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Mass Fragmentations. II. Some Aspects of Mass Spectra from a Series of Compounds Related to Methyl dl-Jasmonate Syntheses

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Synopsis

This paper deals with graphical mass spectral data of the twentyfive compounds related to the preparation of methyl dl-jasmonate and its related materials. The fragmentations from the substituted cyclopentanones and norbornane derivatives can serve basic data for both characterization and elucidation of the structures of complex compounds referring to the preparation of principal components of jasmine flower.

I. Introduction

In the course of the total syntheses of methyl dl-jasmonate and its related compounds starting from both 3a,7a-cis-3a,4,7,7a-tetrahydro-1-indanone[1] and/or 3-carbomethoxynorbornane-2-carboxylic acid,[2] we found some typical aspect on the mass spectral fragmentations of the compounds obtained in the synthetic works. Above all, the similar characteristic fragmentations were observed in the following cases: (Type A) the compounds whose gross structures resemble; (Type B) the compounds whose representative function groups are analogous. In some cases, the appearance of the characteristic base peak also presented useful evidences for the structural elucidation of methyl dl-jasmonate homologues (Type C). On the other hand, nevertheless the resemblance of mutual gross structures apparent correlation on fragment ions can not find in some compounds (Type D). A tentative classification according to the types A, B, C, and D is shown as follows: Type A, the compounds 2 and 3, the compounds 7 and 8, and the compounds 9a, 9b, 9c, 10, 11, and 12; Type B, the compounds cis-4, trans-4, 5, and 6; Type C, the compounds cis-1b, trans-1b, 1c, 14, 15, and 16, the compounds 9a, 9b, 9c, 10, 11, and 12; Type D, 17a, 17b, and 17c.

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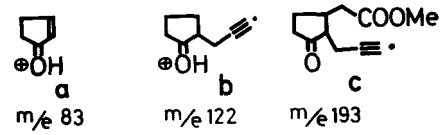
II. Results and Discussion

Mass spectra were measured at 70 eV with a Hitachi RMS-4 spectrometer. Injection temperature are 150-180°C. Mass spectral charts are shown in Fig. 1-25. The mass spectra of the compounds 1a, cis-1b, and trans-1b showed a base peak m/e 83 corresponding to a fragment a (Table 1), whereas methyl dehydrojasmonate (1c)

Table 1
Comparison of Base Peak of Compd 1a, 1b, and 1c

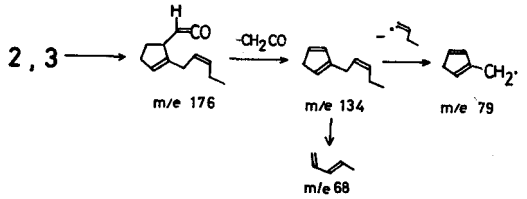
Compd.	1a	trans 1b	cis 1b	1c
Base Peak	83	83	83	122



exhibited a base peak m/e 122 due to a fragment b along with a fragment c m/e 193 (M^+-Et), indicating that the fragmentation of 1c would proceed by elimination of the ethyl group from the pentynyl function. Similar fashion producing m/e 83 was observed in the fragmentation of the compounds 14, 15, and 16.

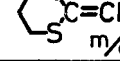
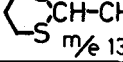
Major fragment ions from jasminebicyclo-δ-lactone 2[3] are well coincide with those of 3, i.e., m/e 134, 119, 105, 93, 79, and 68. This fact reveals that those series of ions would bring from the fragment of m/e 176.

Fragmentation of 2 and 3



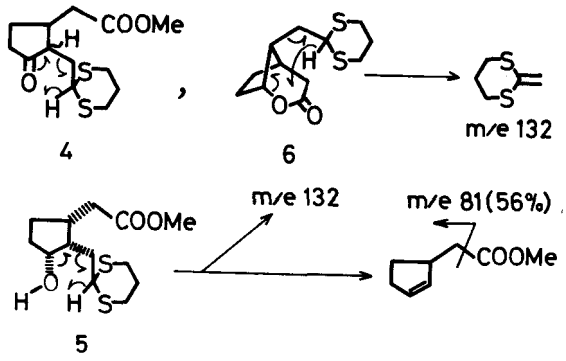
The compounds cis-4, trans-4, 5, and 6 bearing 1,3-dithianyl group could be characterized by an intense fragment ion m/e 119, which resulted in the α fission of the function (see Table 2). While the generation of another intense fragment

Table 2
Mass Spectral Data of Compd. 4, 5, and 6
(rel. int. %)

Compd	 m/e 119	 m/e 132	 m/e 133
4 cis	61	100	66
4 trans	68	100	62
5	100	74	10
6	96	100	18

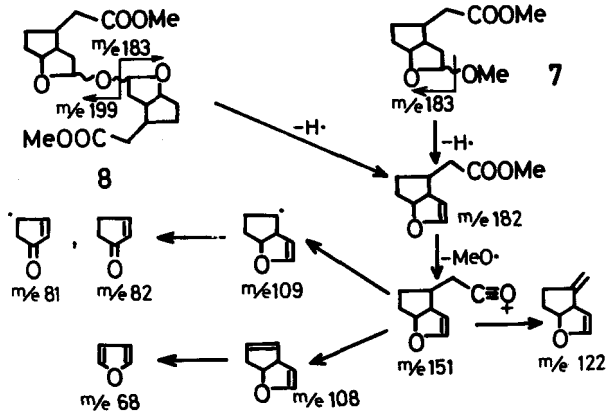
ion m/e 132 due to the 1,3-dithianyl group would cause by an intramolecular hydrogen shift as shown in the following Scheme.

Frgmentation of 4,5 and 6



From the mass spectral patterns 7 and its dimer 8 we found the straight identity on the fragmentations. This results suggest the presence of skeltal similarity which facilitates the structural elucidation of 8. A tentative fragmentation of 7 and 8 is shown in the following Scheme.

Fragmentation of 7 and 8



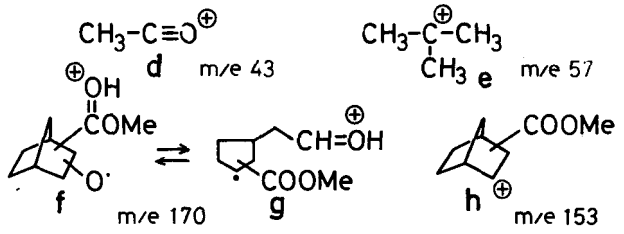
The characteristic mass peaks also appeared at m/e 43, 57, 67, 152, and 170 ascribable to the fragmentations of norbornane derivatives 9a, 9b, 9c, 10, and 11 (see Table 3). The acetates 9a, 9b, and 9c can provide a fragment d m/e 43 as a base peak, whereas the butoxide 10 affords a fragment e m/e 57 (relative intensity 93%) as shown below.

It is noteworthy that the fragmentation of 9a, 9b, 9c, and 10 would start from the formation of the fragment m/e 170 (f and g) in contrast to the expecting ion h m/e 153.

In the case of the tricyclane 13, the strong parent peak m/e 152 is recorded.

Table 3 Mass Spectral Data of Compd. 9,10, and 11

Compd.	9a	9b	9c	10	11
Base Peak m/e	43	43	43	170	67
Typical Fragment m/e(rel.int.)	170 (15)	170 (69)	170 (14)	57 (93)	152 (M^+-H_2O) (78)



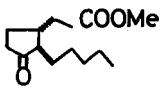
The fragmentation of the alochol 11 provides m/e 152 (M^+-H_2O). Both 11 and 12 bring base peaks m/e 67 corresponding to cyclopentadienyl cation.

In the complex molecules such as 17a, 17b, and 17c attempt of the structural assignment from mass spectral data should be carried out by independent and using another analytical data.

References

1) H. Tanaka and S. Torii, J. Org. Chem., 40, No. 2 (1975).
2) S. Torii, H. Tanaka, and T. Mandai, J. Org. Chem., in contribution.
3) R. Kaiser and D. Lamparsky, Tetrahedron Lett., 1974, 3413.

Fig 1



1a

$C_{13}H_{22}O_3$ MW 226

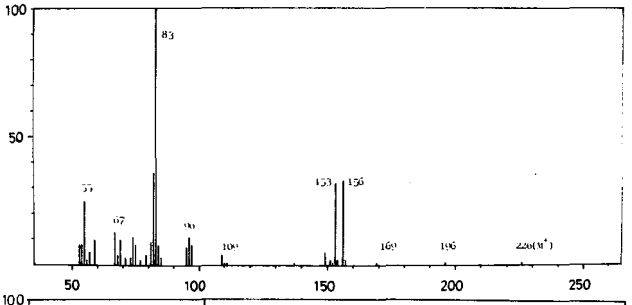
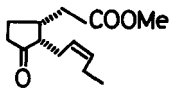


Fig 2



cis 1b

$C_{13}H_{20}O_3$ MW 224

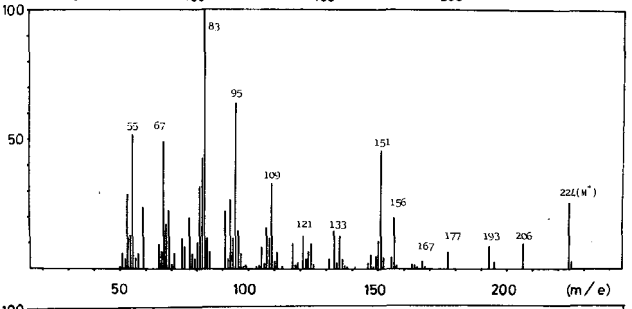
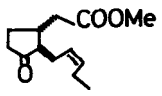


Fig 3



trans 1b

$C_{13}H_{20}O_3$ MW 224

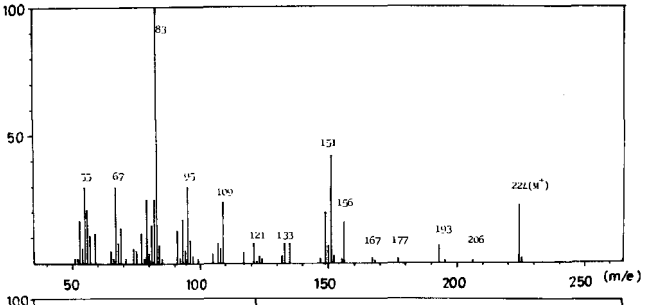
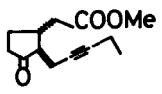


Fig 4



1c

$C_{13}H_{18}O_3$ MW 222

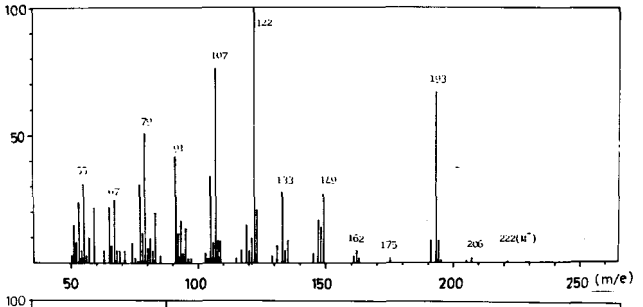
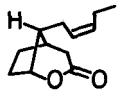
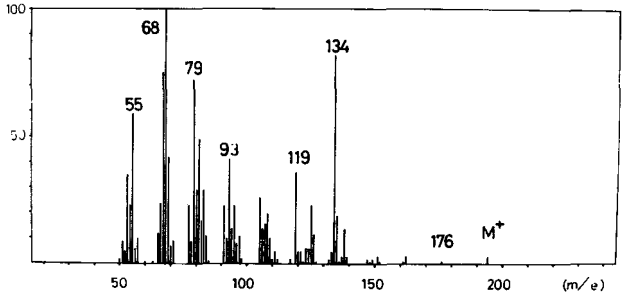


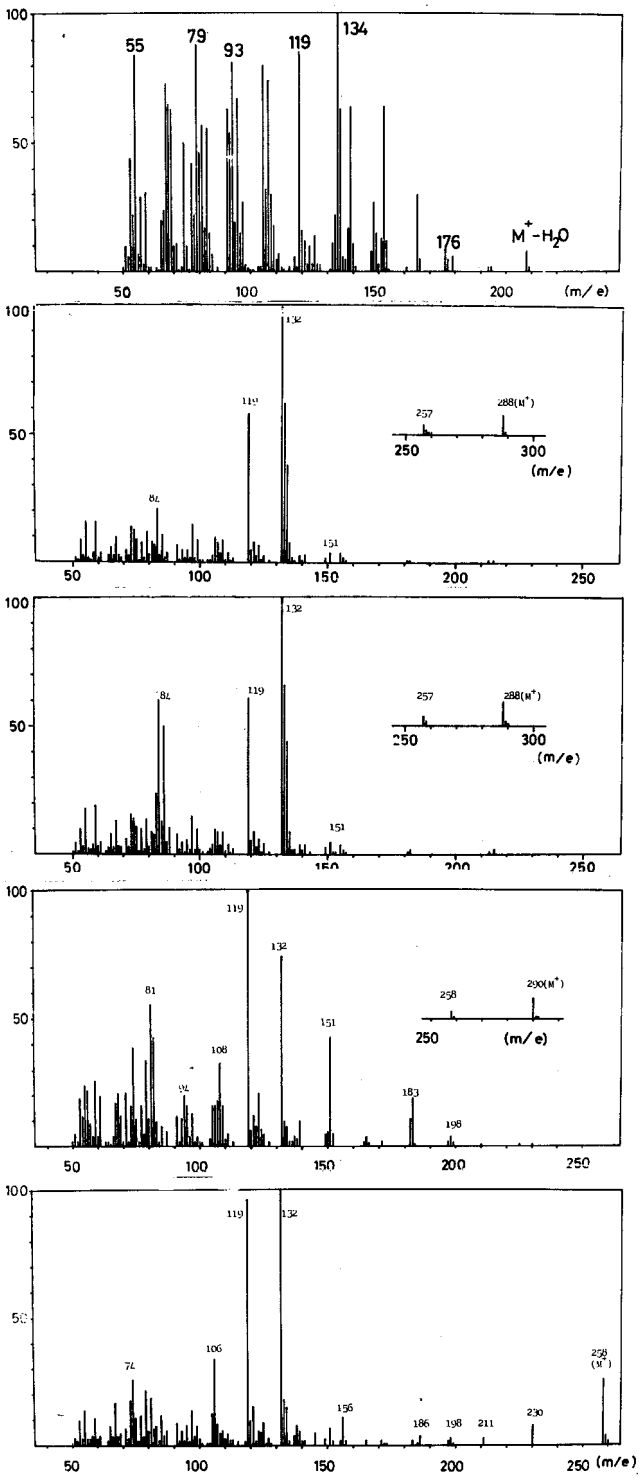
Fig 5



2

$C_{12}H_{18}O_2$ MW 194





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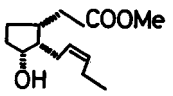
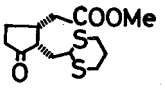


3

$C_{13}H_{22}O_3$ MW 226

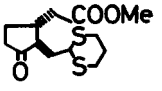
Fig 7



cis 4

$C_{13}H_{20}O_3S_2$ MW 288

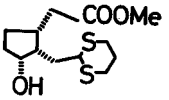
Fig 8



trans 4

$C_{13}H_{20}O_3S_2$ MW 288

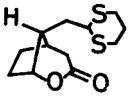
Fig 9



5

$C_{13}H_{22}O_3S_2$ MW 290

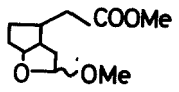
Fig 10



6

$C_{12}H_{18}O_2S_2$ MW 258

Fig 11



7

$C_{11}H_{18}O_4$ MW 214

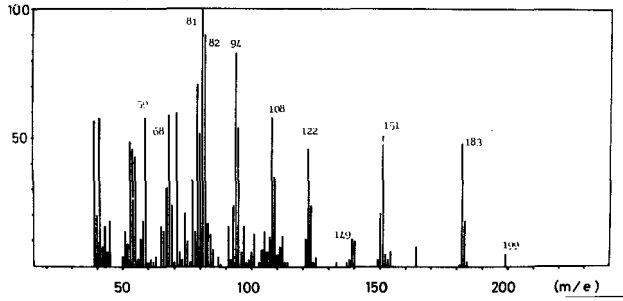
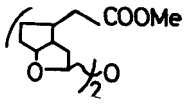


Fig 12



8

$C_{20}H_{30}O_7$ MW 382.5

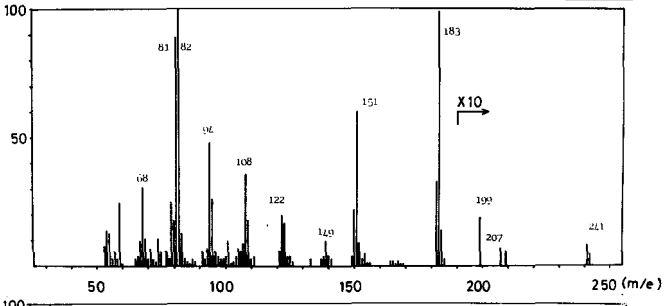
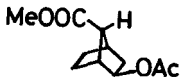


Fig 13



9a

$C_{11}H_{16}O_4$ MW 212

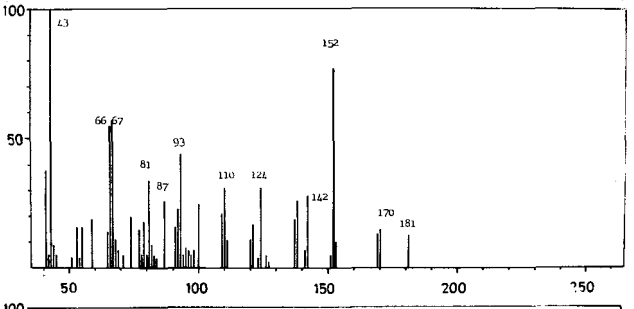
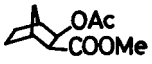
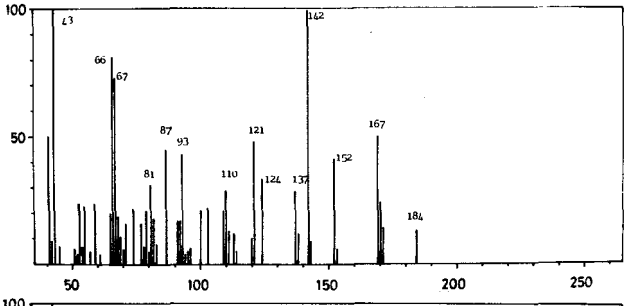


Fig 14



9b

$C_{11}H_{16}O_4$ MW 212



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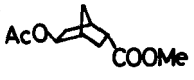
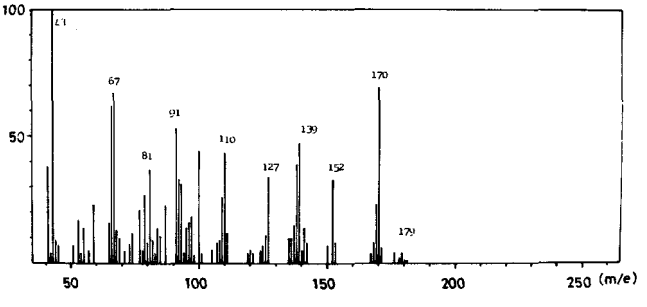


9c

$C_{11}H_{16}O_4$ MW 212



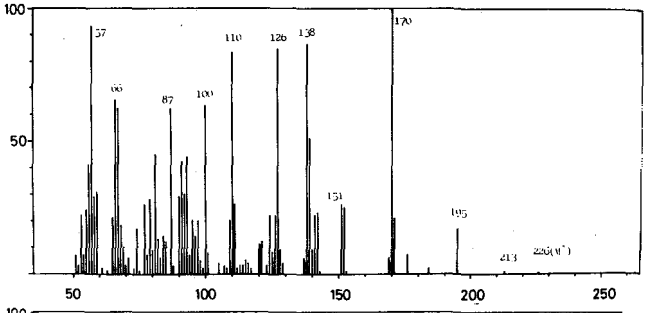
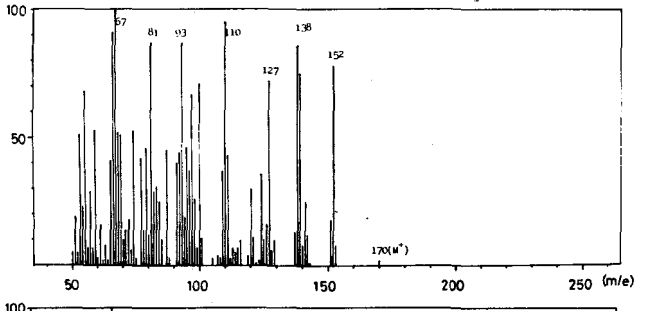


Fig 16

10

$C_{13}H_{22}O_3$ MW 226



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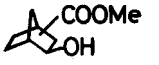
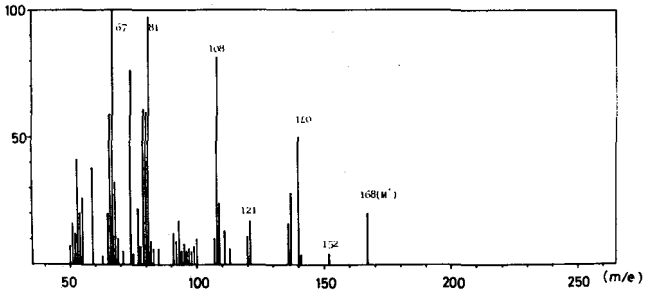


11

$C_9H_{14}O_3$ MW 170



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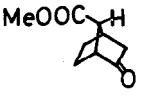

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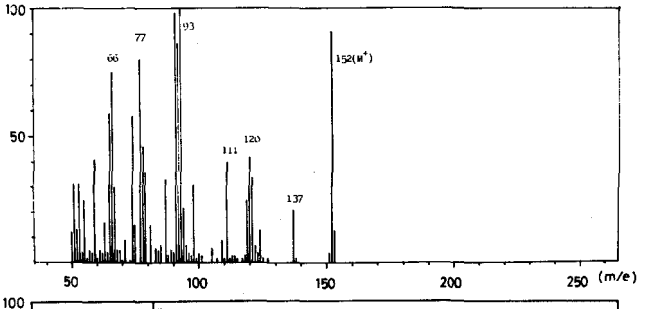
$C_9H_{12}O_3$ MW 168



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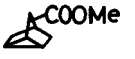


13

$C_9H_{12}O_2$ MW 152

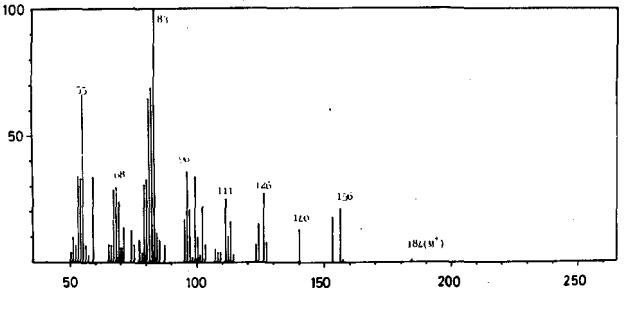
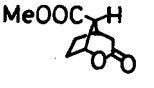


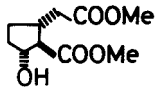
Fig 20



14

$C_9H_{12}O_4$ MW 184

Fig 21



15

$C_{10}H_{16}O_5$ MW 216

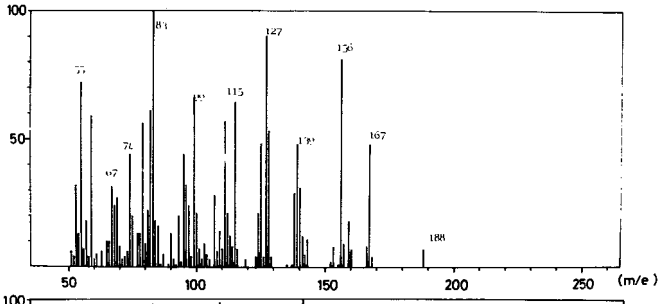
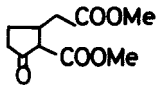


Fig 22



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$C_{10}H_{14}O_5$ MW 214

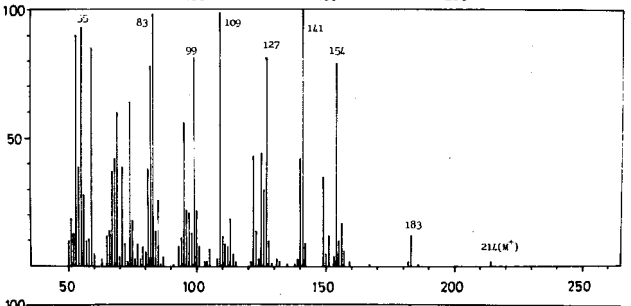


Fig 23

17a

$C_{15}H_{24}O_5$ MW 284

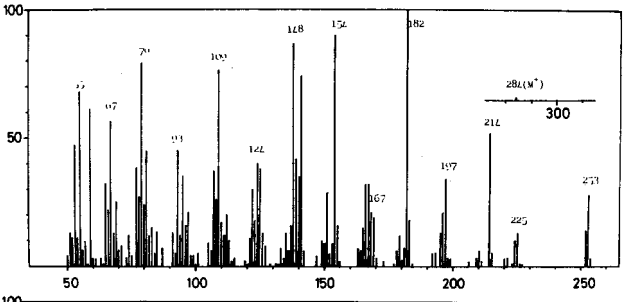
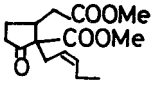


Fig 24



17b

$C_{15}H_{22}O_5$ MW 282

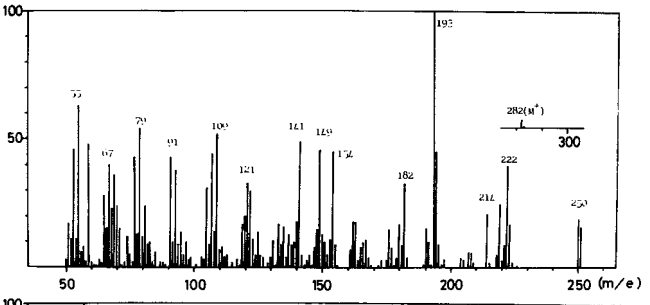
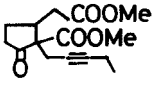


Fig 25



17c

$C_{15}H_{20}O_5$ MW 280