ and $(M-32)^{+\cdot}$ in the EI spectra of alicyclic dimethyl esters, assuming that the fragmentation routes of the TMS esters and dimethyl esters have some common features.

The influence of the *ortho* effect is obvious from the data in Table IV. The specific feature of the fragmentation of alicyclic 1,2-bis(TMS) esters is the origin of $(M-162)^{+\cdot}$ ions, corresponding in mass to positively charged anhydride ions, which have not been found in the mass spectra of alicyclic dimethyl esters[13].

Methane and isobutane mass spectra

The CI mass spectra of dicarboxylic acid TMS esters, monocarboxylic and tricarboxylic acid TMS esters and diol bis(TMS) ethers were measured in order to evaluate the ability of the CI method in both an individual and a group characterization of a compound. The dominant ions in the methane and isobutane CI mass

TABLE V

DOMINANT IONS IN THE METHANE CI MASS SPECTRA OF DICARBOXYLIC ACID BIS(TRIMETHYLSILYL) ESTERS AT AN ION SOURCE TEMPERATURE OF 160–170°C, A METHANE PRESSURE OF *ca.* 25 Pa AND AN ENERGY OF ELECTRONS OF 210 eV FOR $m/z \geqslant$ M−89

Ester	*M−89*	*M−43*	*M−15*	*M−1*	*M*	*M+1*	*M+29*	*M+41*	*M+73*
S2	–	–	32	3	4	100	23	19	(34)
S3	8	–	31	–	3	100	18	14	(26)
S4	100	–	61	–	2	44	19	17	(43)
S5	100	–	80	–	3	42	35	27	(43)
S6	100	–	62	–	3	39	25	18	(30)
S7	100	–	61	3	3	43	23	15	(15)
S8	97	–	79	6	7	100	27	20	(8)
S9	80	–	65	7	8	100	24	15	(10)
S10	47	–	52	8	9	100	20	13	(6)
S11	44	1	53	11	13	100	20	14	(24)
S12	40	–	52	13	13	100	19	14	(20)
S14	42	4	47	18	15	100	17	13	(11)
U4Z	29	–	52	–	7	100	28	28	(24)
U4E	10	–	37	–	6	100	20	15	(61)
U5Z	83	–	100	–	7	100	36	37	(66)
U5E	25	–	40	–	11	100	19	14	(61)
U5I	84	–	55	–	4	79	24	16	(100)
THF	100	–	79	7	9	91	25	19	(60)
MTHF	100	–	49	3	9	67	10	4	(23)
CTHF	100	–	44	3	6	42	10	7	(7)
HHF	100	–	69	6	5	28	14	10	(7)
MHHF	100	–	46	3	6	39	11	8	(9)
NAD	100	–	88	7	21	93	29	35	(18)
A12	71	5	51	–	7	70	16	12	(100)
A13	15	7	52	–	9	100	19	14	(43)
A14	15	8	45	–	9	100	17	13	(32)

spectra are $(M-89)^+$, $(M-15)^+$ and $(M+1)^+$, the adduct ions resulting from the reaction between the alkane plasma and ester molecule, $(M+29)^+$, $(M+41)^+$ (methane) and $(M+41)^+$, $(M+43)^+$ (isobutane), and the ion $(M+73)^+$ (Table V).

The methane CI mass spectra show a greater fragmentation of the quasi-molecular ion $(M+H)^+$ compared with the lower energy isobutane CI mass spectra and with some esters (S4, S5, S6, S7, alicyclic esters) the quasi-molecular ion does not constitute the base peak of the spectrum. With increase in the number of CH_2 groups in the molecular of aliphatic saturated bis(TMS) esters, the intensity of the second quasi-molecular ion $(M-H)^+$ gradually increases. In the isobutane CI mass spectra the quasi-molecular ion $(M+1)^+$ forms the base peak of the spectrum.

The most striking feature of the CI mass spectra of TMS esters is the presence of the ion $(M+73)^+$, the intensity of which varies considerably with the vapour pressure of measured compound, the pressure of the chemical ionization reaction gas in the ionization box, the temperature of the ionization box and the structure of the studied ester. The relative mass of an $(M+73)^+$ ion corresponds to the relative molecular mass of a tris(TMS) derivative of a dicarboxylic acid and this ion is assumed to be the product of persilylation of one ester group via an intermolecular transfer of a TMS group. This phenomenon has also been observed in the mass spectra of monocarboxylic and tricarboxylic acid TMS esters (Fig. 4), but not with alkanediol bis(TMS) ethers.

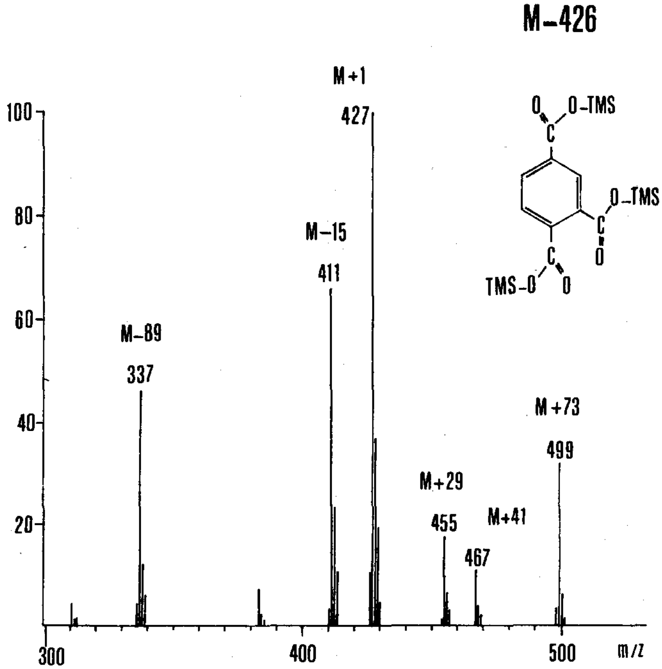


Fig. 4. Characteristic ions in the methane CI mass spectra of carboxylic acid trimethylsilyl esters, $(M-89)^+$, $(M-15)^+$, $(M+1)^+$, $(M+29)^+$, $(M+41)^+$ and $(M+73)^+$, in the methane CI mass spectrum of tris(TMS) trimellitate ($C_{18}H_{30}O_6Si_3$), relative molecular mass 426.

CONCLUSION

The TMS derivatives of dicarboxylic acids have been characterized with the aid of capillary GC and low-resolution MS. The data obtained together with the application of a GC–MS method permit the rigorous identification of polycarboxylic acids in condensation-type polymers and form a basis for developing methods of quantitative analysis.

From the point of view of the separation of isomers and critical pairs on a non-polar capillary column, TMS derivatives seem to be more convenient derivatives than methyl esters.

The EI mass spectra can be used for the reliable identification of the four types of bis(TMS) esters described here when a low-resolution mass spectrometer is connected to a gas chromatograph.

CI mass spectrometry has proved to be a versatile method not only for the identification of a particular derivative but also for a quick search of a chromatogram, which often consists of a large number of component peaks, resulting from the hydrolysis of polymers and derivatization of the liberated monomers, *e.g.*, solvents, blank components, derivatized and underivatized compounds. From the analytical point of view the presence of the $(M+73)^+$ ion indicates that the sample compound is a TMS ester and can serve as supporting evidence for the determination of the relative molecular mass of a compound.

The use of TMS derivatives in the analysis of carboxylic acids in condensation-type polymers is important in connection with the limitations of methods of acid- and base-catalysed condensate alcoholysis[16] and with the fact that effective methods for the quantitative hydrolysis of polymer and isolation of acids are continuously being developed[17].

REFERENCES

1 J. K. Haken, *Prog. Org. Coat.*, 7 (1979) 209.
2 B. J. Allen, G. M. Elsea, K. P. Keller and H. D. Kinder, *Anal. Chem.*, 46 (1977) 741.
3 R. Warthen, A. S. Schurl and R. W. Lenz, *J. Polym. Sci.*, 23 (1979) 3167.
4 S. Mori, M. Furusawa and T. Takeuchi, *Anal. Chem.*, 42 (1970) 959.
5 H. Tengler, *Plaste Verarbeiter*, 22 (1971) 329.
6 A. Jellum, *J. Chromatogr.*, 143 (1977) 427.
7 G. Petersson, *J. Chromatogr. Sci.*, 15 (1977) 245.
8 K. Tanaka and D. G. Hine, *J. Chromatogr.*, 239 (1982) 301.
9 M. Tuchman, L. D. Bowers, K. D. Fregien, P. J. Crippin and W. Krivit, *J. Chromatogr. Sci.*, 22 (1984) 198.
10 O. A. Mammer, J. C. Crawhall and S. S. Thoa, *Clin. Chim. Acta*, 32 (1971) 171.
11 R. Large and K. J. Saunders, *Org. Mass Spectrom.*, 7 (1973) 291.
12 D. L. Corina and K. E. Harper, *J. Chromatogr. Sci.*, 15 (1977) 317.
13 F. Herrmann, O. Dufka and J. Churáček, *J. Chromatogr.*, 360 (1986) 79.
14 M. P. Friocourt, F. Bethou, D. Picart, Y. Dreano and H. H. Floch, *J. Chromatogr.*, 172 (1979) 261.
15 J. Dieckman, J. B. Thomson and C. Djerassi, *J. Org. Chem.*, 33 (1968) 2271.
16 *Test Method D 2455-69*, ASTM, Philadelphia, PA, 1974.
17 J. K. Haken and M. A. Rohanna, *J. Chromatogr.*, 298 (1984) 263.