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

I. DIMETHYL ESTERS

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SUMMARY

Isothermal retention indices for some aliphatic saturated, aliphatic unsaturated, alicyclic and aromatic dicarboxylic acid dimethyl esters on a cross-linked polymethylsiloxane stationary phase at six column temperatures are listed. The characteristic features of their electron impact and methane and isobutane chemical ionization mass spectra and their usefulness for identification purposes are discussed.

INTRODUCTION

Gas chromatography (GC) is often the last step in the analysis of polycarboxylic acids in condensation-type polymers, *e.g.* alkydes, unsaturated polyesters, polyamides, after the polymer chain has been split into the monomer units[1–4].

The use of fused-silica capillary columns with a cross-linked stationary phase has brought about further improvements in the separation of compounds and the accuracy and reproducibility of retention index determination. The combination of mass spectrometry (MS) and high-resolution GC makes the analysis faster and more reliable.

Among the carboxylic acid derivatives suitable for GC analysis the dimethyl esters have been used successfully for more than three decades. However, the GC and MS properties of dimethyl esters of some dicarboxylic acids produced on a large scale have not yet been reported, and the published results of interest, *i.e.* GC retention indices[5–7] and electron impact (EI) and chemical ionization (CI) mass spectra[8–10], are often inadequate for analytical purposes.

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

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TABLE I

KOVÁTS RETENTION INDICES AND THE VALUE OF PARAMETER $\partial I/\mathrm{d}T$ FOR DICARBOXYLIC ACID DIMETHYL ESTERS

Non-polar polymethylsiloxane stationary phase; column temperatures, 75, 100, 125, 150, 175 and 200°C.

Compound	*75°C*		*100°C*		*125°C*		*150°C*		*175°C*		*200°C*	
	I	$\partial I/dT$	*I*	$\partial I/dT$	*I*	$\partial I/dT$	*I*	$\partial I/dT$	*I*	$\partial I/dT$	*I*	$\partial I/dT$
I	890.9	−0.15	887.3	−0.14	884.0	−0.11	881.5	−0.09	—	—	—	—
II	999.3	−0.12	997.1	−0.09	995.2	−0.07	993.7	−0.04	—	—	—	—
III	1103.5	−0.09	1101.7	−0.06	1099.7	−0.04	1098.8	−0.03	—	—	—	—
IV	—	—	1206.9	−0.08	1205.4	−0.07	1203.8	−0.05	1201.8	−0.04	—	—
V	—	—	1309.6	−0.07	1308.0	−0.04	1307.1	−0.02	1306.7	−0.01	—	—
VI	—	—	1411.7	−0.05	1410.3	−0.03	1409.6	−0.01	1409.5	—	—	—
VII	—	—	—	—	1511.6	−0.01	1511.0	—	1511.1	—	1511.6	—
VIII	—	—	—	—	1613.4	—	1612.7	—	1612.9	—	1613.5	—
IX	—	—	—	—	1713.5	—	1713.2	—	1713.6	—	1714.0	—
XI	983.9	−0.08	980.9	−0.06	979.3	−0.05	978.3	−0.09	—	—	—	—
XII	994.0	−0.05	993.2	−0.02	992.8	−0.01	992.9	−0.04	—	—	—	—
XIII	1059.3	−0.07	1057.7	−0.06	1056.4	−0.04	1055.4	−0.03	—	—	—	—
XIV	1085.1	−0.01	1084.8	−0.01	1084.6	—	1084.7	−0.0	—	—	—	—
XV	1064.8	−0.10	1061.4	−0.08	1059.0	−0.07	1056.8	−0.08	—	—	—	—
XVI	—	—	—	—	1358.8	+0.22	1365.2	+0.27	1372.7	+0.32	1381.1	+0.39
XVII	—	—	—	—	1424.2	+0.18	1429.3	+0.22	1435.7	+0.27	1442.2	+0.33
XVIII	—	—	—	—	1521.8	+0.30	1530.1	+0.36	1539.6	+0.41	1550.4	+0.45
XIX	—	—	—	—	1358.9	+0.27	1366.3	+0.31	1374.6	+0.35	1384.0	+0.42
XX	—	—	—	—	1403.1	+0.26	1410.0	+0.30	1417.8	+0.34	1427.0	+0.40
XXI	—	—	—	—	1413.0	+0.35	1422.7	+0.40	1433.8	+0.43	1444.9	+0.49
XXII	—	—	—	—	1409.3	+0.34	1417.9	+0.36	1426.8	+0.41	1437.2	+0.47
XXIII	—	—	—	—	1470.3	+0.36	1479.4	+0.39	1488.5	+0.41	1498.8	+0.44
XXIV	—	—	—	—	1461.1	+0.36	1470.5	+0.41	1480.5	+0.45	1492.1	+0.49

EXPERIMENTAL

Dimethyl esters were prepared by acid-catalysed esterification of commercially available dicarboxylic acids or anhydrides. The 4-methylcyclohex-4-ene 1,2-dicarboxylic acid dimethyl ester were obtained from technical product, methyl tetrahydrophthalanhydride (Veba Chemie, F.R.G.), and the positions of the methyl group and the olefinic bond were confirmed with the aid of NMR spectroscopy.

Gas chromatography

GC experiments were performed on a Model 3700 gas chromatograph with flame ionization detector (Varian Aerograph, Palo Alto, CA, U.S.A.) fitted with a 25 m × 0.20 mm I.D.fused-silica capillary column Ultra 1 (Hewlett-Packard, Vienna, Austria) with a film thickness of cross-linked polymethylsiloxane stationary phase (film thickness 0.32 μm, according to the manufacturer). The split ratio was 1:140, and the linear velocity of the carrier gas (nitrogen) was *ca.* 17 cm/s. No more than 10 ng per component were injected to ensure the capillary column capacity was not overloaded. Retention times were measured with automatic integrator Autolab System IV (Spectra-Physics, Mountain View, CA, U.S.A.) to tenth of seconds. Kovats isothermal retention indices were calculated for the column temperatures given in Table I.

Gas chromatography–mass spectrometry

MS data were taken on the GC–MS System Varian MAT 44S with a quadrupole mass spectrometer coupled with a Model 3700 gas chromatograph. Compounds were introduced into the spectrometer through an Ultra 1 column, and the split ratio was 1:40. The spectrometer was operated at an ion source pressure of 10^{-3}

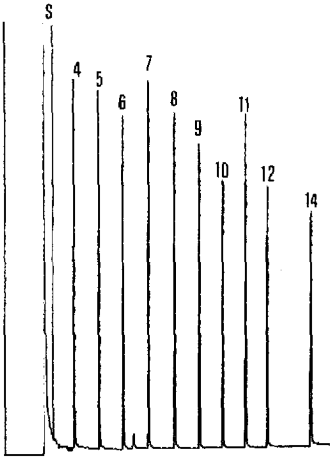


Fig. 1. Chromatogram of the separation of aliphatic saturated dimethyl esters by temperature programming, 120°C for 2 min at 10°C/min, on a non-polar fused-silica capillary column Ultra 1 (25 m × 0.20 mm I.D.). The number of the peak corresponds to the number of carbon atoms in the molecule of the acid: 4 = dimethylsuccinate (II), 5 = dimethylglutarate (III), etc. S = solvent.

Pa with ionization energy 70 eV (EI) or 210 eV (CI), and an ion source temperature of 160–170°C. The pressure of the CI gas, methane or isobutane, was 25 Pa.

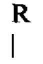
All EI and CI mass spectra were taken at the maximum of overloaded chromatographic peak to ensure approximately constant pressure of the measured compound in the ion source during scanning.

RESULTS

The compounds studied were divided into four classes according to their chemical structure: aliphatic saturated (I–X), aliphatic unsaturated (XI–XV), alicyclic (XVI–XXI) and aromatic (XXII–XXIV) dicarboxylic acid dimethyl esters.

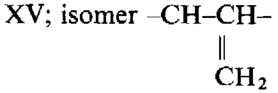
$CH_3OOC(CH_2)_nCOOCH_3$

I; $n = 1$
II; $n = 2$
III; $n = 3$
:
X; $n = 10$

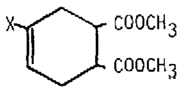


$CH_3COOCH{=}\overset{\overset{R}{|}}{C}{-}COOCH_3$

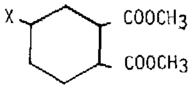
XI; R = H (*Z*)
XII; R = H (*E*)
XIII; R = CH_3 (*Z*)
XIV; R = CH_3 (*E*)



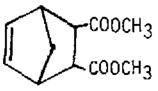
XV; isomer $-CH-\underset{\underset{CH_2}{\|}}{CH}-$



XVI; X = H
XVII; X = CH_3
XVIII; X = Cl



XIX; X = H
XX; X = CH_3



XXI

Compounds XXII, XXIII and XXIV were dimethyl phthalate, isophthalate and terephthalate, respectively.

The saturated dimethyl esters (I–X) form a homologous series and can be well separated on a non-polar fused-silica capillary column by programmed temperature analysis; 120°C for 2 min with a temperature gradient of 10°C/min (Fig. 1). With the higher homologues in the series the methylene increment ΔI_{CH_2} approaches the value 100, whereas with the lower homologues this parameter increases to 111.2 for I and II (malonate and succinate) at 125°C (Table II). The curvature in the lower part of the plot of I *vs.* number of carbon atoms in the molecule of dimethyl ester is apparent from the data at Table II. This phenomenon has also been observed with other homologous series[11].

The values of the parameter $\partial I/\mathrm{d}T$ that characterize the temperature dependence of Kovats retention index were obtained from the plot and are given in Table I. This parameter is negligible for saturated aliphatic dimethyl esters and only for the lowest member of the series it reaches value -0.15.

The unsaturated aliphatic dimethyl esters (XI–XV) have lower retention indices than the corresponding saturated analogues. The *trans* isomers, dimethyl fu-

TABLE II

VALUES OF METHYLENE INCREMENTS IN THE HOMOLOGOUS SERIES OF ALIPHATIC SATURATED DIMETHYL ESTERS ON A NON-POLAR STATIONARY PHASE

ΔI_{CH_2}	*75°C*	*100°C*	*125°C*	*150°C*	*175°C*	*200°C*
II–I	104.4	109.8	111.2	112.2	–	–
III–II	104.2	104.6	104.5	105.1	–	–
IV–III	–	105.2	105.7	105.0	–	–
V–IV	–	102.7	102.6	103.3	104.9	–
VI–V	–	102.1	102.3	102.5	102.8	–
VII–VI	–	–	101.3	101.4	101.6	102.1
VIII–VII	–	–	101.8	101.7	101.8	101.9
IX–VIII	–	–	100.1	100.5	100.7	100.5

marate (XII) and mesaconate (XIV) elute after the *cis* isomers, dimethyl maleate (XI) and citraconate (XIII) whereas on polar stationary phases this elution order is reversed. The values of $\partial I/\mathrm{d}T$ are generally small, with the values for *trans* isomers being lower than those for *cis* isomers.

Three aromatic isomers, dimethyl phthalate, isophthalate and terephthalate (XXII–XXIV), were well separated on the efficient capillary column together with dimethyl suberate (VI) and dimethyl azelate (VII) and there is no need to use polar or mixed stationary phases (Fig. 2)[12]. Owing to the aromatic character of these isomers their retention indices are strongly temperature dependent.

The cyclic character of the alicyclic group compounds (XVI–XXI), which are mostly methylated *cis* products of Diels–Alder cycloaddition reactions, results in a

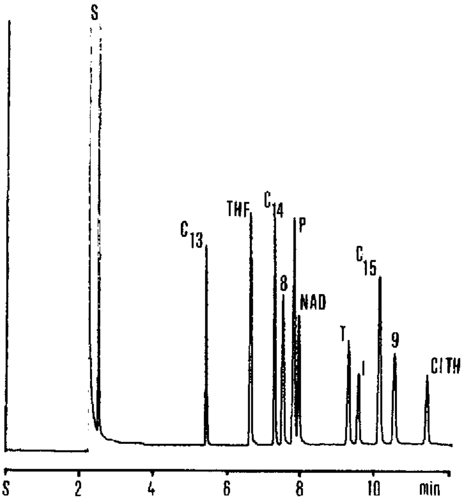


Fig. 2. The isothermal separation of aromatic, alicyclic and saturated dimethyl esters in the C_{14}–C_{15} region. Peaks: P = phthalate (XXII); I = isophthalate (XXIII); T = terephthalate (XXIV); 8 = suberate (VI); 9 = azelate (VII); THF = tetrahydrophthalate (XVI); NAD = nadicate (XXI); ClTHF = chlorotetrahydrophthalate (XVIII). Conditions: non-polar polymethylsiloxane fused-silica capillary column Ultra 1; temperature, 162°C.

TABLE III

DOMINANT AND CHARACTERISTIC IONS IN THE EI MASS SPECTRA OF DICARBOXYLIC ACID DIMETHYL ESTERS WITH THEIR RELATIVE INTENSITIES

Ion source temperature, 170°C; electron energy 70 eV.

Compound	*Mol.wt.*	*Ions (relative intensity, %)*
I	132	15(100), 27(6), 29(16), 42(16), 43(8), 57(12), 59(28), 74(12), 101(14)
II	146	15(100), 26(9), 27(24), 29(14), 31(5), 41(6), 42(7), 45(10), 55(76), 56(9), 57(8), 59(52), 87(20), 114(19), 115(67)
III	160	15(94), 27(14), 29(20), 39(13), 41(31), 42(40), 43(24), 55(49), 58(10), 59(100), 69(5), 72(5), 74(9), 87(15), 97(5), 100(41), 101(29), 128(25), 129(37)
IV	174	15(64), 27(25), 29(28), 31(10), 39(12), 41(32), 42(25), 43(41), 54(14), 55(75), 56(11), 59(100), 69(7), 72(8), 82(10), 83(19), 87(9), 101(45), 111(38), 114(44), 115(9), 142(13), 143(34)
V	188	15(100), 27(24), 29(26), 31(8), 39(18), 41(49), 42(31), 43(61), 45(12), 48(11), 49(12), 55(81), 59(56), 68(21), 69(45), 73(31), 74(65), 83(38), 87(15), 97(19), 100(8), 111(8), 114(6), 115(56), 124(12), 125(20), 128(16), 156(6), 157(21)
VI	202	15(83), 27(31), 29(41), 31(14), 39(20), 41(80), 45(13), 54(11), 55(100), 56(20), 59(63), 67(11), 68(28), 69(87), 73(11), 74(90), 82(13), 83(37), 84(10), 87(32), 96(7), 97(72), 110(16), 111(17), 114(6), 127(7), 129(59), 138(59), 142(5), 170(6), 171(33)
VII	216	15(80), 27(19), 29(31), 39(15), 41(56), 42(22), 43(63), 45(8), 55(100), 59(47), 67(9), 68(8), 69(29), 73(7), 74(67), 81(6), 82(8), 83(49), 84(21), 87(19), 96(8), 97(17), 98(11), 101(5), 110(5), 111(29), 124(12), 125(10), 143(19), 152(43), 153(5), 185(17)
VIII	230	15(69), 27(18), 29(30), 39(13), 41(58), 42(18), 43(67), 55(100), 59(44), 67(10), 69(31), 73(9), 74(72), 81(8), 83(28), 84(35), 87(20), 96(6), 97(31), 98(43), 101(5), 111(4), 115(4), 121(4), 124(6), 125(36), 138(17), 139(7), 157(17), 166(13), 199(18)
IX	244	15(100), 29(51), 39(23), 41(82), 42(28), 43(79), 45(10), 53(7), 54(10), 55(98), 59(48), 67(12), 68(8), 69(48), 70(6), 73(7), 74(61), 81(8), 83(15), 84(30), 87(20), 95(5), 96(5), 97(20), 98(48), 112(7), 113(8), 121(5), 139(16), 152(6), 171(7), 213(4)
X	258	15(100), 29(59), 31(17), 39(15), 41(64), 42(17), 43(71), 45(9), 55(85), 57(17), 59(35), 68(6), 69(51), 70(6), 73(6), 74(65), 75(5), 81(11), 83(26), 84(45), 87(24), 97(17), 98(83), 101(4), 111(12), 112(25), 135(8), 152(6), 153(18), 185(12)
XI	144	15(100), 26(29), 27(7), 29(15), 30(4), 39(4), 53(9), 54(13), 55(6), 59(37), 85(15), 113(63), 114(6)
XII	144	15(100), 26(41), 27(10), 29(32), 30(7), 31(6), 39(5), 41(4), 53(19), 54(16), 55(4), 59(28), 85(35), 113(46), 114(8)
XIII	158	15(100), 27(12), 29(60), 30(9), 31(6), 37(6), 38(17), 39(60), 41(9), 53(10), 55(6), 59(57), 67(7), 68(14), 98(5), 99(25), 127(64), 128(6)
XIV	158	15(68), 27(16), 29(57), 30(8), 31(10), 37(7), 38(23), 39(100), 41(10), 53(12), 55(5), 59(54), 67(15), 68(29), 69(20), 98(8), 99(7), 126(14), 127(7)
XV	158	15(100), 27(9), 29(36), 30(6), 37(5), 38(14), 39(51), 41(25), 42(6), 45(7), 53(6), 55(17), 59(63), 67(6), 68(10), 69(26), 71(8), 99(18), 113(6), 126(14), 127(16)
XVI	198	15(66), 27(14), 29(8), 33(8), 39(13), 41(6), 45(5), 51(8), 52(4), 53(7), 55(4), 59(14), 77(21), 78(37), 79(100), 80(10), 106(3), 107(7), 138(20), 166(6), 167(7)
XVII	212	15(57), 27(8), 29(7), 39(12), 41(8), 45(3), 51(4), 53(6), 55(4), 59(11), 65(5), 77(19), 79(9), 91(19), 92(30), 93(100), 94(9), 121(3), 138(2), 152(21), 180(4), 181(6), 212(2)
XVIII	232	15(100), 27(10), 33(15), 39(10), 45(5), 51(17), 52(5), 53(7), 59(28), 77(65), 78(11), 79(16), 112(27), 113(64), 114(13), 115(19), 137(4), 172(26), 174(8), 200(5), 201(9), 203(2)

TABLE III (*continued*)

Compound	*Mol.wt.*	*Ions (relative intensity, %)*
XIX	200	15(100), 26(4), 27(21), 29(17), 31(4), 39(22), 41(28), 43(4), 45(6), 53(15), 54(13), 55(19), 59(21), 66(6), 67(18), 68(5), 77(5), 79(18), 80(41), 81(75), 82(10), 108(27), 109(15), 111(4), 140(31), 141(5), 168(14), 169(11)
XX	214	15(100), 27(13), 29(24), 39(22), 41(29), 42(5), 43(5), 45(5), 53(14), 54(10), 55(28), 59(21), 67(17), 68(8), 69(4), 75(6), 77(13), 78(7), 79(16), 93(10), 94(43), 95(57), 96(7), 113(6), 122(16), 123(8), 154(17), 182(9), 183(6)
XXI	210	15(54), 27(5), 39(15), 59(11), 65(16), 66(100), 67(10), 85(4), 91(17), 113(36), 119(12), 145(16), 151(4), 179(3)
XXII	194	15(38), 27(4), 29(6), 39(4), 50(25), 51(7), 64(5), 74(6), 75(5), 76(21), 77(42), 92(15), 104(7), 105(4), 133(8), 135(7), 163(100), 164(11), 194(8)
XXIII	194	15(23), 29(4), 39(4), 50(17), 51(5), 52(7), 66(8), 74(5), 75(13), 76(19), 77(12), 103(11), 104(5), 119(6), 120(8), 135(32), 149(2), 163(100), 164(11), 194(26)
XXIV	194	15(27), 50(19), 52(7), 66(6), 74(6), 75(12), 76(17), 77(11),103(16), 104(9), 119(5), 120(6), 135(25), 163(100), 164(11), 179(2), 194(23)

considerable temperature dependence of their retention indices but the values of the $\partial I/\mathrm{d}T$ parameter do not reach the values of aromatic diesters.

When the methylene increment is due to substitution of hydrogen by methyl leading to aliphatic or alicyclic chain branching, differences of only 65, 44 and 77 index units were found between tetrahydrophthalate (XVI) and methyl tetrahydrophthalate (XVII), hexahydrophthalate (XIX) and methyl hexahydrophthalate (XX) and maleate (XI) and citraconate (XIII), respectively.

Mass spectrometry

The saturated aliphatic dimethyl esters have been studied most exhaustively[8–10]. The most striking feature of their EI mass spectra is the absence of a molecular ion, the loss of a methoxy group giving the ion $(M - OCH_3)^+$ at m/z M − 31, the loss of two methanol molecules giving an ion at m/z M − 64, and ions at m/z M − 73, M − 92, M − 105, M − 115, M − 123. In the lower part of the spectrum ions are apparent at m/z 15, 27, 29, 41, 55 and 69, ion $C_2H_3O_2{}^+$ or $C_3H_7O^+$ at m/z 59, the series of ions at m/z 87, 101, 115 and odd-electron ion series at m/z 74, 84, 98 and 112 (Table III).

The EI spectra of unsaturated dimethyl esters (XI–XV) are simple owing to the small number of carbon atoms in the molecule. The common features of the spectra are the ions at m/z M − 31, M − 59 and M − 89. The peaks at m/z M − 64, M − 73 and the odd-electron ion series are absent.

Besides the ion $(M - CH_3O)^+$, which forms the base peak in the spectra of aromatic dimethyl esters, the presence of a molecular ion (at m/z 194) is characteristic of the spectrum of the molecule with a high level of resonance stabilization. The further ions are $(M - CO_2CH_3)^+$ and $(M - CH_3CO_2CH_3)^{+\cdot}$ at m/z 135 and 120. Isomers are distinguishable from small differences in their mass spectra. The *ortho* isomer has $(M - OCH_3 - OCH_2)^+$ at m/z 133, and the *para* isomer $(M - CH_3)^+$ at m/z 179 (low intensity). The mass spectrum of the *meta* isomer is very similar to that of the *para* isomer but the peak at m/z 179 is absent and a low intensity ion $(M - OCH_3 - CH_2)^+$ appears at m/z 149[13].

The alicyclic dimethyl esters have not been studied previously and only the analogy with the mass spectral fragmentation of free acids[14] can be used in this discussion. The minor fragmentation route involves elimination of a methoxy group and methanol from the molecular ion to give ions at m/z M $-$ 31 and M $-$ 32. The major fragmentation routes give rise to the ions $(M - 60)^{+\cdot}$, $(M - 119)^{+}$ and $(M - 120)^{+\cdot}$, which were not observed in the mass spectra of aliphatic and aromatic dimethyl esters. The Diels–Alder products (XVI $-$ XVIII and XXI) show ions at m/z M $-$ 91, and the saturated analogues (XIX and XX) show ions at m/z M $-$ 92. Only the spectrum of nadic acid dimethyl ester (XXI) differs from the above-mentioned spectra by the presence of ions at m/z 66 and 113, presumably positively charged cyclopentadiene and methylated maleic anhydride, formed by a retro-Diels–Alder reaction by analogy with fragmentation processes of nadic anhydride[15].

Methane and isobutane CI mass spectra

The dominant ions in the methane CI mass spectra are summarized in Table IV. In contrast to EI mass spectra the quasimolecular ion MH^+ is present in the CI spectrum, constituting the base peak in the spectra of dimethyl malonate (I), fumarate (XII), mesaconate (XIV), isophthalate (XXIII) and terephthalate (XXIV). The main fragmentation reaction is the loss of methanol from the quasimolecular ion to give the $(MH - CH_3OH)^+$ ion, which forms the base peak in the mass spectra of the

TABLE IV

DOMINANT IONS IN THE METHANE CI MASS SPECTRA OF DICARBOXYLIC ACID DIMETHYL ESTERS

Ion source temperature, 160–170°C; methane pressure, 25 Pa; energy of electrons, 210 eV.

Compound	*Mol.wt.*	$(MH - CH_3OH)^+$	$(M + H)^+$	$(M + C_2H_5)^+$	$(M + C_3H_5)^+$
I	132	21	100	0	2
II	146	100	7	1	1
III	160	100	8	5	6
IV	174	100	16	8	8
V	188	100	12	11	8
VI	202	100	22	12	8
VII	216	100	23	14	8
VIII	230	100	27	16	9
IX	244	100	30	15	8
X	258	100	23	9	6
XI	144	100	13	1	1
XII	144	11	100	6	7
XIII	158	100	6	2	2
XIV	158	13	100	6	1
XV	158	100	9	2	0
XVI	198	100	16	6	1
XVII	212	100	20	10	2
XVIII	232	100	14	5	0
XIX	200	100	9	6	4
XX	214	100	10	8	5
XXI	210	100	23	1	4
XXII	194	100	5	4	3
XXIII	194	14	100	7	6
XXIV	194	10	100	9	5

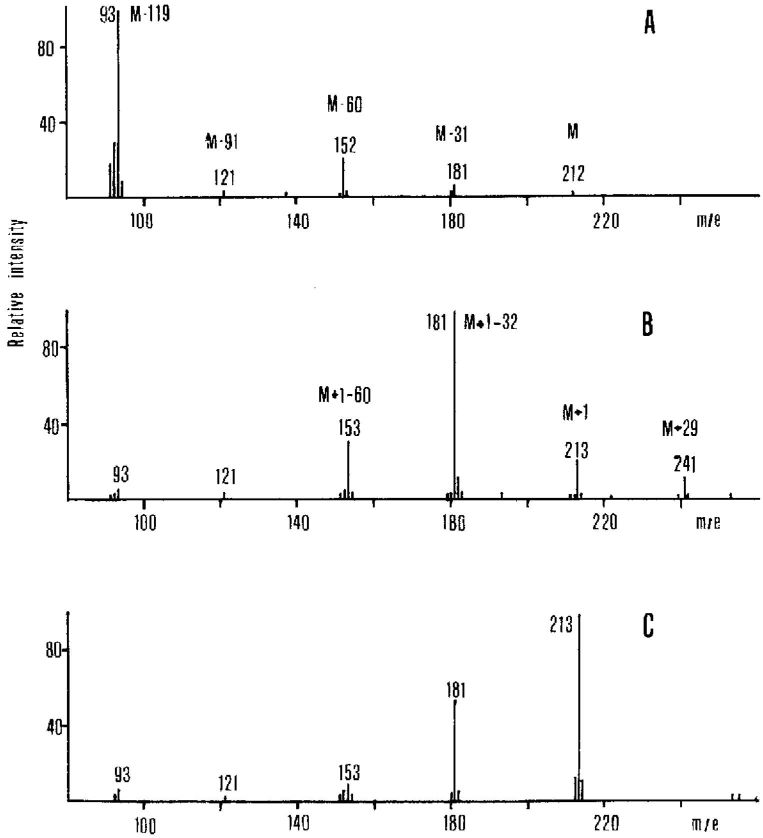


Fig. 3. The comparison of electron impact (A), and methane (B) and isobutane (C) chemical ionization mass spectra of 4-methylcyclohex-4-ene 1,2-dicarboxylic acid dimethyl ester in the mass unit range 90–260. The molecular weight of the compound is 212.

remaining compounds (II–XI, XIII, XV–XXII). The adduct ions, $(M + C_2H_5)^+$ and $(M + C_3H_5)^+$, resulting from the reaction between methane plasma and ester molecules serve to confirm the relative molecular weight of the compound; this is generally impossible with the EI spectrum.

The slight differences between the mass spectra within individual groups are not shown in Table IV: *e.g.* the ion $(M - 13)^+$ appears with dimethyl suberate (VI) approaching the relative intensity of 6% with dimethyl dodecanedioate (X). The alicyclic dimethyl esters show a signal at *m/z* M − 59, and the Diels–Alder products show signals at *m/z* M + 9 of very low intensity.

A typical (lower energy) isobutane mass spectrum is shown in Fig. 3C. The extent of fragmentation is much less than in the methane CI mass spectrum, and the quasimolecular ion $(M + H)^+$ is the base peak in the spectrum of most dimethyl esters studied. The next dominant ion is $(MH - CH_3OH)^+$. The adduct ion, when it appears, is generally at *m/z* M + 41.

DISCUSSION

The CI mass spectra provide information on the molecular weight of the compound and the major fragmentation route. The relative molecular mass is an important parameter in the identification of sample components. With the exception of isomers, the dimethyl esters studied differ in molecular weight. The main fragmentation route helps to differentiate the main classes of compound. Thus dominant peaks at M − 31 indicate particularly strongly the presence of at least two methoxycarbonyl groups in the molecule.

The EI mass spectra help to differentiate dimethyl esters and methyl esters of fatty acids, because the ions in the spectra of fatty acid methyl esters[16] at *m/z* M − 29 and M − 43 were not found in the spectra of dimethyl esters.

In the case of aliphatic saturated dimethyl esters, the EI spectrum provides a highly specific reflection of the chemical structure. The EI spectra of aromatic isomers are similar to each other, but have small distinctive differences.

On the basis of published data[14] and our unreported experiments, the EI mass spectra of the isomers of tetrahydrophthalic acid dimethyl esters are very similar, and the retention indices system be used to distinguish between them.

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