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SEPARATION AND IDENTIFICATION OF *cis–trans* ISOMERIC DIMETHYL ESTERS BY A GAS CHROMATOGRAPHY–MASS SPECTROMETRY–CALCULATOR SYSTEM

F. W. KARASEK* and M. F. TCHIR

Guelph-Waterloo Graduate Center, University of Waterloo, Chemistry Department, Waterloo, Ontario (Canada)

and

W. D. BOWERS

Department of Chemistry, Arizona State University, Tempe, Ariz. 85281 (U.S.A.)

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SUMMARY

Four *cis*- and *trans*-dimethyl ester isomers resulting from the photolysis of *o*-isopropenylbenzophenone with dimethyl maleate or dimethyl fumarate were separated by gas chromatography (GC) with sufficient resolution for qualitative and quantitative analysis using a glass column packed with Aue packing. Both the GC–mass spectrometry (MS) analysis and Kováts' retention indices of these compounds were obtained. Only one of the four mass spectra exhibited significant differences from the others, primarily in the intensity of the molecular and base ions. Analytical methods are described for rapid analysis of mixtures of these compounds by either GC or GC–MS.

INTRODUCTION

Among the various chromatographic methods used to separate and identify isomeric compounds, gas chromatography (GC) has proven to be a most rapid, reliable method. Fairly good separation of *cis–trans*-alkenes has been attained with a GC column containing a sulfobenzyl derivative of Porasil C converted from the H^+ to the Ag^+ form[1]. The use of nematic liquid crystals as liquid phases has also been described as capable of isomer separation[2–4]. These phases must be operated within a narrow temperature range, with limits determined by their melting point and the temperature at which column bleed becomes excessive. This requirement limits their use and flexibility. Lane *et al.*[5] achieved good separation of polynuclear aromatic hydrocarbons (PAHs) using a 1% coating of OV-7 on Chromosorb W. Due to solvent interaction with the liquid phase, the solvent peak possessed excessive tailing, and sample injections less than 1 μl had to be used.

* To whom correspondence should be addressed.

The GC packing used in this study was developed by Aue[6,7]. The packing is formed by creating an ultrathin layer of a Carbowax 20M polymer (*ca.* 15 Å of 0.2%, w/w) physically bonded to a Chromosorb surface. It is especially free of active sites and gives no perceptible bleed at 250°. With this packing Aue *et al.*[8] have shown separation of the two isomers benefin and trifluralin and of PAH isomers. The packing has also been successfully used in this laboratory for the separation of complex mixtures of PAHs found in airborne particulate matter[9].

The objective of this work is to report an analytical method for the four methyl ester isomers obtained from the photolysis of *o*-isopropenylbenzophenone with dimethyl maleate or dimethyl fumarate which involves their GC separation, Kováts' retention indices and mass spectra. These four compounds are the isomers 3,4-dihydro-9,10-dimethoxycarbonyl-4-methyl-1-phenyl-1,4-ethano-1H-2-benzopyran which differ from each other only in the *cis* and *trans* positions of the dimethyl ester groups. Both a digital gas chromatograph and a GC–mass spectrometry (MS)–calculator system were used to obtain the analytical data. The analytical methods described provide rapid analyses of mixtures of these compounds by either GC or GC–MS to facilitate studies of their synthesis reactions.

EXPERIMENTAL

Chemicals

The four ester isomers were prepared by M. F. Tchir at the University of Waterloo, Chemistry Department. The purity and structure of these compounds were characterized by elemental analysis, melting points, nuclear magnetic resonance (NMR) and infrared (IR) spectra. Their preparation has been described elsewhere[10,11]. The Aue column packing which consists of a physically bonded thin layer (*ca.* 0.2%, w/w) coating of Carbowax 20M on exhaustively acid washed Chromosorb W (100–120 mesh) was prepared in our laboratory. For the GC and GC–MS analyses a sample solution was prepared containing a mixture of *ca.* 0.2 μg/μl of each methyl ester isomer in an ethyl acetate solvent.

Instrumentation

A Hewlett-Packard 5830A digital chromatograph, equipped with a flame ionization detector (FID), was used to explore the proper conditions necessary to achieve separation of the ester mixture. A Pyrex glass column (1.8 m × 2 mm I.D.) packed with Aue packing (100–120 mesh) was used. The following GC conditions gave the desired separation: 3-μl injection of the sample solution of mixed isomers; helium flow-rate, 30 ml/min; injection port temperature, 240°; column temperature held isothermally at 190°; FID temperature, 300°; hydrogen flow-rate, 42 ml/min; air flow-rate, 250 ml/min. A calculated value of 2566 plates per meter was obtained for this column using the GC peak for compound II.

The ester mixture was also analyzed with the bench top Hewlett-Packard 5992A GC–MS–calculator system equipped with a membrane interface. The GC section of the GC–MS instrument contained another Pyrex glass column (1.8 m × 2 mm I.D.) packed with the same type of Aue packing as above. The GC conditions used were: 2-μl injection of the sample solution containing the isomer mixture; helium flow-rate, 25 ml/min; injection port temperature, 240°; column temperature held isothermally

at 190°. A calculated value of 3300 plates per meter was obtained for this column using the GC peak for compound II. The quadrupole mass spectrometer was automatically calibrated with a perfluorotetrabutylamine (PFTBA) reference compound to a fixed set of mass spectral conditions using an AUTOTUNE program. The ratio of the intensities of the peaks at *m/e* 69, 219 and 502 were adjusted to 100:52:7. Ionizing conditions used were 70 eV at 170°. Under the conditions of this analysis the background spectrum was almost non-existent. It showed little perceptable bleed from either the column or the membrane. Its total abundance was 5 counts for a *m/e* 259 ion, and it was not necessary to subtract it from the recorded spectra.

The mass spectra of the four compounds was also determined for a solid sample of each purified compound using the solid probe inlet of the VG micromass 7070 high resolution magnetic mass spectrometer. Ionizing conditions used were 70 eV at 200°.

RESULTS AND DISCUSSION

The four methyl ester isomers differ only in their *cis–trans* configuration of the methyl ester groups relative to the bridged ether as indicated in Fig. 1. The chromatogram shown in Fig. 2 obtained from the 5830A digital chromatograph indicates that all of the isomers were separated adequately for qualitative and quantitative analysis. The symmetrical well separated narrow peaks seen in the chromatogram are typical of the separating efficiency obtainable with the Aue packing for isomeric compounds.

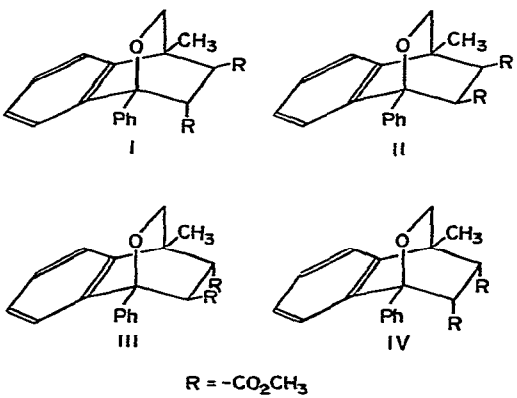

Fig. 1. Structures of the four isomeric methyl ester compounds analyzed in the chromatograms of Figs. 2 and 3.

Comparison of the chromatogram from the digital chromatograph seen in Fig. 2 with the reconstructed chromatogram seen in Fig. 3 obtained from the GC–MS system shows that the same degree of separation of the methyl esters is achieved with both instruments, although the GC–MS instrument gives shorter retention times and slightly narrower peaks. The difference in retention times could result from a combination of several factors; a different packing density of the columns, a different average temperature actually experienced by each column and the effect of the membrane separator on the measured carrier gas flow-rate. The carrier flow-rates of

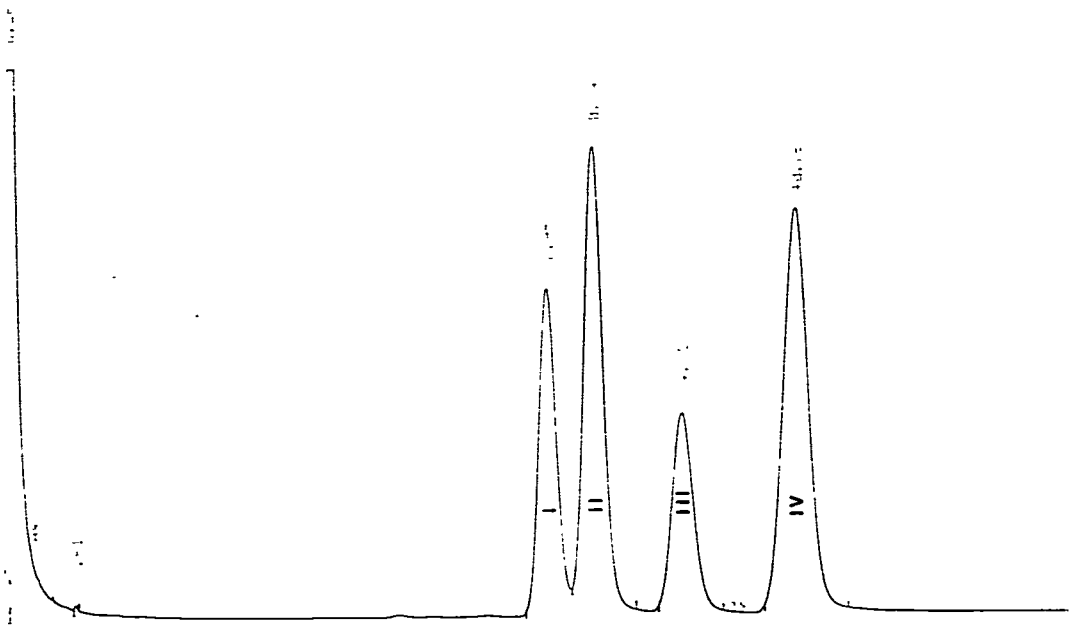

Fig. 2. The chromatogram obtained with the HP 5830A digital chromatograph for a 3-μl injection of the sample solution of the four isomers shown in Fig. 1. Retention times are automatically printed at the top of each GC peak and the beginning and end of integration of peak areas is shown at the peak bases.

both instruments were measured by a bubble flow meter, but the flow measured for the digital chromatograph is that actually flowing through the FID detector while that of the GC–MS system was the flow measured after the membrane separator where the split occurs to divert some GC effluent into the mass spectrometer. Although there is a considerable difference in retention time displayed between the chromatograms from the two instruments, the important variables of plate efficiency and Kováts' retention indices are in close agreement. The slightly better plate value obtained for the GC–MS chromatogram indicates that no measureable peak broadening occurs through the GC–MS interface system.

The Kováts' retention indices were determined for these four compounds using both the digital chromatograph and the GC–MS–calculator instruments. The agreement in retention indice values between duplicate runs and between both instruments was better than 1 %. The average retention indice values are reported in Table I.

The advantages of using a mass spectrometer as a detector for a gas chromatograph has been well established. With the HP 5992A GC–MS–calculator system a mass spectrum is taken automatically at the top of each GC peak and stored on a cassette tape. At the end of the GC–MS analysis, the mass spectra in both a plotted and tabulated format are retrieved from the tape. The normalized, plotted mass spectra of the isomeric esters are presented in Fig. 3 and their tabulated ionic abundance values are listed in Figs. 5–8. Examination of the close correspondence in spectral patterns of the four mass spectra confirms that these compounds are isomers, with

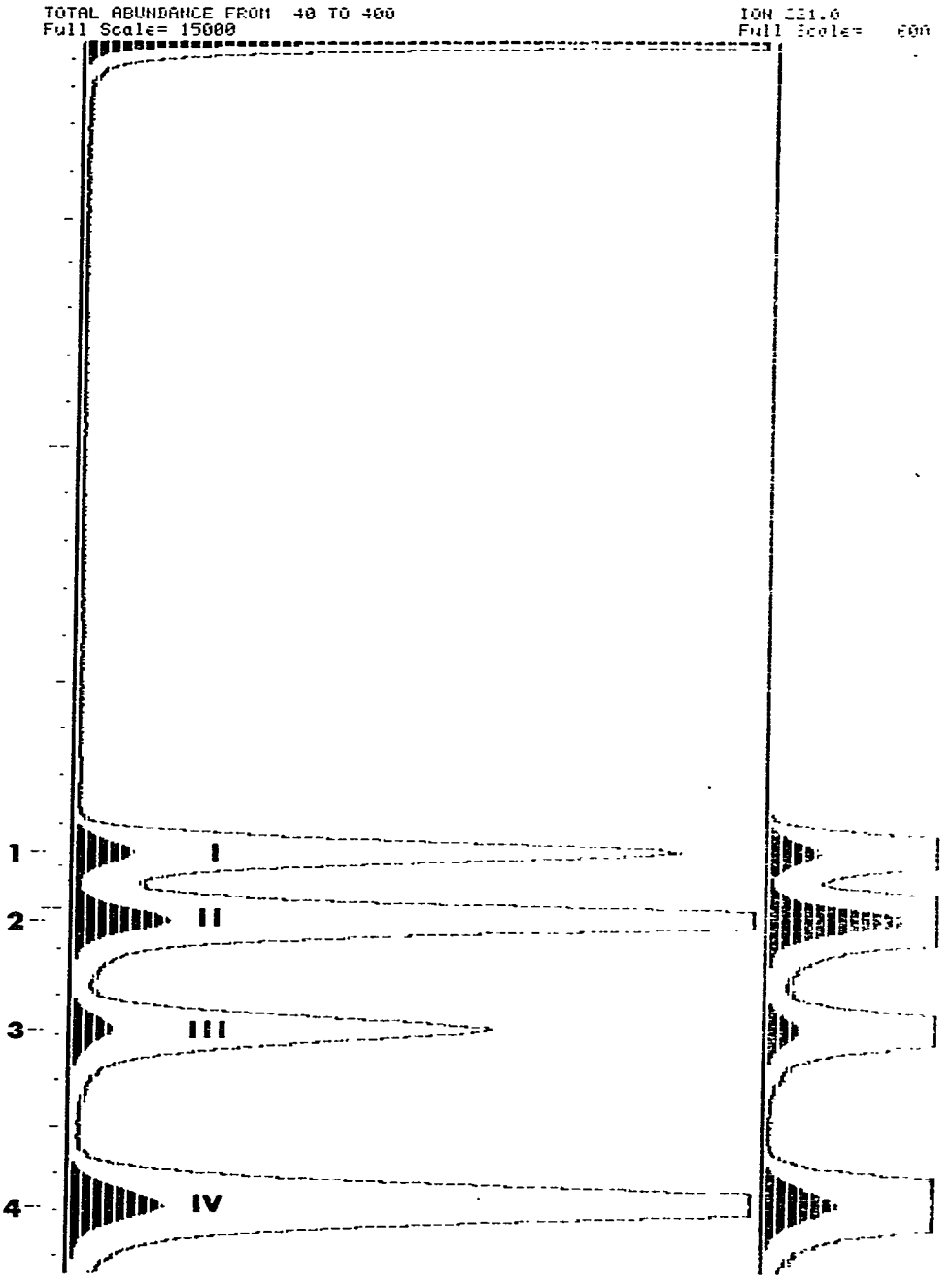

Fig. 3. The reconstructed chromatogram obtained with the HP 5992A GC–MS–calculator system for a 2-μl injection of the sample solution of the four isomers shown in Fig. 1 is recorded at two different sensitivities along with corresponding mass chromatograms for the *m/e* 221 ion. Positions where the four mass spectra shown in Fig. 4 were taken are indicated by number. Minutes of retention time are indicated by baseline dash marks.

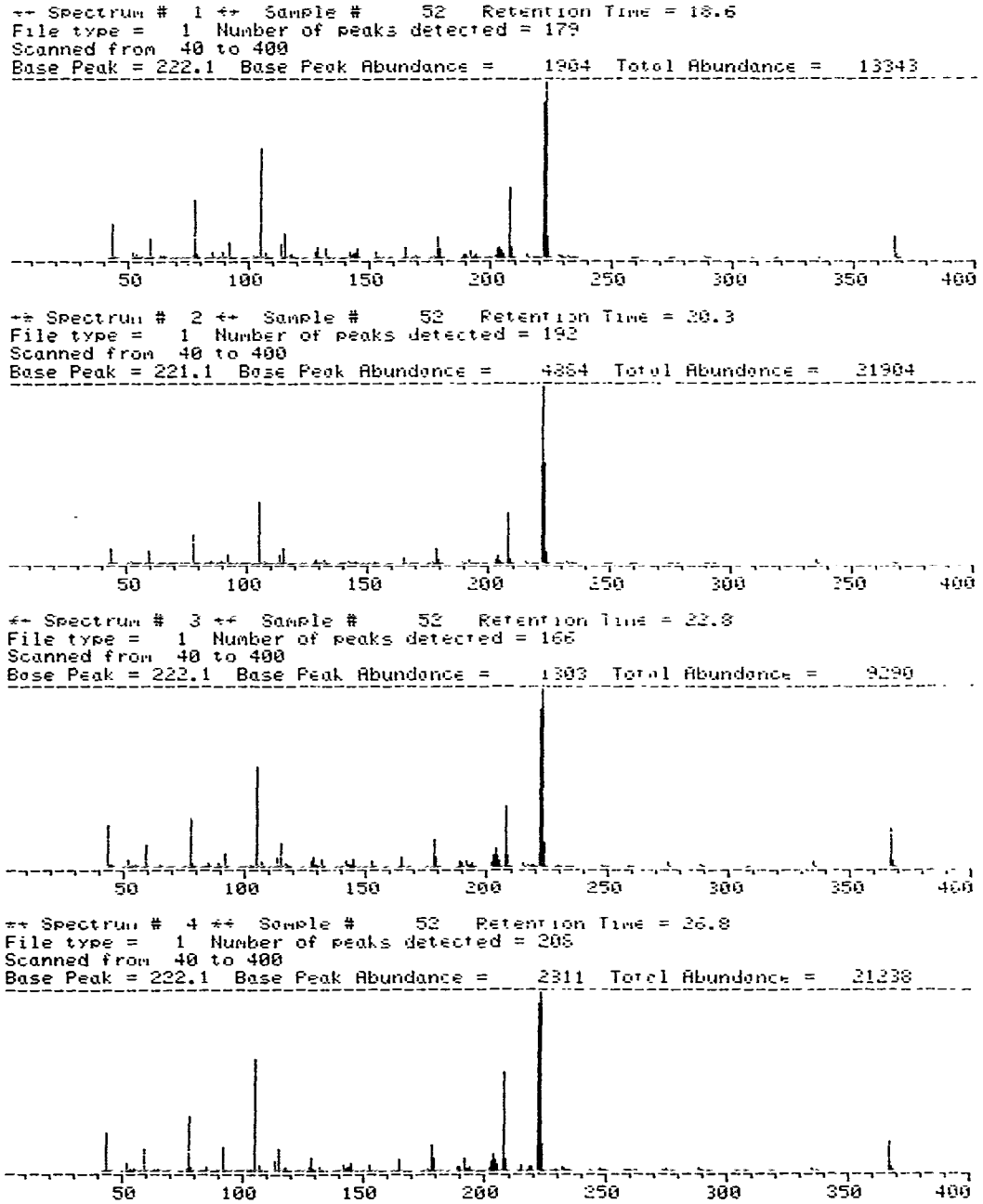

Fig. 4. Mass spectra obtained during the GC–MS analysis of Fig. 3 as plotted by the GC–MS–calculator system.

TABLE I

KOVÁTS' RETENTION INDICES FOR DIMETHYL ESTER ISOMERS

Compound	*Index*
I	2837
II	2858
III	2897
IV	2938

++ Spectrum # 1 ++ Sample # 52 Retention Time = 18.6
File type = 1 Number of peaks detected = 179
Scanned from 40 to 400
Base Peak = 222.1 Base Peak Abundance = 1904 Total Abundance = 13343
Lower Abundance Cutoff Level = 0.8

MASS	ABUNDANCE	MASS	ABUNDANCE	MASS	ABUNDANCE
41.1	1.5	115.0	15.1	194.1	3.8
43.1	20.1	116.0	2.9	195.1	1.8
44.1	1.8	117.0	3.0	197.1	1.5
45.1	1.5	118.0	0.9	200.1	1.3
51.1	4.9	126.0	1.0	201.1	2.1
53.0	3.6	127.0	4.2	202.1	6.0
55.1	2.5	128.0	7.1	203.1	7.7
59.0	12.5	129.0	1.3	204.2	5.8
63.1	2.1	130.0	1.8	205.2	3.0
65.1	2.7	131.1	5.1	206.2	1.1
69.1	0.9	139.1	1.6	207.0	40.8
70.1	0.9	141.1	4.3	208.1	7.8
75.0	1.1	142.1	2.9	209.0	0.8
76.1	2.4	143.1	3.2	215.1	3.6
77.1	32.9	144.1	3.3	216.1	1.8
78.1	3.3	145.1	6.1	218.1	1.6
79.1	0.9	146.0	1.5	219.1	1.6
81.1	0.9	150.0	0.9	221.1	87.3
82.0	0.9	151.1	1.8	222.1	100.0
84.1	0.8	152.1	4.3	223.1	13.2
85.0	4.7	153.1	1.0	224.1	1.1
89.0	4.1	157.1	0.8	228.1	1.0
90.0	1.1	164.0	0.9	229.1	2.3
91.0	10.4	165.0	7.7	231.1	3.0
92.1	1.1	166.1	1.7	232.1	1.1
94.6	0.8	169.0	2.0	233.1	1.2
97.1	1.3	176.0	2.1	245.1	1.0
99.0	1.0	177.0	1.6	247.1	1.7
101.1	2.3	178.1	13.6	257.1	1.4
102.1	1.6	179.1	6.4	259.0	1.0
103.1	2.1	180.2	1.3	275.0	1.8
105.0	62.1	189.1	3.0	288.1	2.4
106.0	4.8	190.1	3.1	335.1	3.5
107.1	0.9	191.2	5.0	366.1	13.1
113.0	9.3	192.1	1.5	367.1	3.0
114.0	1.7	193.1	2.6		

Fig. 5. Tabulated mass spectrum of compound I.

some interesting differences in the spectrum of the isomer producing the II GC peak. The intensity of the molecular ion and the *m/e* 221, 222 pair differ from those found in the spectra of the other three compounds, all of which exhibit almost identical spectra.

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** Spectrum #   2 **   Sample #      52   Retention Time = 20.3
File type =    1   Number of peaks detected = 192
Scanned from  40 to 400
Base Peak = 221.1   Base Peak Abundance =     4884   Total Abundance =    21994
Lower Abundance Cutoff Level =   0.5
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MASS	ABUNDANCE	MASS	ABUNDANCE	MASS	ABUNDANCE
41.1	1.0	126.0	0.5	194.1	2.9
43.1	9.4	127.0	2.0	195.1	0.9
44.1	0.8	128.0	3.4	197.1	0.6
45.1	1.0	129.1	1.7	200.1	0.6
51.1	2.9	130.0	0.9	201.1	1.2
53.0	1.5	131.1	3.1	202.1	3.8
55.1	1.6	139.1	1.0	203.1	5.2
59.1	8.4	141.1	2.4	204.1	2.3
63.0	1.4	142.1	1.5	205.2	1.9
65.1	1.3	143.1	1.6	206.1	0.8
69.0	0.7	144.1	2.0	207.1	29.3
75.1	0.9	145.1	2.8	208.1	3.9
77.1	17.2	146.0	0.7	215.1	2.4
78.1	1.7	150.1	0.6	216.0	0.7
85.0	2.5	151.1	1.1	217.1	0.5
88.0	0.6	152.0	2.4	218.1	0.9
89.0	2.2	153.3	0.8	219.1	1.3
90.0	0.5	157.1	0.6	221.1	100.0
91.1	6.8	163.0	0.5	222.1	55.7
92.1	0.7	165.0	4.9	223.1	7.2
99.1	0.8	166.0	0.7	228.1	0.6
101.0	1.6	169.1	1.0	229.1	1.1
102.1	1.1	176.1	2.1	231.1	2.1
103.1	1.1	177.1	1.6	232.1	0.9
105.0	35.0	178.1	9.7	233.1	0.6
106.0	2.6	179.1	3.9	247.1	0.9
107.0	0.6	180.1	0.6	259.0	0.5
113.0	6.2	189.1	2.3	275.0	0.9
114.0	0.9	190.1	1.6	288.1	1.1
115.0	10.0	191.1	3.0	335.1	3.2
116.0	1.8	192.1	0.9	336.1	0.6
117.0	1.7	193.1	1.7	366.1	0.8
118.0	0.6				

Fig. 6. Tabulated mass spectrum of compound II.

All four adducts have been isolated as pure crystalline compounds. The two maleate (*cis*) adducts (GC peaks II and IV) have been shown by NMR and IR studies to have the structures given in Fig. 1. The stereochemistry of the two fumarate adducts (peaks I and III) has not been definitely established as yet; so that differentiation between these two compounds by the assignment given is tentative.

The mass spectra of all four adducts have been measured also on a conventional magnetic mass spectrometer using the solid probe inlet. These spectra gave excellent agreement with those obtained by the GC–MS system, although there were the minor variations which one would expect between spectra from a magnetic and quadrupole mass spectrometer. The ion at *m/e* 221 or 222 (*m/e* 222 appears to be due to a retro Diels–Alder rearrangement) were the base peaks in both systems. The molecular ion was found for all spectra from both instruments, ranging from 7 to 45% relative abundance. However, other high mass fragments, particularly *m/e* 247 and 275, were more abundant on the magnetic instrument. Conversely, the lower mass fragments of *m/e* 77 and 105 were about one-half the relative abundance of these ions found with the GC–MS quadrupole system. Relative intensities of ions in clusters matched very well. Neither spectra gave any obviously doubly charged ions. The magnetic mass

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** Spectrum #   3 **  Sample #      52   Retention Time = 22.8
File type =    1  Number of peaks detected = 166
Scanned from  40 to 400
Base Peak = 222.1  Base Peak Abundance =    1303  Total Abundance =    9290
Lower Abundance Cutoff Level =   0.8
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MASS	ABUNDANCE	MASS	ABUNDANCE	MASS	ABUNDANCE
41.1	2.1	116.0	3.1	197.1	1.4
43.1	24.0	117.0	2.6	200.1	0.9
44.1	2.4	118.0	0.8	201.1	3.2
45.1	2.1	126.0	1.0	202.1	7.7
50.1	1.1	127.0	4.6	203.1	11.7
51.1	5.5	128.0	6.0	204.2	7.1
52.1	1.0	129.0	2.1	205.2	4.3
53.0	2.4	130.0	2.2	206.1	1.0
55.1	2.9	131.1	5.5	207.0	35.5
57.0	1.0	139.1	2.0	208.1	8.0
59.1	13.7	141.1	4.7	209.1	1.0
63.1	1.8	142.1	2.6	215.1	3.2
65.1	2.6	143.1	2.0	216.1	2.0
69.1	1.5	144.1	2.6	218.1	2.4
70.1	1.0	145.1	5.1	219.1	3.0
71.1	1.0	146.0	1.7	220.1	1.2
75.1	1.3	151.1	1.9	221.1	88.1
76.1	2.1	152.1	4.1	222.1	100.0
77.1	28.2	153.1	1.1	223.1	14.4
78.1	3.2	155.1	0.9	224.2	1.7
79.1	0.8	157.1	0.9	228.1	1.0
82.0	0.8	163.0	0.9	229.1	2.4
84.0	1.1	165.0	6.2	231.1	2.9
85.0	3.6	166.0	1.2	232.1	1.9
89.0	3.3	169.0	1.5	233.1	1.1
90.0	0.9	176.0	1.7	235.1	0.8
91.0	8.7	177.0	1.5	247.1	2.1
92.0	1.1	178.1	16.3	249.1	1.6
97.2	1.8	179.1	6.8	250.2	0.9
99.0	1.2	180.2	1.5	257.1	1.4
101.1	3.4	189.1	4.2	259.0	1.2
102.0	2.2	190.1	3.3	274.1	1.1
103.1	1.9	191.1	5.0	275.1	3.4
105.0	56.9	192.1	2.4	288.1	2.3
106.0	4.8	193.1	2.5	335.1	4.1
107.0	1.1	194.1	3.7	366.1	32.3
113.0	6.7	195.1	1.8	367.1	4.7
115.0	14.3				

Fig. 7. Tabulated mass spectrum of compound III.

spectrum gives a metastable peak at *m/e* 193.1 corresponding to the decomposition reaction of *m/e* 222 with loss of CH_3 to give *m/e* 207.

These data provide the basis of an analytical method for both qualitative and quantitative analysis of these compounds by either GC or GC–MS instrumentation. Use of the GC–MS instrumentation is quite clearly the method of choice because of the qualitative mass spectra and mass chromatograms available which would identify these compounds in a more complex mixture. However, because of the almost identical nature of mass spectra the Kováts' retention indices are necessary so that combined with the mass spectra a positive identification can be obtained. When the GC method alone is used, then the retention indices provide the primary means of identification. In many cases of samples from studies of the synthesis of these compounds this could be adequate.

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** Spectrum #  4 **  Sample #     52   Retention Time = 26.8
File type =   1  Number of peaks detected = 202
Scanned from  40 to 400
Base Peak. = 222.1  Base Peak Abundance =    2811  Total Abundance =   21238
Lower Abundance Cutoff Level =   0.8
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MASS	ABUNDANCE	MASS	ABUNDANCE	MASS	ABUNDANCE
41.1	1.4	117.0	3.0	201.1	2.8
43.1	21.6	118.0	0.9	202.1	6.8
44.1	1.1	126.0	0.9	203.1	10.8
45.1	1.6	127.0	3.4	204.2	7.6
50.0	1.1	128.1	8.9	205.2	4.6
51.2	5.7	129.1	2.4	206.2	1.6
52.1	1.0	130.0	1.7	207.1	55.1
53.0	2.3	131.0	4.0	208.1	7.5
55.1	2.3	139.1	1.7	215.1	4.0
59.1	13.3	141.1	4.1	216.0	1.5
63.1	2.0	142.1	2.6	218.1	3.8
65.1	2.1	143.1	3.2	219.1	3.6
69.1	0.9	144.1	3.1	221.1	93.0
75.1	1.5	145.1	5.6	222.1	100.0
76.1	2.6	146.2	1.5	223.1	15.0
77.1	31.9	151.1	1.8	224.1	1.4
78.1	3.0	152.1	4.2	228.1	0.9
81.9	0.8	153.1	1.5	229.1	2.9
84.0	1.0	163.0	0.9	230.1	0.9
85.0	3.3	165.0	7.0	231.1	3.4
88.0	0.8	166.0	1.5	232.1	2.1
89.0	2.9	169.0	1.5	233.1	1.5
90.0	1.1	176.1	2.6	235.1	1.4
91.0	14.1	177.0	1.7	247.1	2.2
92.1	1.9	178.1	15.7	249.1	2.0
97.1	1.3	179.1	8.7	250.1	1.4
99.0	1.1	180.1	1.3	257.1	1.2
101.0	2.3	189.1	3.5	259.0	1.0
102.1	1.7	190.1	3.3	275.0	2.7
103.1	2.2	191.1	8.2	288.1	2.5
105.0	61.9	192.1	2.5	289.1	0.9
106.0	4.1	193.1	2.8	291.1	0.8
107.0	0.9	194.1	3.8	303.1	2.1
112.9	6.1	195.1	1.3	335.0	2.5
115.0	13.5	197.1	1.3	366.1	16.9
116.0	2.8	200.1	1.4	367.1	3.9

Fig. 8. Tabulated mass spectrum of compound IV.

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