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SOME APPLICATIONS OF MASS SPECTROMETRY TO ORGANIC CHEMISTRY.

A thesis presented by

THOMAS ALEXANDER BRYCE

to the University of Glasgow for the degree of Doctor of Philosophy.

The Chemistry Department.

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C O N T E N T S.

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CHAPTER 1.

I N T R O D U C T I O N.

Thomson [1], in 1910, was the first to separate the different mass components of an element by passing a collimated beam of ions through a combined electrostatic and magnetic field. The ions, emerging from this field in a series of parabolic curves, were sorted according to their mass to charge ratios and were detected by a photographic plate. Aston [2], in 1919, extending the work of Thomson, demonstrated conclusively the existence of the two isotopic forms of neon using an instrument which had consecutive electrostatic and magnetic fields. Photographic detection of the ion beams was possible in Aston's apparatus as the locus of foci of ions of different mass was a plane. Such instruments, which were used for accurate measurement of mass but which were not suitable for measurement of the relative abundance of the ionic species, became known as mass spectrographs.

At about the same time, Dempster [3] was constructing the first mass spectrometer. In this instrument an essentially mono-energetic beam of ions was split into its different mass components by deflection through 180° in a homogeneous magnetic field. Instruments like this which used electrical detection of the ion beam and which, therefore, were capable of accurately measuring relative ionic abundances were known as mass spectrometers.

A convenient way of distinguishing the different kinds of instruments is the method employed to focus the ion beam. Velocity focusing is the focusing of a beam of ions, homogeneous in mass, moving in the same initial direction but at different speeds, while direction focusing is the focusing of a beam of ions, homogeneous in mass, moving at the same speed but in different initial directions. Double-focusing is that in which a beam of ions of different initial speed and direction is brought to a focus. Aston's spectrograph and Dempster's spectrometer, which were the fore-runners of modern instruments, had only single-focusing properties, the former having velocity, but not direction focusing; the latter had direction, but not velocity focusing of the ion beam.

The general theory of the double-focusing of an ion beam was derived by Herzog [4] and the design used by Mattauch and Herzog [5] for a double-focusing mass spectrograph is still widely used today. Modern double-focusing mass spectrometers are usually of the design of Johnson and Nier.[6] Double-focusing mass spectrographs and spectrometers are capable of much higher resolution than single-focusing instruments as the arrangement of electrostatic and magnetic fields compensates for any spread in the energy of the ions leaving the source.

Although it was shown by Barber [7] and by Stephens [8] in 1933 that the focusing action of 180° deflection in a homogeneous magnetic field,

as in Dempster's mass spectrometer, was a particular case of the focusing action of any wedge-shaped magnetic field; it was not until 1940 that Nier reported [9] the construction of a 60° sector mass spectrometer. Single-focusing mass spectrometers which employ a magnetic field to disperse an essentially mono-energetic beam of ions are widely used today in chemical analysis.

Most of the mass analysers that have been constructed to study the mass spectra of organic molecules make use of the electron-bombardment source developed by Nier[10] to produce the ions, and a magnetic field to separate them. However, ions of organic molecules have also been produced by photon impact[11], by a strong electrostatic field (field ionization)[12] and by a high voltage spark.[13] In addition, mass analysis has been accomplished by selection in a radio-frequency field,[14] and by the time-of-flight of the ions.[15]

The use of mass spectrometers in the analysis of chemical compounds was realised by Thomson; but the unreliability of the early instruments, together with the difficulties of manipulation, deterred chemists from applying mass spectrometry to their problems. However, the demand for rapid, accurate analysis of hydrocarbons by the petroleum industry together with advances in electronic methods led to the production of reliable mass spectrometers. The mass spectrometer was used to determine quantitatively the amounts of hydrocarbons or

types of hydrocarbon which were known to be present in a gaseous mixture. The first example of such an analysis was given by Hoover and Washburn[16] and it was later shown[17] that the method was not restricted to hydrocarbons. This method of analysis is dependent on (i) the reproducibility of the mass spectrum of a given compound under fixed operating conditions; (ii) the mass spectrum of a mixture being a linear superposition of the mass spectra of the components of the mixture; and (iii) the direct proportionality of the sensitivity for the reference peak of a component to the partial pressure of that component in the mixture. The first use of electronic digital computers in mass spectrometry[18] was in reducing the time required for this kind of quantitative analysis.

The need for any compound under examination in a mass spectrometer to be in the vapour state prevented the early workers in this field from examining those compounds which were not gases under normal conditions of temperature and pressure. In the usual gas system the pressure is maintained at approximately 10^{-2} torr in a glass reservoir of 2-3 litres volume and allowed to diffuse through a leak under conditions of molecular flow to the ionization chamber, where the pressure is of the order of 10^{-6} torr. The introduction of systems of this type that could be operated at elevated temperatures by O'Neal and Wier[19] and Caldecourt[20] increased the range of compounds which

could be admitted into a mass spectrometer. Nevertheless, many involatile or thermally unstable compounds could still not be examined because a sufficient sample pressure could not be attained in the reservoir to obtain a mass spectrum. Organic compounds in the vapour phase tend to decompose in contact with heated metals, thus heated reservoir systems made entirely of glass have been developed.

The difficulty in obtaining the mass spectra of involatile or thermally unstable compounds was finally overcome by the development of methods of introducing the sample directly into the ionization chamber.[21] By this means a sufficient sample pressure to obtain a mass spectrum can be attained at approximately 100° less than the temperature required using a heated reservoir system. The speed of operation of a direct inlet system may be greatly increased if it allows samples to be changed without breaking the mass spectrometer vacuum. The problem of keeping the sample pressure constant during the recording of the spectrum when employing a direct inlet system has been largely overcome by the use of fast scanning. The main advantages to the organic chemist of such systems are that the mass spectrum of almost every kind of organic compound can be determined, and that as little as 10^{-6} gm. of sample is required, whereas 10^{-3} gm. of sample may be required for a reservoir system.

From the time that the mass spectra of propane and butane were

reported by Stewart and Olson[22], a vast amount of data has been accumulated concerning the behaviour of organic molecules under electron impact. Two approaches to a theory of mass spectra have been made. The more fundamental approach is the quasi-equilibrium theory of Rosenstock, Wallenstein, Wahrhaftig and Eyring[23]. The two principal assumptions of this theory are that the processes leading to the formation of a mass spectrum are a series of competing, consecutive, unimolecular reactions, and that the rate constants for each of these reactions can be calculated by an appropriate form of the absolute reaction rate theory. The absolute reaction rate theory proposes that the rate of a reaction is determined by the concentration and properties of the activated complexes which are in equilibrium with the reactant species. If sufficient information about the parameters of the activated complexes is known, it is possible to perform quantitative calculations of mass spectra and compare them with experimentally determined values. In spite of the difficulties involved, such calculations have been made for small molecules; however, the problems associated with these calculations for larger molecules means that the theory in its present state has little application to the bulk of organic compounds. A recent review and assessment of the future of the theory has been made[24].

The second and more useful approach for the analytical chemist is

that developed by McLafferty. McLafferty postulated[25] that the factors which determine the formation of abundant ions in mass spectra are the relative stabilities of (i) the ion and neutral fragment, (ii) the bonds of the decomposing ion; and (iii) the possibility of fragmentation through a cyclic transition state. This approach, which is of a more intuitive and empirical nature, also attempts to rationalize fragmentations observed in a mass spectrometer in terms of such concepts of physical-organic chemistry as resonance; inductive effects; stabilities of carbonium; oxonium ions etc. The evidence that mass spectral reactions parallel those of solution chemistry is growing. Indeed, it has been shown that substituent effects in the mass spectra of certain benzoyl compounds can be quantitatively related to the Hammet "sigma" constants for these substituents.[26] The theory also requires that the positive charge be localized at favoured positions in the molecule, i.e., at hetero-atoms or other functional groups in the molecule, an idea due to Cummings and Bleakney.[27] The localized charge then dictates the course of the subsequent decomposition of the molecule.

Djerassi and his associates[28] have developed the localized charge concept and have often applied it with considerable success in the extensive studies they have made. As an aid to the understanding of mass spectrometer processes the same group has, by the use of compounds suitably labelled with heavy isotopes, elucidated the mechanisms of

many hydrogen atom rearrangement reactions[28] which are often observed in the mass spectra of organic molecules. However, deficiences in the localized charge concept have been pointed out[29] and have limited its acceptance.

Biemann[30], using the physical-organic chemistry approach but not using the localized charge theory, has given a set of empirical rules which attempt to summarize known fragmentation processes.

Recently, McLafferty[31] has described a "a generalized mechanism for mass spectral reactions." This mechanism which is a modification of his original theory considers that the positive charge and unpaired electron of an odd-electron ion can be positioned at different sites in the ion and that each exerts a separate influence on the course of fragmentation of the ion.

A different approach, of some use to the analytical chemist, is that of chemically modifying a functional group such that it will then cause the molecule to fragment by known and predictable paths. In this way it is hoped that the position of the functional group in the molecule can be readily ascertained. Such derivatives which have been used successfully include ethylene ketal[32] and thioketal[33], N,N-dimethylamino[34], and O-isopropylidene[35] groups.

The use of high resolution mass spectrometers in organic chemistry was pioneered by Beynon[36] who realized that, because of the differences

in the nuclear packing fraction[37] of the elements, it was possible to distinguish ions that were of the same nominal mass but differing chemical composition. Thus, if an instrument of sufficiently high resolving power were available, not only could the molecular formula of the compound be obtained by accurately measuring the mass of the molecular ion, but also a great deal of information concerning the structure of the compound by mass measuring the abundant fragment ions. This technique was also extremely useful in studying the mass spectra of compounds whose structures were known. For example, Beynon[38] was able to show that the ion of mass twenty-eight units less than the molecular ion of phenol was formed by the loss of carbon monoxide and not ethylene. Many similar applications of high resolution mass spectrometry have been described.[36]

It was soon obvious that more information would be forthcoming if the elemental compositions of all the ions in a mass spectrum were known. The time required to do this by the peak-matching[39] method commonly employed in double-focusing mass spectrometers was prohibitive. Thus, until 1964 only a few complete high resolution mass spectra of low molecular weight compounds had been reported.[40] At this time, however, Biemann[41] described a rapid, accurate method for precise mass determination of all ions in a spectrum obtained from a double-focusing mass spectrograph. In this method the high resolution mass spectra of

the sample and of a calibration compound are recorded on a photographic plate. One set of lines on the photographic plate corresponds to the ions of known mass from the calibration compound, while the other set of lines corresponds to ions of unknown mass from the sample. Therefore it is possible to relate the distances between the lines on the plate to the difference in mass of the ions which produce the lines. By making use of a suitably programmed computer the calculation of the masses of the ions of the sample can be rapidly performed. The term "element map" was used to describe the particular way that the final data, i.e., the elemental compositions of the ions, was arranged.

A system suitable for use in mass spectrometers has recently been described.[42] In this system the mass spectra of the sample and calibration compound are recorded on magnetic tape, the time interval between the ions being related to the mass difference of the ions.

When using an "element map" to determine the structure of an organic compound it is obviously necessary to have a knowledge of those rearrangements which involve the migration of alkyl groups and which involve the elimination of small molecules, the atoms of which are not chemically bonded in the neutral molecule. The migration of alkyl groups was originally thought to be of rare occurrence, but recent investigations[43] have shown that such migrations may be more common than imagined. Similarly, reactions like the elimination of carbon monoxide from the molecular ion of 1- nitronaphthalene[44] must be fully

documented for the full potential of the "element mapping" technique to be utilised.

REFERENCES.

1. J. J. Thomson, "Rays of positive electricity and their application to chemical analyses." Longmans, Green and Co., Ltd., London, 1913.

2. F. W. Aston, Phil.Mag., 1919, 38, 709.

3. A. J. Dempster, Phys. Rev., 1918, 11, 316.

4. R. K. F. Herzog, Z. Physik, 1934, 89, 447.

5. J. Mattauch and R. F. K. Herzog, Z. Physik, 1934, 89, 786.

6. E. G. Johnson and A. O. Nier, Phys. Rev., 1953, 91, 10.

7. M. Barber, Proc. Leeds phil. lit. Soc., 1933, 2, 427.

8. W. E. Stephens and A. L. Hughes, Phys. Rev., 1934, 45, 123; W. E. Stephens, ibid., 1934, 45, 513.

9. A. O. Nier, Rev. Sci. Instr., 1940, 11, 212.

10. A. O. Nier, Rev. Sci. Instr., 1947, 18, 398.

11. See for example, V. H. Dibeler, R. M. Reese and M. Krauss in "Advances in Mass Spectrometry," Vol III, W. L. Mead, ed., p.471, The Institute of Petroleum, London, 1966.

12. A. J. B. Robertson and B. W. Viney in ref. 11, p. 23; H. D. Beckey, H. Knoppel, G. Metzinger and P. Schulze in ref. 11, p.35.

13.(a) F. N. Hodgson, M. Desjardins and W. L. Baun, J. Phys. Chem., 1963, 67, 1250; (b) J. H. Beynon in "Mass Spectrometry," R. I. Reed, ed., p. 359, Academic Press, London, 1965.

14. See for example, C. Brunnee in ref. 13(b) p.37.

15. A. E. Cameron and D. F. Eggers, Rev. Sci. Instr., 1948, 19, 605; W. C. Wiley and H. M. McLaren, ibid., 1955, 26, 1150.

16. H. Hoover and H. W. Washburn, Amer. Inst. Min. Met. Engineers, 1940, Technical Publication No. 1205; H. Hoover and H. W. Washburn, Calif. Oil World, 1941, 34, 21.

17. H. W. Washburn, H. F. Wiley, S. M. Rock and C. E. Berry, Ind. Eng. Chem., Analyt., 1945, 17, 74; A. K. Brewer and V. H. Dibeler, J. Res. Nat. Bur. Stand., 1945, 35, 125.

18. G. P. Barnard and L. Fox, The Institute of Petroleum, Conference on Applied Mass Spectrometry, October, 1953.

19. M. J. O'Neal and T. P. Wier, Analyt. Chem., 1951, 23, 830.

20. V. J. Caldecourt, Analyt. Chem., 1955, 27, 1670.

21. R. I. Reed, J. Chem, Soc., 1958, 3432; J. H. Beynon, R. A. Saunders and A. E. Williams, Appl. Spectroscopy, 1963, 17, 63.

22. H. R. Stewart and A. R. Olson, J. Amer. Chem. Soc., 1931, 53, 1236.

23. H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, Proc. Nat. Acad. Sci., Wash., 1952, 38, 667.

24. H. M. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions", F. W. McLafferty, ed., p.2, Academic Press, New York, 1963.

25. F. W. McLafferty in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, eds., p.93, Academic Press, New York, 1962; F. W. McLafferty in ref. 24, p.309.

26. F. W. McLafferty, Analyt. Chem., 1959, 31, 477; M. M. Bursey and F. W. McLafferty, J. Amer. Chem. Soc., 1966, 88, 529.

27. C. S. Cummings and W. Bleakney, Phys. Rev., 1940, 58, 787.

28. See for example (a) H. Budzikiewicz, C. Djerassi and D. H. Williams, "Interpretation of the Mass Spectra of Organic Compounds," and (b) "Structure Elucidation of Natural Products by Mass Spectrometry, Vol.I and II," Holden-Day, San Francisco, 1964.

29. G. Spiteller and M. Spiteller-Friedmann, Monatsh., 1964, 95, 257.

30. K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, 1962.

31. F. W. McLafferty, Chem. Comm., 1966, 78.

32. See for example, H. Audier, J. Bottin, A. Diara, M. Fetizon, P. Foy, M. Golfier and W. Vetter, Bull. Soc. chim. France, 1964, 2292; Z. Pelah, D. H. Williams, H. Budzikiewicz and C. Djerassi, J. Amer. Chem. Soc., 1964, 86, 3722.

33. ref. 28(a), pp. 54 - 58, 78 - 80; ref. 28(b) Ch. 18.

34. See for example ref. 28(b) Ch. 18.

35. J. A. McCloskey and M. J. McClelland, J. Amer. Chem. Soc., 1965, 87 5094.

36. J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier, Amsterdam, 1960.

37. F. W. Aston, "Mass Spectra and Isotopes," p.80, Edward Arnold and Co., London, 1942.

38. ref. 36, p. 352.

39. K. S. Quisenberry, T. T. Scolman and A. O. Nier, Phys. Rev., 1956, 102, 1071.

40. J. H. Beynon, R. A. Saunders and A. E. Williams, Appl. Spectroscopy, 1960, 14, 95; Analyt. Chem., 1961, 33, 221.

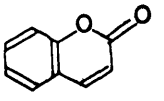
41. K. Biemann, P. Bommer and D. M. Desiderio, Tetrahedron Letters, 1964, 1725; K. Biemann, P. Bommer, D. M. Desiderio and W. J. McMurray, in ref. 11, p. 639.

42. C. Merritt, P. Issenberg, M. L. Bazinet, B. N. Green, T. O. Merron and J. G. Murray, Analyt. Chem., 1965, 37, 1037; P. Issenberg, M. L. Bazinet and C. Merritt, ibid., 1965, 37, 1074.

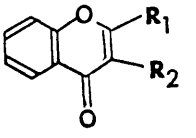
43. Recent examples include, F. Komitsky, Jr., J. E. Gurst and C. Djerassi, J. Amer. Chem. Soc., 1965, 87, 1398; A. K. Bose, I. Kugajevsky, P. T. Funke, K. G. Das, Tetrahedron Letters, 1965, 3065; C. Djerassi, A. M. Duffield, F. Komitsky, Jr., L. Tokes, J. Amer. Chem. Soc., 1966, 88, 860;

44. J. H. Beynon, B. E. Job and A. E. Williams, Z. Naturforsch., 1966, 21a, 210; J. Harley-Mason, T. P. Toube and D. H. Williams, J. Chem. Soc. (B) 1966, 396.

FIGURE I.



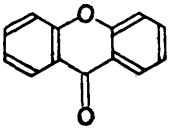
Coumarin



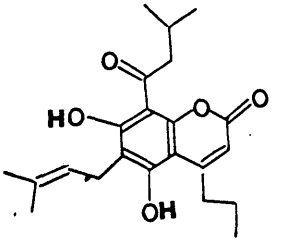
Chromone $R_1 = H$, $R_2 = H$

Flavone $R_1 = Ph$, $R_2 = H$

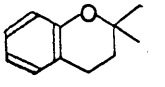
Isoflavone $R_1 = H$, $R_2 = Ph$



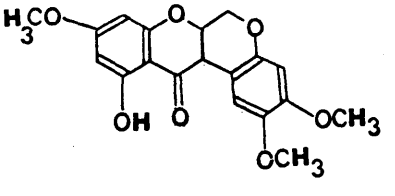
Xanthone



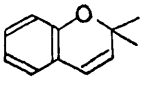
Mammein



2,2-Dimethylchroman



Sermundone (a Rotenoid)



2,2-Dimethylchromene

CHAPTER 2.

THE MASS SPECTRA OF CHROMONES.

Introduction.

The majority of chromones found in Nature are derivatives of 2-phenylchromone, i.e., flavone (Fig.I) and 3-phenylchromone, i.e., isoflavone (Fig.I). The remainder, some fifteen in number, are derivatives of 2-methylchromone. Although these compounds have a limited distribution, six being found in one plant, Ammi visnaga, and four in another, Eugenia caryophyllata, it is thought that their lack of physiological activity and of striking chemical properties may have resulted in some being overlooked. However they are not devoid of interest as, for example, one such compound, rubrofusarin, is based, not on resorcinol or phloroglucinol as are other compounds of this type, but on naphthalene; and, in addition, it has recently been shown[1] that siphulin, an acid isolated from the lichen, Siphula ceratities, is a 2-benzylchromone, the only one of its type known.

Many naturally occurring compounds are oxygen containing heterocycles and naturally occurring derivatives of benzopyran have been studied fairly extensively by mass spectrometry.[2] Thus, investigations of the mass spectra of coumarins[3,4] (benzo-α-pyrones, Fig.I), flavones[3,5] (2-phenylbenzo-γ-pyrones, Fig.I), isoflavones[3,5] (3-phenylbenzo-γ-pyrones, Fig.I), xanthones,[6] chromans[7] and chromenes[7] have been made.

One of the principal features of the mass spectra of oxygenated aromatic compounds is the elimination of the oxygen atoms as carbon monoxide or as formyl radicals. For example, peaks corresponding to $(M-CO)^+$ and $(M-CHO)^+$ are observed in the mass spectrum of phenol[8] and both coumarin[3,4] and anthraquinone[9] decompose by successive loss of two molecules of carbon monoxide. The introduction of substituents, however, may greatly reduce the importance of this type of fragmentation. In the mass spectrum of the coumarin, mammein (Fig.I) the most abundant ions are formed by fission of the valeryl and δ,δ-dimethylallyl side chains.[10]

As might be expected the mass spectrum of chromone[11] (benzo-γ-pyrone, Fig.I) is similar to that of coumarin in the respect that both spectra contain ions formed by expulsion of one and two molecules of carbon monoxide. Chromone, however, can decompose in a way not possible for coumarin. This decomposition corresponds to cleavage of the 1,2 and 3,4 bonds of the pyrone ring and can be represented as a retro-Diels-Alder reaction. A recent investigation[11] has shown that such a reaction can be used to explain the behaviour, under electron impact, of widely differing types of compounds, and that it is often possible to predict which of the two species formed by the reaction will retain the positive charge. Retro-Diels-Alder fragmentation is an important feature of the mass spectra of flavones,[3,5]

isoflavones,[3,5] rotenoids[5] (Fig.I) and 4-hydroxy-3-phenylcoumarins.[12] Ions corresponding to both species formed by this reaction are observed in every case.

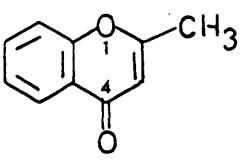
In the present study the mass spectra of a number of 2-methylchromones and 2-hydroxymethylchromones of natural and synthetic origin have been examined to investigate the correspondence between cracking pattern and structure. In addition, the possibility of applying known fragmentations of this type of compound to the chromones has been considered.

Discussion.

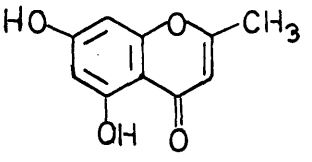
(A) Simple Substituted 2-Methylchromones.

In the mass spectrum of chromone itself two distinct fragmentation pathways are observed. The first gives rise to peaks at m/e 118 and m/e 90 corresponding to the expulsion of one and two molecules of carbon monoxide respectively. As the mass spectrum of chromone at masses less than 118 contains all the ions, with approximately the same relative intensity, as encountered in the mass spectrum of benzofuran, it is possible to suggest that m/e 118 is formed by loss of the carbonyl group from the pyrone ring followed by ring closure to give the molecular ion of benzofuran. While it is realised that such an observation does not constitute a proof of the mechanism of elimination of carbon monoxide from chromone, a similar argument has previously been used to explain the genesis of the $(M-CO)^+$ ion in the mass spectra

FIGURE II.



I



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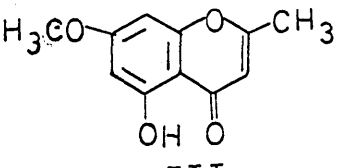
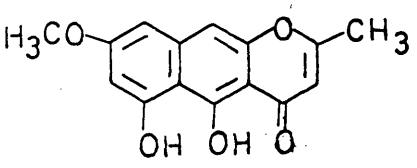
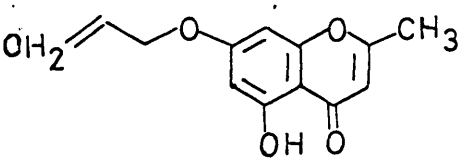


III



IV



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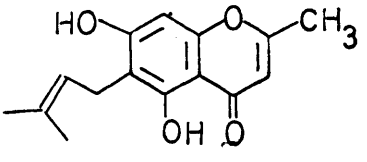

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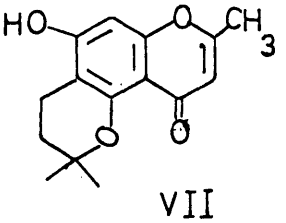
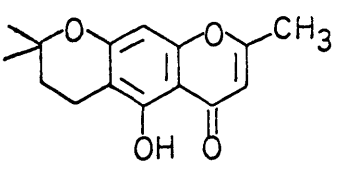
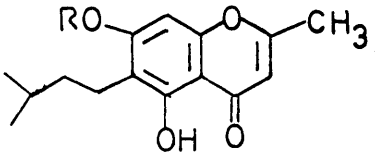


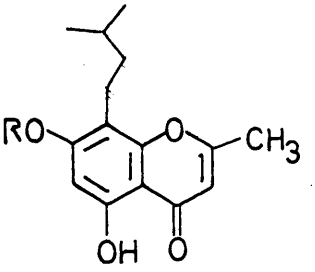
VII



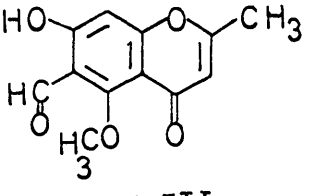
VIII



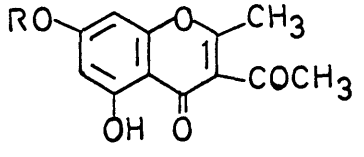
IX, R=H
X, R=CH3



XI, R=H
XII, R=CH3



XIII



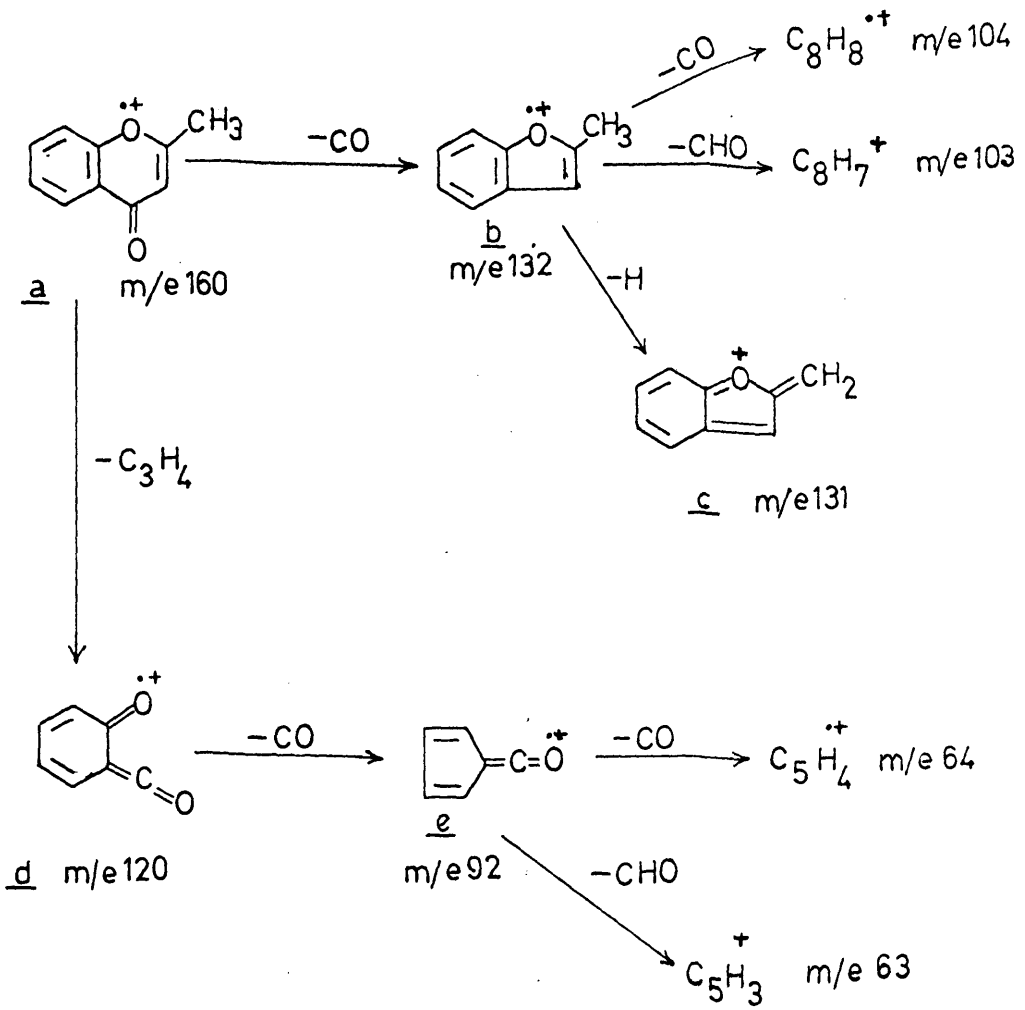
XIV, R=H
XV, R=CH3CO

of many compounds including coumarins,[3,4] α-pyrones,[13] γ-pyrones[14] and anthraquinones.[9] However, it has been recently shown, by the use of suitably labelled derivatives, that the $(M-CO)^+$ ion in the mass spectrum of α-pyrone does not have a furan structure.[15]

The second decomposition pathway of chromone involves cleavage of the γ-pyrone ring by a retro-Diels-Alder reaction, the positive charge remaining with the oxygenated species of mass 120 units. The ion of mass 120 then undergoes sequential loss of two molecules of carbon monoxide.

As expected, the mass spectral fragmentation of 2-methylchromone (I, Fig.II) is similar to that of chromone. Thus peaks are observed at m/e's 132, 120 and 92 corresponding to $(M-CO)^+$, $(M-C_3H_4)^+$ and $(M-C_3H_4-CO)^+$ respectively. However, two additional fragmentations are noted in the mass spectrum of 2-methylchromone. The $(M-CO)^+$ ion breaks down by loss of a hydrogen atom, forming m/e 131, rather than by loss of another molecule of carbon monoxide. A metastable ion at m/e 130.0 confirms that m/e 131 is formed directly from m/e 132. This difference in the behaviour of chromone and 2-methylchromone is exactly that encountered in the mass spectra of γ-pyrone and 2,6-dimethyl-γ-pyrone.[14] If the hydrogen atom is lost from the 2-methyl group in the formation of m/e 131 in the mass spectrum of 2-methylchromone, m/e 131 can be represented by a conjugated oxonium ion such as c (Fig.III). A driving

FIGURE III.



A = a → b → c

B = a → d → e

force for this step is presumably the conversion of an odd electron ion radical (m/e 132) into an even electron ion (m/e 131).

The second difference is observed in the retro-Diels-Alder fragmentation. In the mass spectrum of chromone the abundance of m/e 121 can be accounted for completely on the basis of the isotopic contribution[16] of m/e 120, the ion which is formed by the retro-Diels-Alder reaction. However, in the mass spectrum of 2-methylchromone the abundance of m/e 121 is 5% greater than the calculated isotopic contribution of m/e 120. All other compounds examined which form an ion by a retro-Diels-Alder reaction also form an ion one mass unit greater than that derived by the simple reaction. Since chromone has no such ion in its mass spectrum the presence of a 2-methyl group is a necessary condition for its formation. The complete fragmentation pattern of 2-methylchromone is shown in Fig.III.

Substitution of hydroxyl groups in the benzene ring does not alter the general fragmentation pathways already described for 2-methylchromone. Thus, the mass spectrum (Fig.1Va) of 2-methyl-5,7-dihydroxychromone (II, Fig.II) shows that it decomposes by routes analogous to A and B (Fig.III). It is possible that the $(M-CO)^+$ ion in the spectrum of 2-methyl-5,7-dihydroxychromone is formed by loss of carbon monoxide from one of the phenolic hydroxyl groups rather than from the pyrone ring. It has been suggested,[3] as the appearance potential of the $(M-CO)^+$ ion

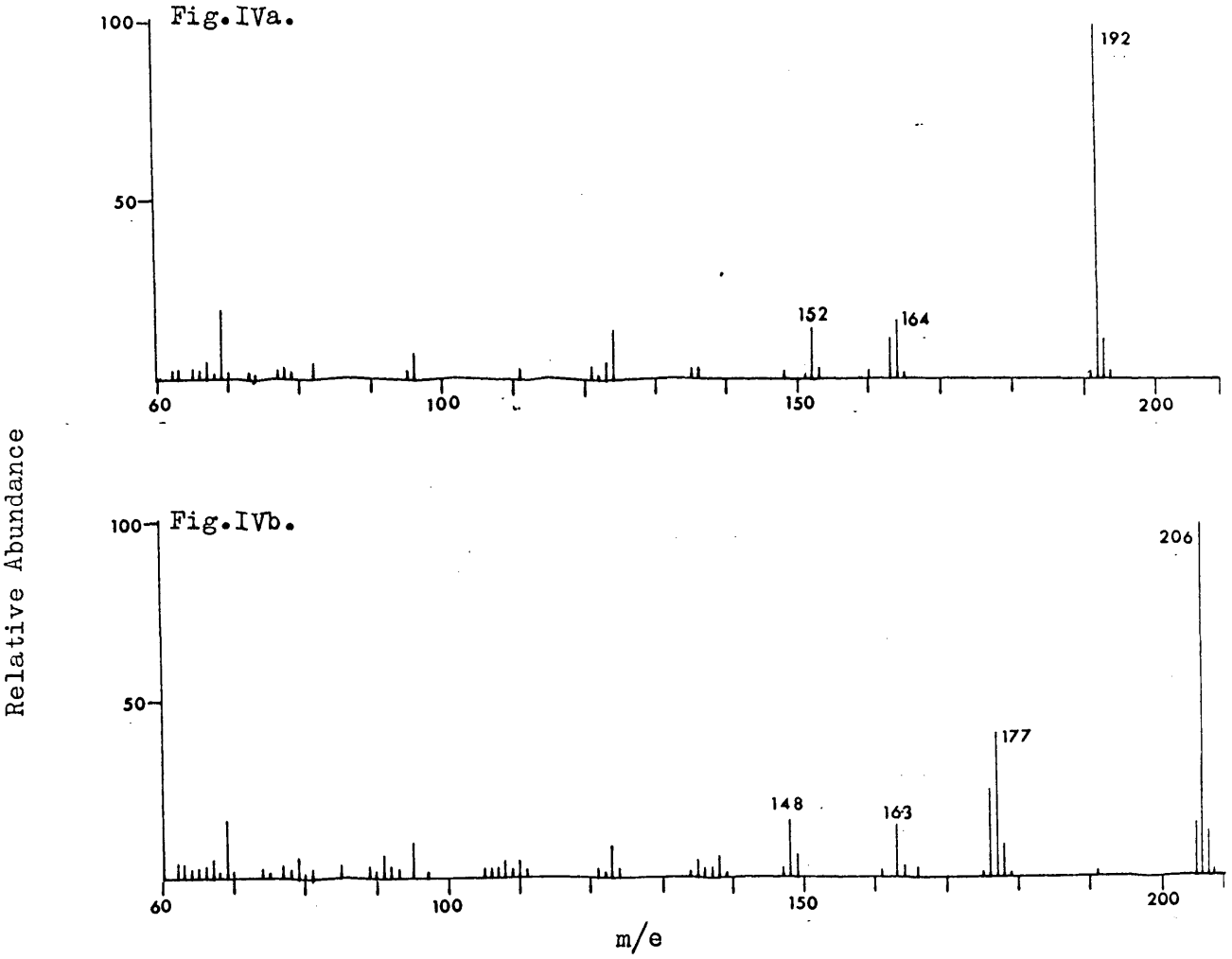


Fig.IVa: Mass Spectrum of 2-Methyl-5,7-dihydroxychromone.

Fig.IVb: Mass Spectrum of 2-Methyl-5-hydroxy-7-methoxychromone

in the mass spectrum of umbelliferone (7-hydroxycoumarin) is nearer the value of the corresponding ion in the spectrum of coumarin than in the spectrum of phenol, that the carbon monoxide molecule lost is from the lactone carbonyl and not from the phenolic substituent. In addition, Beynon and Williams[9] showed that for hydroxyanthraquinones the $(M-CO)^+$ ion is formed by loss of carbon monoxide from the ketonic portion of the molecule. Therefore, it is likely that hydroxychromones behave in the same manner, although no absolute decision could be made without studying suitably labelled derivatives.

Introduction of a methoxyl group, however, into the aromatic nucleus has a marked effect on the spectrum. Consideration of the mass spectrum (Fig.IVb.) of eugenin (2-methyl-5-hydroxy-7-methoxychromone, III, Fig.II) shows that "chromone-type" fissions (A, B Fig.III) operate only to a very small extent. Instead the mass spectrum resembles that of m-methoxyphenol. The main features of the mass spectrum of m-methoxyphenol[17] are (i) a small peak corresponding to loss of a methyl radical; (ii) intense peaks corresponding to losses of a formyl radical and formaldehyde; and (iii) an intense peak corresponding to the combined loss of a methyl radical and carbon monoxide. This behaviour is to be compared with that[17] of the ortho-and para- isomers, the mass spectra of which contain abundant $(M-CH_3)^+$ and $(M-CH_3CO)^+$ ions, no $(M-CHO)^+$ and $(M-CH_2O)^+$ ions being observed. Ions formed by the three processes outlined for m-methoxyphenol are present in the mass spectrum

of eugenin giving peaks at m/e's 191 ($M-CH_3$), 177 (M-CHO), 176 ($M-CH_2O$) and 163 ($M-CH_3CO$). Because of the close similarity between the two spectra it is reasonable to assume that the γ-pyrone system makes no contribution to the loss of a formyl radical observed in the mass spectrum of eugenin. The $(M-CH_3CO)^+$ ion is worthy of some comment. Although no metastable ion is observed for its formation it is most likely formed by explusion of carbon monoxide from the $(M-CH_3)^+$ ion. Analogous cleavages are noted in the mass spectra of 2-methoxynaphthalene[18] and m-dimethoxybenzene.[17] The suggestion has been made[19] that the carbon-oxygen bond fission giving rise to the $(M-CH_3)^+$ ion in such compounds occurs only to a small extent because the $(M-CH_3)^+$ ion cannot be stabilised by formation of an oxonium ion, and because of the preferred elimination of carbon monoxide from the $(M-CH_3)^+$ ion to form the ion $(M-CH_3CO)^+$. Weakly abundant ions of mass 166 and 123, in the mass spectrum of eugenin, arise from retro-Diels-Alder cleavage of the molecular ion and the $(M-CH_3CO)^+$ ion respectively. A metastable ion at m/e 124.5 shows that the $(M-CH_2O)^+$ ion breaks down further by elimination of carbon monoxide (m^* calculated for $176^+ \rightarrow 148^+ = 124.5$).

Rubrofusarin (IV, Fig.II), on electron bombardment, behaves in exactly the same way as eugenin. Thus ions are observed at m/e 243, m/e 242 and m/e 229 corresponding to $(M-CHO)^+$, $(M-CH_2O)^+$ and $(M-CH_3CO)^+$ respectively. M/e 189, in the mass spectrum of rubrofusarin, is formed

by retro-Diels-Alder decomposition of m/e 229. Evidence for this transition is a metastable ion at m/e 156.0 (m^* calculated for $229^+ \rightarrow 139^+ = 155.9$).

In the mass spectrum of 2-methyl-5-hydroxy-7-allyloxychromone (V, Fig.II) fission of the carbon-oxygen bond of the allyloxyl group is an important feature. The stability of the allyl ion (m/e 41), which forms the base peak of the spectrum, accounts for the prominence of this fragmentation. At higher masses ions are observed for the loss of carbon monoxide and methylacetylene from the molecular ion, thus demonstrating that this compound fragments in a manner typical of a 2-methylchromone. One point of interest in the mass spectrum of 2-methyl-5-hydroxy-7-allyloxychromone is the high abundance (80%) of the $(M-CH_3)^+$ ion. No $(M-CH_3)^+$ ion is observed in the mass spectrum of 2-methylchromone, hence it is reasonable to assume that the carbon atom lost in the formation of this ion is the terminal carbon of the allyl chain. The formation of this $(M-CH_3)^+$ ion requires the rearrangement of a hydrogen atom followed by a vinylic cleavage and there is no obvious reason why it should occur. It should be noted, however, that the mass spectrum of phenyl allyl ether contains an abundant $(M-CH_3)^+$ ion.[20]

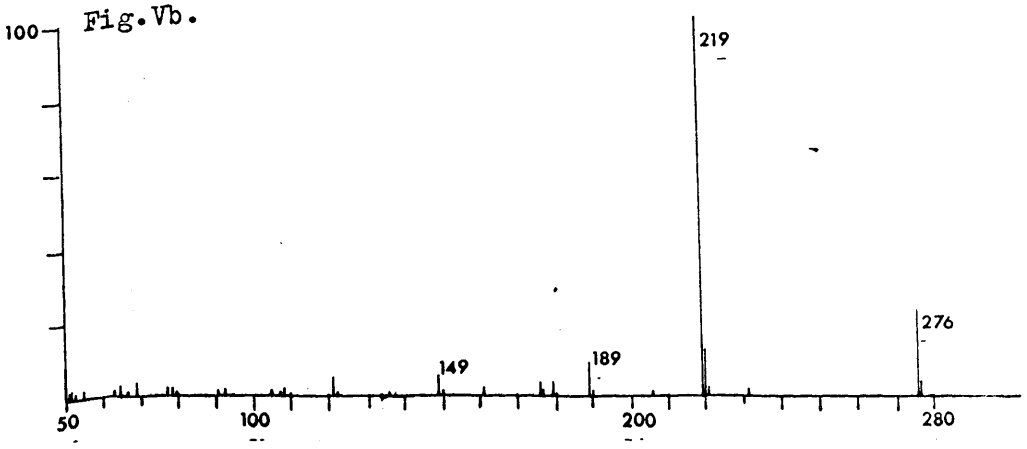
Substitution of a γ,γ-dimethylallyl group in the benzene ring or the presence of a 2,2-dimethylchroman system is also sufficient to

suppress to a great extent "chromone-type" fissions (A, B Fig.III). This is evident from the mass spectra of peucenin (VI, Fig.II) isopeucenin (VIII, Fig.II) and allopeucenin (VII , Fig.II). The mass spectra of these three compounds are very similar. A metastable ion at m/e 132.8, in all three spectra, shows that fragmentation of the γ-pyrone ring by a retro-Diels-Alder mechanism takes place from m/e 205, the base peak. (m^* calculated for $205^+ \rightarrow 165^+$ = 132.8). M/e 205 is formed by expulsion of a C_4H_7 radical from the molecular ion (m^* calculated for $260^+ \rightarrow 205^+$ = 161.6, observed 161.6) Although this fragmentation is somewhat surprising, especially in the mass spectrum of peucenin where is involves a vinylic fission, it agrees with the previously reported behaviour of γ,γ-dimethylallyl[3,4,5,21] and 2,2-dimethylchroman[3,7] systems. Only in the spectrum of isopeucenin is an abundant ion recorded for the loss of a C_4H_8 molecule. The genesis of this ion, m/e 206, can be regarded as a retro-Diels-Alder decomposition of the 2,2-dimethylchroman ring.

The ion of mass 217 in the mass spectra of peucenin, isopeucenin and allopeucenin corresponds to the loss of 43 mass units from the molecular ion, m/e 260. Observation of the appropriate metastable ion (m^* calculated for $260^+ \rightarrow 217^+$ = 181.1, observed 181.1) shows that it is formed, in every case, directly from the molecular ion. This suggests that a C_3H_7 radical is expelled in the formation of m/e 217, and

explains the greater abundance of m/e 217 in the spectrum of peucenin that in the spectra of isopeucenin and allopeucenin. The $(M-43)^+$ ion in the mass spectrum of osthol (7-methoxy-8-γ,γ-dimethylallylcoumarin) was shown, by the presence of the appropriate metastable ion, to be formed by loss of a fragment of 28 mass units from the $(M-CH_3)^+$ ion.[3] The neutral fragment of mass 28 was assumed to be carbon monoxide. On the other hand, Willhalm[7] and co-workers report that the $(M-43)^+$ ion in the mass spectrum of 2,2-dimethylchroman (Fig.I) arises by loss of a molecule of ethylene from the $(M-CH_3)^+$ ion. Exact mass measurement of m/e 217 (calculated 217.0501; found 217.0493) confirms that for peucenin, isopeucenin and allopeucenin that the $(M-43)^+$ ion consists of a single species formed by loss of a C_3H_7 radical. It would obviously be of interest to examine the mass spectra of osthol and 2,2-dimethylchroman under high resolving power conditions.

Cleavage of the alkyl side chain is also the most important fragmentation process in the mass spectrum of dihydropeucenin (1X,Fig.II). Thus peaks **are** observed at m/e's 219 $(M-C_3H_7)$, 206 $(M-C_4H_8)$ and 205 $(M-C_4H_9)$. M/e 205 is formed by β-cleavage to the ring and m/e 206 is formed by β-cleavage accompanied by migration of a hydrogen atom to the ring-containing product, in agreement with the behaviour of 1-phenylalkanes. McCollum and Meyerson[22] found that β-cleavage with hydrogen migration occurs in the mass spectra of 1-phenylpropane and



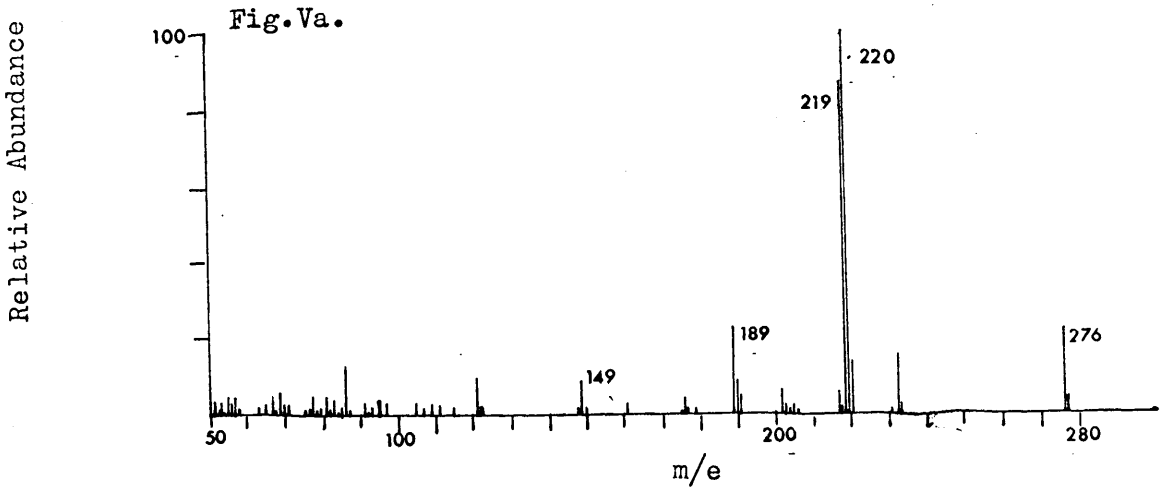


Fig.Vb: Mass Spectrum of Dihydroheteropeucenin-7-methyl ether

Fig.Va: Mass Spectrum of Dihydropeucenin-7-methyl ether.

higher homologues, and that 95% of the hydrogen which migrates is originally attached to the γ-carbon of the alkyl chain. Formation of a substituted tropylium ion would explain the high abundance of m/e 205.

A metastable ion at m/e 133.0 confirms that m/e 165, the only other ion of any importance, in the mass spectrum of dihydropeucenin, is formed by a one-step fission of m/e 205 and that this reaction corresponds to a retro-Diels-Alder decomposition of m/e 205 (m^* calculated for $205^+ \rightarrow 165^+ = 132.8$).

In contrast to the mass spectrum of eugenin (III, Fig.II), the mass spectrum (Fig.Va) of dihydropeucenin 7-methyl ether (X, Fig.II) does not contain ions corresponding to $(M-CHO)^+$ and $(M-CH_2O)^+$. Dihydropeucenin methyl ether, under electron impact, breaks down in the same manner as dihydropeucenin. Thus, the major fragmentation pathway is fission of the alkyl side chain, ions being observed at m/e's 233 ($M-C_3H_7$), 220 ($M-C_4H_8$) and 219 ($M-C_4H_9$). Decompositions involving the methoxyl and γ-pyrone functional groups are noted at lower masses as indicated by metastable ions at m/e 163.1 and m/e 117.5 corresponding to the transitions $219^+ \rightarrow 189^+ + 30$ and $189^+ \rightarrow 149^+ + 40$ respectively. Hence. m/e 219 fragments by expulsion of a formaldehyde molecule to form m/e 189 which subsequently undergoes a retro-Diels-Alder reaction to yield m/e 149. The high abundance of the ion formed by simple β-cleavage of the side

chain (m/e 219) in the mass spectrum of dihydropeucenin methyl ether may also be explained by the formation of a substituted tropylium ion.

As might be expected, the decompositions observed in the mass spectra of dihydropeucenin and dihydropeucenin methyl ether are also observed in the mass spectrum of dihydroheteropeucenin (XI, Fig.II) and in the mass spectrum (Fig.Vb) of dihydroheteropeucenin 7-methyl ether (XII, Fig.II). However, one significant difference is observed. The abundance of m/e 206 in the mass spectrum of dihydroheteropeucenin can be accounted for solely on the basis of the isotopic contribution[16] of m/e 205 i.e. no ion corresponding to β-cleavage and migration of a hydrogen atom is formed. The abundance ratio, corrected for naturally occurring isotopes, of the ion m/e 206 to m/e 205 in the mass spectrum of dihydropeucenin is 1.2/1, demonstrating that each process occurs with almost equal probability. Similarily, β-cleavage accompanied by the rearrangement of a hydrogen atom does take place in the mass spectrum of dihydroheteropeucenin methyl ether, whereas the abundance ratio, corrected for the contribution of naturally occurring isotopes, of m/e 220 to m/e 219 in the mass spectrum of dihydropeucenin methyl ether is 1/1. If the explanation for the difference in behaviour of the dihydropeucenin compounds and the dihydroheteropeucenin compounds is to be based on steric grounds, then it seems likely that the C-5 hydroxyl group must be involved in the rearrangement reaction observed in the mass

FIGURE VI.

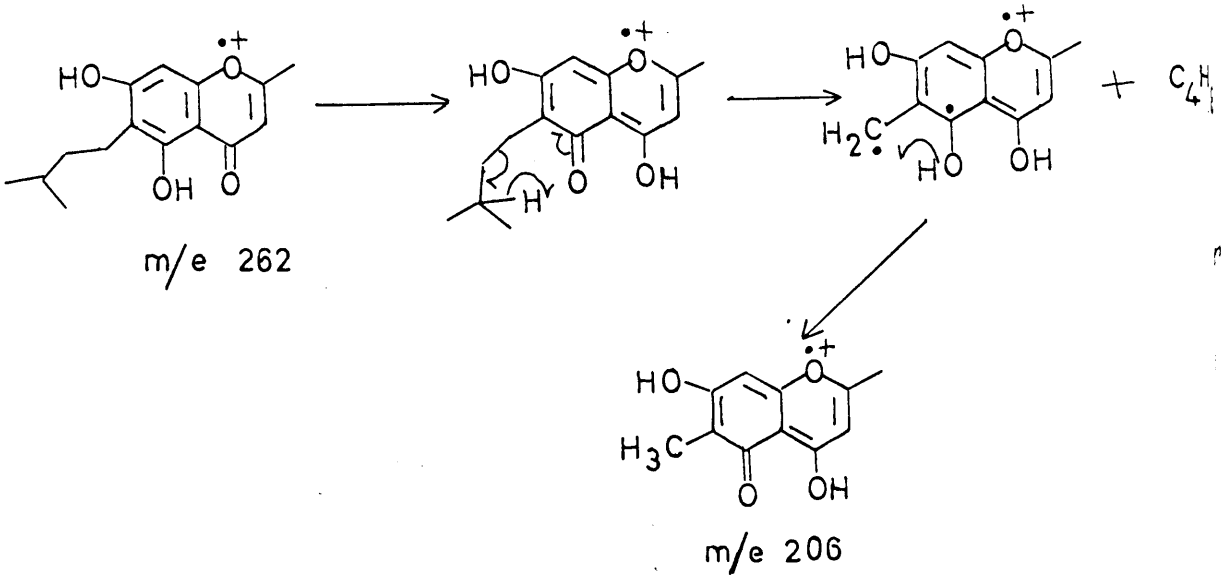
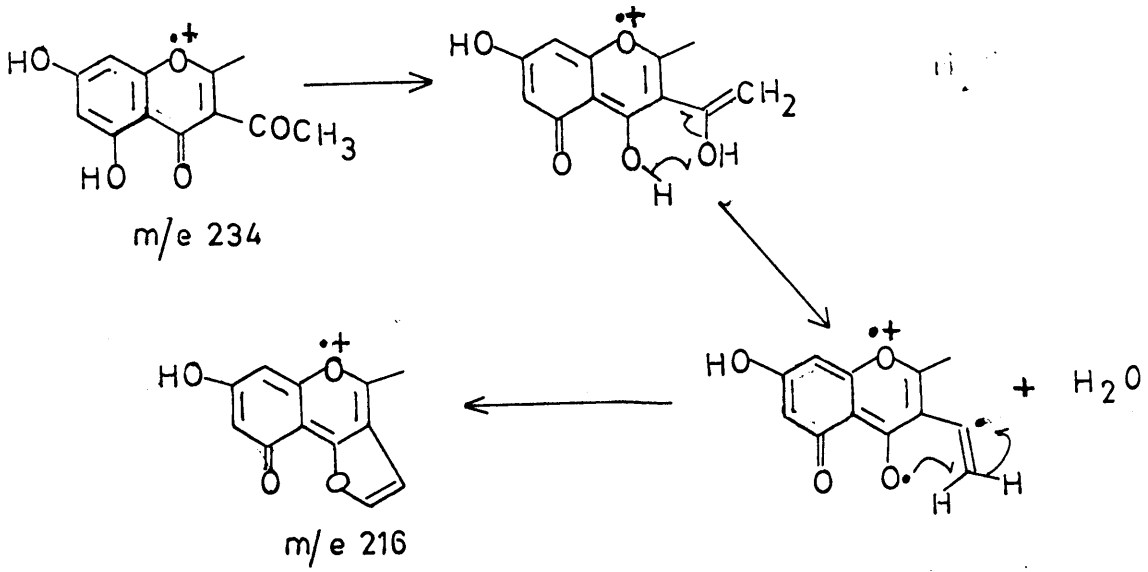


FIGURE VII.



spectra of the dihydropeucenin compounds. A plausible mechanism which requires the participation of the C-5 substituent is shown in Fig.VI. This mechanism, however, requires a seven-membered transition state, rather than the four-[23] or six-membered[24] transition states which have been suggested for the rearrangement of 1-phenylalkanes. An alternative explanation may lie in the different thermodynamic stabilities of the dihydropeucenin compounds and the dihydroheteropeucenin compounds. It is possible to isomerize dihydropeucenin to dihydroheteropeucenin by treatment with hydroiodic acid, whereas the reverse reaction does not occur under the same conditions.[25] Therefore, it is likely that dihydropeucenin is thermodynamically less stable than its isomer. It is possible, then, that the additional energy possessed by dihydropeucenin is sufficient to allow the rearrangement process to occur.

It is not suprising that the molecular ion of a highly substituted compound like 2-methyl-5-methoxy-6-formyl-7-hydroxychromone (XIII, Fig.II) does not decompose by a retro-Diels-Alder reaction, especially when it is recalled that such a decomposition does not occur in the mass spectrum of a simple chromone like eugenin (III,Fig.II). Instead the main fragmentation pathways involve the functional groups other than the pyrone ring. Thus, in the spectrum are ions of m/e's 233 (M-H), 219 ($M-CH_3$), 217 (M-OH), 218 ($M-H_2O$) and 203 ($M-CH_3O$). The

base peak of the spectrum, m/e 206, is formed by the loss of a molecule of carbon monoxide from the molecular ion. The carbon monoxide molecule could come, either wholly or partly, from the carbonyl group of the pyrone ring, from the 6-formyl group or from the 7-hydroxyl group. Observation of the appropriate metastable ions shows that there are at least three paths by which m/e 206 can decompose, namely :-

(1) m/e 206 $\xrightarrow{-H}$ m/e 205 $\xrightarrow{-CHO}$ m/e 176

(calculated for $206^+ \rightarrow 205^+$ = 204.0, observed = 204.0)

(2) m/e 206 $\xrightarrow{-CHO}$ m/e 177 $\xrightarrow{-CHO}$ m/e 148 $\xrightarrow{-H}$ m/e 147.

(calculated for $206^+ \rightarrow 177^+$ = 152.0; observed = 152.0;

" " $177^+ \rightarrow 148^+$ = 123.7; " = 123.9;

" " $148^+ \rightarrow 147^+$ = 146.0; " = 146-147.)

(3) m/e 206 $\xrightarrow{-H_2O}$ m/e 188 $\xrightarrow{-CO}$ m/e 160

(calculated for $206^+ \rightarrow 188^+$ = 171.6; observed = 171.5

" " $188^+ \rightarrow 160^+$ = 136.1; " = 136.0)

Paths (1) and (2) agree well for ions of mass 206 containing a 6-formyl group. The mass spectra of salicylaldehyde[26] and o-methoxybenzaldehyde[27] both contain ions corresponding to $(M-H_2O)^+$ which suggests that path (3) could be followed by ions of mass 206 containing a 6-formyl group. However, it will be shown later that a molecule of water may be eliminated by a reaction that involves an interaction of the 4-carbonyl group with the 5-methoxyl group of a chromone.

Hence, without the use of suitably labelled analogues, it is not possible to decide the exact nature of the $(M-CO)^+$ ion in the mass spectrum of XIII.

The only compounds which were available for examination, in this study, which possess additional substituents in the pyrone ring are 2-methyl-3-acetyl-5,7-dihydroxychromone (XIV, Fig.II) and its 7-acetylated derivative (XV, Fig.II). The primary fission of the 7-acetylated derivative is expulsion of a molecule of ketene to give an ion, m/e 234, which can be considered to be identical with the molecular ion of 2-methyl-3-acetyl-5,7-dihydroxychromone, in agreement with the known behaviour of phenyl acetates.[28] Thus it is found that the spectra of both compounds are the same in normal and metastable ions, except for some variation in ion intensities. Therefore only the mass spectrum of 2-methyl-3-acetyl-5,7-dihydroxychromone will be discussed.

Although the molecular ion of 2-methyl-3-acetyl-5,7-dihydroxychromone does decompose by elimination of a molecule of carbon monoxide from the pyrone ring the main fragment ions are observed at m/e 219 $(M-CH_3)$ and m/e 216 $(M-H_2O)$. The methyl radical lost in the formation of m/e 219 is almost certainly that of the 3-acetyl group for two reasons. Firstly, no $(M-CH_3)^+$ ion is present in the spectrum of 2-methyl-5,7-dihydroxychromone, and secondly, fission of the carbon-carbon bond adjacent to a carbonyl function is known to be a favourable

process as the positive charge can be readily stabilised in the resulting ion.

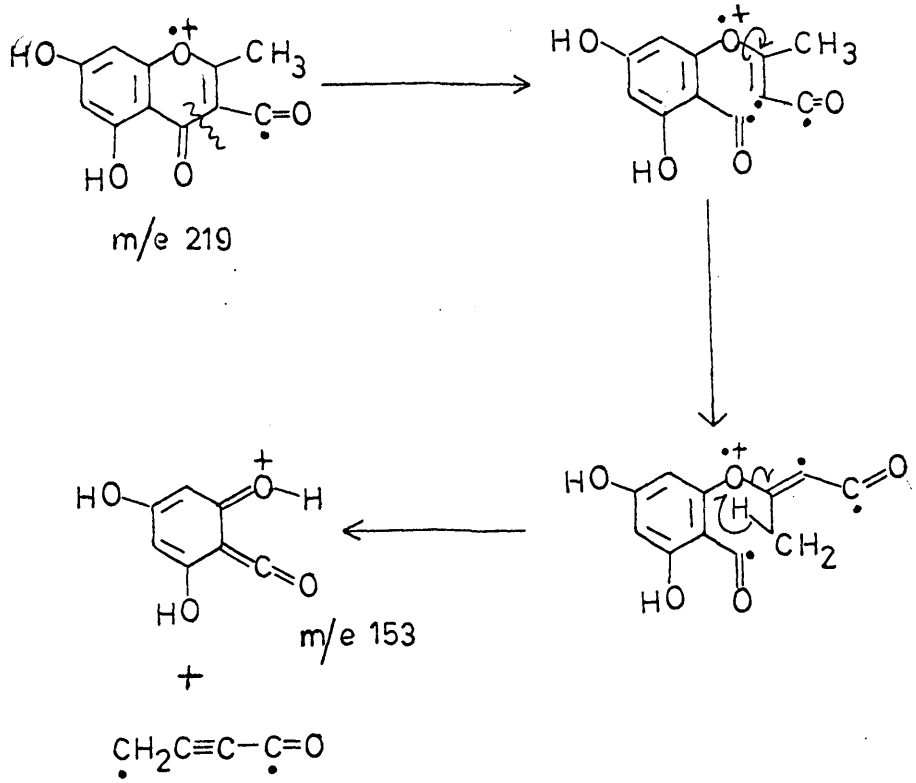
A metastable ion at m/e 199.4 confirms that the $(M-H_2O)^+$ ion results from an electron impact induced dissociation of the molecular ion, m/e 234 (m^* calculated for $234^+ \rightarrow 216^+$ = 199.4). Examination of the mass spectrum of 2-methyl-5,7-dihydroxychromone shows that it does not decompose in this way; hence the observed elimination of a molecule of water in the mass spectrum of the corresponding 3-acetyl compound must arise from some interaction of the 3-acetyl group with either the 2-methyl or the 4-carbonyl groups. If it is possible for the 3-acetyl group to exist in the enol form a reasonable mechanism for the elimination of water can be proposed as shown in Fig. V11. The driving force for this decomposition would then be provided by the formation of the cyclic, conjugated daughter ion at m/e 216. M/e 216 subsequently fragments by elimination of a molecule of carbon monoxide to form the ion m/e 188. (m^* calculated for $216^+ \rightarrow 188^+$ = 163.6; observed = 163-164.)

A metastable peak at m/e 106.9 in the mass spectrum of 2-methyl-3-acetyl-5,7-dihydroxychromone could arise from either of the transitions :-

(1) $219^+ \rightarrow 153^+ + 66$; m^* calculated = 106.89.

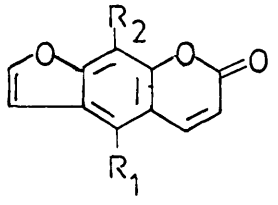
(2) $216^+ \rightarrow 152^+ + 64$; m^* calculated = 106.89.

FIGURE VIII.


HO
CH3
C=O
HO
O
m/e 219
HO
CH3
C=O
HO
O
HO
C=O
H
CH2
HO
O
HO
H
C=O
HO
m/e 153
+
CH2C≡C−C=O

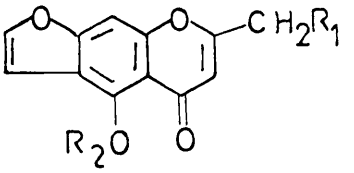
Exact mass measurement showed that the elemental composition of the ion m/e 153 is $C_7H_5O_4$ (calculated 153.0188; found 153.0195), while the composition of the ion m/e 152 is one hydrogen less i.e. $C_7H_4O_4$ (calculated 152.0110; found 152.0109). Thus the fragment of mass 66 eliminated in (i) would be C_4H_2O and the fragment of mass 64 eliminated in (2) would be C_5H_4. As the expulsion of a C_5H_4 fragment from m/e 216 is considered extremely unlikely, the metastable ion at m/e 106.9 must arise from transition (1). Therefore, the ion of mass 153 is formed by fission of the 1:2 and 3:4 bonds of the pyrone ring in the $(M-CH_3)^+$ ion accompanied by the migration of a hydrogen atom to the charge retaining species. Although, as previously pointed out, an ion arising by retro-Diels-Alder cleavage of the pyrone ring of a 2-methylchromone is always accompanied by a weakly abundant satellite ion one mass unit greater, this is the sole example where the abundance of the satellite ion is larger than the abundance of the ion formed by the simple reaction. The same type of fragmentation, observed in the mass spectrum of 4-hydroxy-3-phenylcoumarin, was interpreted in terms of the transfer of the hydrogen atom attached to C-3 in the 4-keto tautomer of this compound.[12] A mechanism, similar to that proposed to take place in the mass spectrum of 4-hydroxy-3-phenylcoumarin, is shown in Fig.VIII. In the mass spectrum of 2-methyl-3-acetyl-5,7-dihydroxychromone the ion of m/e 152 can be formed either by

FIGURE IX.



XVI; R_1=H, R_2=OCH_3.

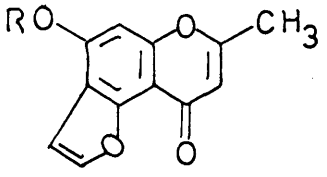
XVII ; R_2=H, R_1=OCH_3.



XVIII; R_1=H, R_2=H .

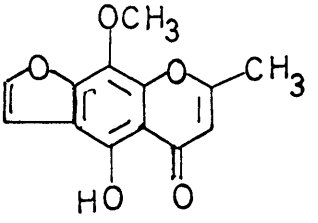
XIX ; R_1=H , R_2=CH_3.

XX ; R_1=OH, R_2=CH_3.

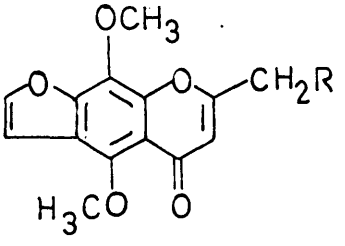


XXI; R=H .

XXII; R=CH_3.



XXIII



XXIV; R=H .

XXV; R=OH.

loss of a hydrogen atom from m/e 153, or by a simple retro-Diels-Alder cleavage of m/e 219. The latter alternative is preferred as the ion m/e 67, the composition of which was confirmed to be C_4H_3O (calculated 67.01839; found 67.01843), corresponds to the other product of the retro-Diels-Alder reaction.

(B) Furochromones.

Recent investigations have shown that the electron impact induced dissociations of furocoumarins[3,29] are not greatly different from those of simple coumarins. In addition it was shown that, although the fragmentation of a methoxyl substituent may be superimposed on the fragmentation of the α-pyrone ring, the mass spectra are independent of the position of the methoxyl group. For example, the mass spectra of xanthotoxin (XVI, Fig.IX) and bergapten (XVII, Fig.IX) are almost identical, ions being observed at $(M-CH_3)^+$, $(M-CO)^+$, $(M-COCH_3)^+$ and $(M-C_2O_2CH_3)^+$.[3] It will be seen, however, that the mass spectrum of a furochromone can depend largely on the position of a methoxyl substituent.

Examination of the mass spectrum of norvisnagin (XVIII, Fig.IX) shows that the fragmentation of this compound is not greatly different from that of a simple chromone such as 2-methyl-5,7-dihydroxychromone. Thus retro-Diels-Alder cleavage of m/e 216, the molecular ion, gives rise to the ion m/e 176 which decomposes further by sequential

elimination of two molecules of carbon monoxide, ions being observed at m/e's 148 and 120. Metastable ions at m/e 143.4 (calculated for $216^+ \rightarrow 176^+ = 143.4$), at m/e 124.5 (calculated for $176^+ \rightarrow 148^+ = 124.4$), and at m/e 97.3 (calculated for $148^+ \rightarrow 120^+ = 97.2$) confirm each step of this degradation route. One difference in the mass spectrum of norvisnagin is noted when compared with that of 2-methyl-5,7-dihydroxychromone. Metastable ions at m/e 162.0 and m/e 186.0, in the mass spectrum of norvisnagin, show that m/e 187 (M-CHO) can be formed from both the molecular ion (m^* calculated for $216^+ \rightarrow 187^+ = 161.8$) and from m/e 188 (M-CO) (m* calculated for $188^+ \rightarrow 187^+ = 186.0$); whereas, in the mass spectrum of 2-methyl-5,7-dihydroxychromone, a metastable ion is only observed for the formation of the $(M-CHO)^+$ ion from the $(M-CO)^+$ ion. It is realised that the absence of a metastable ion for a particular transition does not necessarily mean that the transition does not take place. Nevertheless, the possibility that the $(M-CHO)^+$ ion in the mass spectrum of norvisnagin is formed by two different reactions, while the same ion in the mass spectrum of 2-methyl-5,7-dihydroxychromone is formed by one reaction only, would explain the differences in the abundance ratio of $(M-CO)^+$ to $(M-CHO)^+$ in the two spectra. The abundance ratios of $(M-CO)^+$ to $(M-CHO)^+$ are 0.2/1 and 1.3/1 in the mass spectra of norvisnagin and 2-methyl-5,7-dihydroxychromone respectively.

Precise mass determination of the ion m/e 160 in the mass spectrum of norvisnagin showed that its composition is $C_{10}H_8O_2$ (calculated 160.0524; found 160.0518), and thus originates from the molecular ion by expulsion of two molecules of carbon monoxide.

The fragmentation sequence involving retro-Diels-Alder decomposition of the molecular ion followed by successive losses of two molecules of carbon monoxide is also noted in the mass spectrum of norisovisnagin (XXl, Fig.lX). Loss of carbon monoxide from the molecular ion is confirmed by a broad metastable ion centred at 163.8 (calculated for $216^+ \rightarrow 188^+ = 163.6$). No metastable ion is detected for the direct loss of a formyl radical, but one at 186.0 shows that the $(M-CHO)^+$ ion arises from the ion m/e 188 by the loss of a hydrogen atom. The abundance ratio of the ions $(M-CO)^+$ to $(M-CHO)^+$ is 0.9/1, which is much closer to the value of this ratio in the mass spectrum of 2-methyl-5,7-dihydroxychromone than to the value in the spectrum of norvisnagin.

The most abundant ion in the mass spectrum (Fig.Xlla) of khellinol (XXlll, Fig.lX) corresponds to the loss of a methyl radical from the molecular ion. Barnes and Occolowitz,[17] in a study of the mass spectra of phenyl methyl ethers, showed that when it is possible to write quinonoid structures for ions derived by the loss of a methyl radical from each compound there is no fission between the aromatic ring and

the ether oxygen. In a later investigation, the same authors noted that abundant ions are observed for the loss of a methyl radical from a methoxyl group in the mass spectra of those coumarins for which the $(M-CH_3)^+$ ion could be represented by a conjugated oxonium ion.[3] Recently, Shapiro and Djerassi[30] pointed out that the $(M-CH_3)^+$ ion in the mass spectrum of 6,7-dimethoxycoumarin could be represented by a conjugated oxonium ion only if the methyl radical were lost from the C-6 methoxyl group, and by appropriate deuterium labelling they were able to prove the methyl radical is indeed lost preferentially from the C-6 methoxyl group.

In the light of all this evidence there is no doubt that the $(M-CH_3)^+$ ion in the mass spectrum of khellinol is formed by the loss of a methyl radical from the C-8 methoxyl group rather than from the C-2 methyl group, and the formation of a conjugated oxonium ion explains its high abundance. Weakly abundant ions of m/e's 218 and 203 can be attributed to the elimination of carbon monoxide from the molecular ion and the $(M-CH_3)^+$ respectively. Retro-Diels-Alder decomposition of the molecular ion of khellinol does not take place; however, the $(M-CH_3)^+$ ion does cleave by this mechanism to give the ion m/e 191 which subsequently expels a molecule of carbon monoxide forming the ion of mass 163. Metastable ions of m/e 157.9 (calculated for $231^+ \rightarrow 191^+ = 157.9$) and m/e 139.0 (calculated for

FIGURE X.

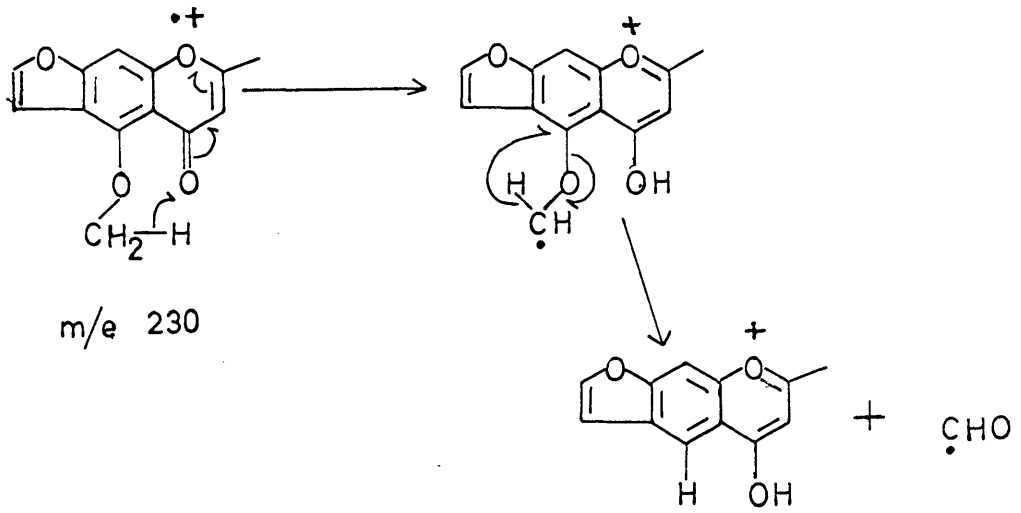
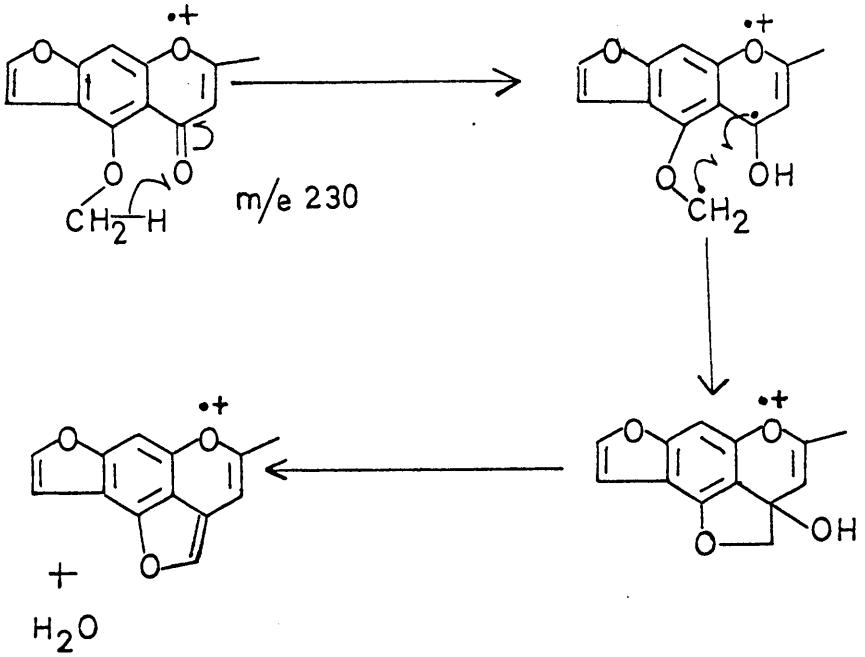


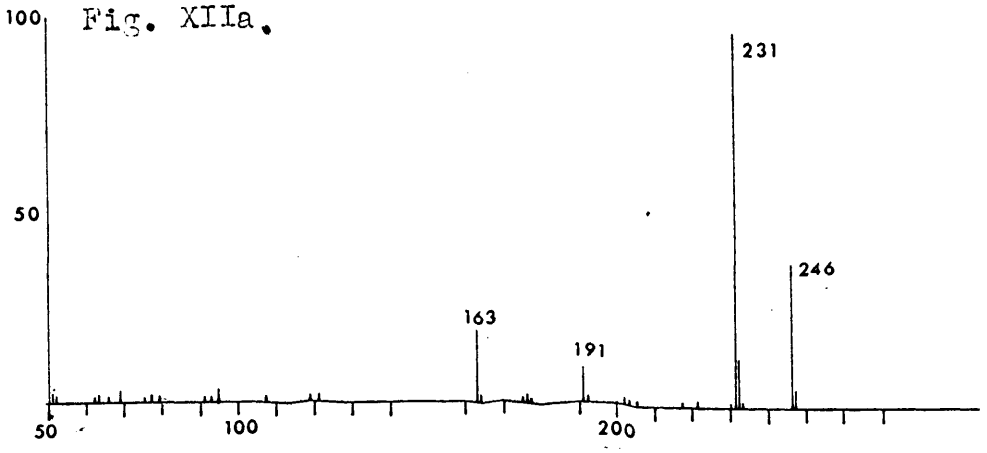
FIGURE XI.

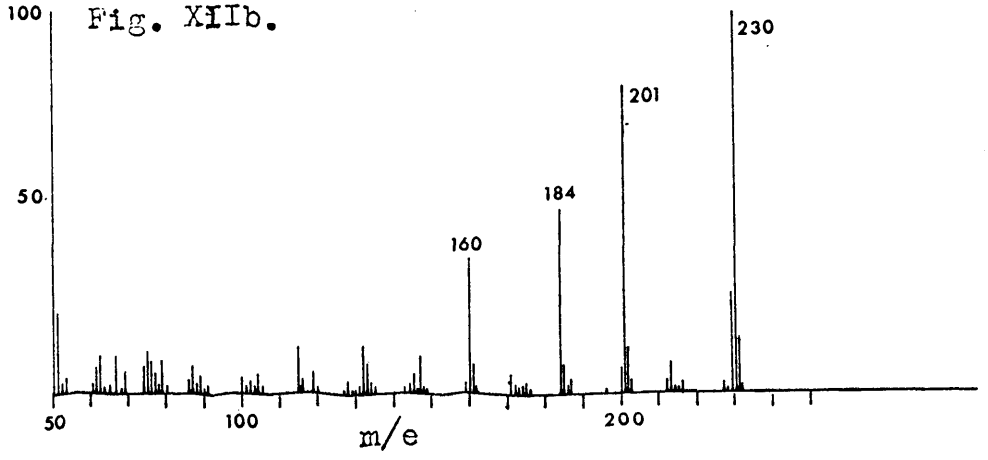


$191^+ \rightarrow 163^+ = 139.1$) substantiate these transitions.

It is very surprising that, even although it can be represented by a conjugated oxonium ion, the $(M-CH_3)^+$ ion in the mass spectrum (Fig.XIIb.) of visnagin (XIX,Fig.IX) only amounts to 1% of the base peak intensity. The fragment ion of greatest abundance is m/e 201 corresponding to the loss of a formyl radical from the molecular ion. No loss of carbon monoxide is observed, but a weakly abundant ion of m/e 200 corresponds to the loss of formaldehyde from the molecular ion. It is suggested, as no $(M-CO)^+$ ion is formed and as a $(M-CH_2O)^+$ ion is recorded, that the elements of the formyl radical lost in the formation of m/e 201 originate from the C-5 methoxyl group. The different modes of fragmentation of methoxyl groups on the C-5 and C-8 positions of a furochromone may be due to an interaction between the C-5 methoxyl group and the C-4 carbonyl group of the pyrone ring. Thus, it is possible that the initial step in the formation of m/e 201 involves transfer of a hydrogen atom from the methoxyl group to the carbonyl function as shown in Fig.X.

Transfer of a hydrogen atom from the C-5 methoxyl group to the carbonyl group may also be the initial step in the formation of the $(M-H_2O)^+$ ion in the mass spectrum of visnagin. A metastable ion of m/e 195.4 confirms that this loss of water is induced by electron impact (m^* calculated for $230^+ \rightarrow 212^+ = 195.5$). A plausible mechanism





Relative Abundance

Fig.XIIa: Mass Spectrum of Khellinol.

Fig.XIIb: Mass Spectrum of Visnagin.

for the loss of water is shown in Fig.XI. The mechanisms suggested for the loss of a molecule of water and the formyl radical in the mass spectrum of visnagin would also account for the differences in the mass spectra of the isomeric methoxyanthraquinones. Beynon and Williams[9] found that the mass spectrum of 1-methoxyanthraquinone contained $(M-OH)^+$ and $(M-H_2O)^+$ ions, the abundance of each being approximately 9% of the base peak, while the corresponding peaks in the spectrum of 2-methoxyanthraquinone were undetectable. In addition, they found that the loss of a formyl radical from the molecular ion was more probable for the 1-methoxy than for the 2-methoxy compound. However, the fact that 2-methoxyanthraquinone does have a $(M-CHO)^+$ ion in its mass spectrum could mean that the suggested mechanism is not the complete explanation. One further example of methoxyl groups fragmenting in a different manner depending on their position in the molecule may be quoted. It was found that the mass spectra of those furoquinoline alkaloids which have a C-8 methoxyl substituent contain abundant $(M-CHO)^+$ ions, whereas the mass spectra of those furoquinoline alkaloids which have methoxyl groups substituted at other positions contain $(M-CHO)^+$ ions which are of very weak intensity.[31]

The remaining important peaks in the mass spectrum of visnagin are found at masses 184 and 160. The composition of m/e 184 was found to be $C_{12}H_8O_2$ (calculated 184.0527; found 184.0524), and although no metastable

ion is recorded for its formation it can be formed by the loss of a molecule of carbon monoxide from the $(M-H_2O)^+$ ion. A metastable ion at m/e 128.0 shows that the ion of mass 160 is derived from the $(M-CH_2O)^+$ ion (m^* calculated for $200^+ \rightarrow 160^+ = 128.0$), and that m/e 160, therefore, arises from a retro-Diels-Alder decomposition of the $(M-CH_2O)^+$ ion.

The mass spectrum of khellol (XX, Fig.IX) shows that it cleaves in the same manner as visnagin under electron bombardment. Thus the $(M-CHO)^+$ ion, m/e 217, is the most abundant fragment ion in the spectrum. Accompanying m/e 217 are ions of mass 216 and 215 corresponding to losses of formaldehyde and a methoxyl group respectively. It is possible, however, that the elements of formaldehyde, the formyl radical and the methoxyl group all originate in the 2-hydroxymethyl group. As the same fissions are noted in the mass spectrum of visnagin, it is likely that fragmentation of the 2-hydroxymethyl group of khellol plays little or no part in the formation of these ions. Additional support for this theory is provided by the mass spectrum of khellol obtained in the presence of deuterium oxide. When the spectrum of khellol was recorded in the presence of deuterium oxide a mixture of non-deuteriated and mono-deuteriated species was formed. Analysis of abundances of the molecular ions showed that 53% of the molecules were labelled. Similarily it was found that 53% of the $(M-CHO)^+$ ions were labelled. Therefore, either the $(M-CHO)^+$ ion is

formed preferentially by loss of 29 mass units from the methoxyl group, or that in any loss of 29 mass units from the alcohol function there is complete retention of the alcoholic hydrogen atom. It has been shown that the results obtained for the $(M-CHO)^+$ ion in the mass spectra of various deuteriated derivatives of benzyl alcohol could best be explained if all the hydrogen lost came with equal probability from the three hydrogen atoms of the hydroxymethyl group.[32] Hence less than 100% retention of the label would be expected in the mass spectrum of deuteriated khellol, if the alcohol group made a significant contribution to the $(M-CHO)^+$ ion. Furthermore, a metastable ion at m/e 119.5 corresponding to the transition $217^+ \rightarrow 161^+ + 56$ (m^* calculated for $217^+ \rightarrow 161^+ = 119.4$) confirms that the $(M-CHO)^+$ ion can undergo retro-Diels-Alder decomposition of the pyrone ring, thus additionally demonstrating that the hydroxymethyl group is retained in m/e 217.

The molecular ion of khellol also fragments by loss of a molecule of water to form m/e 228 which subsequently breaks down with loss of carbon monoxide to give m/e 200. M/e 171 is formed by the loss of a formyl radical from m/e 200. Metastable ions at m/e 211.2 (calculated for $246^+ \rightarrow 228^+ = 211.3$), at m/e 175.4 (calculated for $228^+ \rightarrow 200^+ = 175.4$) and at m/e 146.4 (calculated for $200^+ \rightarrow 171^+ = 146.2$) confirm this decomposition path. Loss of a formyl radical is also

noted from the ion m/e 216 ($M-CH_2O$) (m^* calculated for $216^+ \rightarrow 187^+$ = 161.8; observed = 161.9).

A comparison of the mass spectrum of khellinol with the mass spectra of visnagin and khellol makes it possible to predict that a linear furochromone with methoxyl groups at C-5 and C-8 will exhibit two distinct fragmentations of the methoxylgroups, namely; (1) loss of a methyl radical from the C-8 methoxyl; and (2) loss of a formyl radical from the C-5 methoxyl group. The mass spectrum of khellin (XXlV, Fig.lX) is in excellent agreement with this prediction. Thus the abundance of the $(M-CH_3)^+$ ion is 98% of the base peak (the molecular ion), while the relative abundance of the $(M-CHO)^+$ ion is 38%. However, in contrast to the mass spectra of khellol and visnagin, the mass spectrum of khellin contains an ion derived by the loss of water from the $(M-CH_3)^+$ ion, rather than from the molecular ion. Nevertheless, the same mechanism that was described for the loss of water from the molecular ions of khellol and visnagin can be used to explain the loss of water from the $(M-CH_3)^+$ ion in the spectrum of khellin, if it is accepted that the methyl radical is lost solely from the C-8 methoxyl group. Observation of the appropriate metastable ions shows that the remaining abundant ions in the mass spectrum of khellin can be derived by eliminations of carbon monoxide, formyl radicals and methyl radicals from the $(M-CH_3)^+$ and $(M-CHO)^+$ ions (Fig.Xlll).

FIGURE XIII.

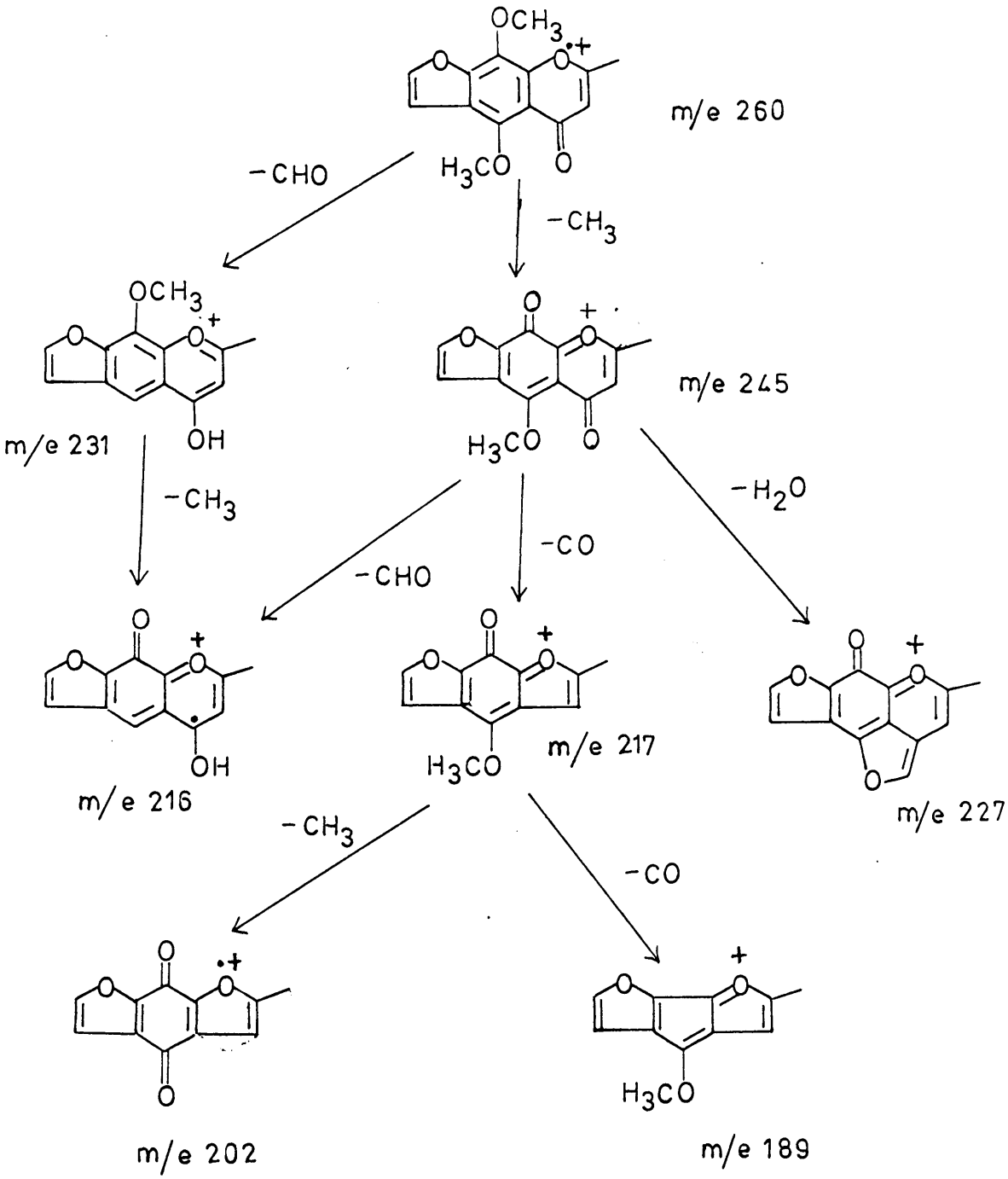

m/e 260
-CHO
-CH3
m/e 231
m/e 245
-CH3
-H2O
-CO
-CHO
m/e 216
m/e 217
m/e 227
-CH3
-CO
m/e 202
m/e 189

FIGURE XIII.

Transition	Observed m*	Calculated m*
$260^{+} \rightarrow 245^{+} + 15$	231.0	230.8
$260^{+} \rightarrow 231^{+} + 29$	205.2	205.2
$231^{+} \rightarrow 216^{+} + 15$	202.0	201.9
$245^{+} \rightarrow 217 + 28$	192.1	192.2
$245^{+} \rightarrow 216^{+} + 29$	190.4	190.4
$217^{+} \rightarrow 202^{+} + 15$	188.0	188.0
$217^{+} \rightarrow 189^{+} + 28$	164.5	164.4

Further confirmation of the behaviour, under electron impact, of this type of compound is provided by the mass spectrum of ammiol (XXV,Fig.1X) which also contains abundant $(M-CH_3)^+$ and $(M-CHO)^+$ ions. It is possible that the formyl radical is lost from the 2-hydroxymethyl group. However, the arguments used to exclude this possibility in the mass spectrum of khellol may be applied to the mass spectrum of ammiol. Metastable ions at m/e's 208.0, 206.1 and 177.5 in the mass spectrum of ammiol show that m/e 233 is formed by the loss of carbon monoxide from the $(M-CH_3)^+$ ion (m^* calculated for $261^+ \rightarrow 233^+$ = 208.0), that m/e 232 is derived by the loss of a formyl radical from the $(M-CH_3)^+$ ion (m^* calculated for $261^+ \rightarrow 232^+$ = 206.2) and that m/e 203 is derived by loss of a formyl radical from m/e 232 (m^* calculated for $232^+ \rightarrow 203^+$ = 177.6).

In view of the mass spectral behaviour of eugenin (III,Fig.II) and rubrofusarin (IV,Fig.II) it might be expected that isovisnagin (XXII,Fig.1X), which has the same oxygenation pattern as eugenin, would also give the mass spectral reactions associated with a m-methoxyphenol. However, the mass spectrum of isovisnagin does not contain a $(M-CH_2O)^+$ ion, and the $(M-CHO)^+$ ion is weakly abundant. In addition, no $(M-CH_3)^+$ ion is detectable, even though any such ion could be represented as a conjugated oxonium ion. Instead it is found that the pyrone function determines the course of fragmentation of isovisnagin. Thus ions are

observed at m/e 202, m/e 201, m/e 190 and m/e 162 corresponding to $(M-CO)^+$, $(M-CHO)^+$, $(M-C_3H_4)^+$ and $(M-C_3H_4CO)^+$ respectively, i.e., isovisnagin cleaves in a way typical of a simple chromone. Metastable ions at m/e 173.0, m/e 160.1 and m/e 133.5 corresponding to the transitions

$$202^+ \rightarrow 187^+ + 15 \quad (m^* \text{ calculated} = 173.1)$$

$$190^+ \rightarrow 175^+ + 15 \quad (m^* \text{ calculated} = 160.1)$$

$$162^+ \rightarrow 147^+ + 15 \quad (m^* \text{ calculated} = 133.3)$$

show that carbon-oxygen bond fission with loss of a methyl radical does take place from several fragment ions.

Conclusions.

Previous investigations had established that a likely dissociation, induced by electron impact, of compounds containing a γ-pyrone ring is decomposition of the molecular ion by a retro-Diels-Alder reaction. It is, therefore, a reasonable assumption that such a reaction would be a prominent feature of the mass spectra of chromones. Some support for this assumption is found in the mass spectrum of chromone, the parent compound of the class, which does contain an abundant ion formed by this means. However, the results obtained in the present study show that retro-Diels-Alder cleavage often takes place from a fragment ion, rather than from the molecular ion, thus indicating the unfavourable

nature of the process. Indeed, it was found that no such decompositions were evident in the mass spectra of several of the more highly substituted compounds examined. It is likely, therefore, that it will not always be possible to distinguish a chromone from an isomeric coumarin solely on the basis of their mass spectra.

The mass spectra of linear furochromones were found to be particularly sensitive to the position of methoxyl substituents. Thus, the results obtained show that a methoxyl group on the C-8 position fragments by elimination of a methyl radical, whereas a methoxyl group on the C-5 position cleaves with loss of a formyl radical. This difference in behaviour may be explained by an interaction between the C-5 methoxyl and the C-4 carbonyl groups.

REFERENCES.

1. T. Bruun, Acta Chem. Scand., 1965, 19, 1677.

2. For a review see, H. Budzikiewicz, C. Djerassi and D. H. Williams "Structural Elucidation of Natural Products by Mass Spectrometry," Ch. 29, Holden-Day, San Francisco, 1964.

3. C. S. Barnes and J. L. Occolowitz, Austral. J. Chem., 1964, 17, 975.

4. N. S. Wulfson, V. I. Zaretskii and V. G. Zyakoon, Izvest. Akad. Nauk SSSR, Ser. Khim., 1963, 2215.

5. R. I. Reed and J. M. Wilson, J. Chem. Soc., 1963, 5949.

6. E. Clayton, Ph.D. Thesis, Glasgow 1964.

7. B. Willhalm, A. F. Thomas and F. Gautschi, Tetrahedron, 1964, 20, 1185.

8. T. Aczel and H. E. Lumpkin, Analyt. Chem., 1960, 32, 1819; J. H. Beynon "Mass Spectrometry and its Applications to Organic Chemistry," p.352, Elsevier, Amsterdam, 1960.

9. J. H. Beynon and A. E. Williams, Appl. Spectroscopy, 1960, 14, 156.

10. A. McCormick, Ph.D. Thesis, Glasgow 1966.

11. H. Budzikiewicz, J. I. Brauman and C. Djerassi, Tetrahedron, 1965, 21, 1855.

12. A. P. Johnson, A. Pelter and M. Barber, Tetrahedron Letters, 1964, 1267.

13. H. Nakata, Y. Hirata and A. Tatematsu, Tetrahedron Letters, 1965, 123.

14. P. Beak, T. H. Kinstle and G. A. Carls, J. Amer. Chem. Soc., 1964, 84, 3833.

15. W. H. Pirkle, J. Amer. Chem. Soc., 1965, 87, 3023.

16. J. H. Beynon and A. E. Williams "Mass and Abundance Tables for use in Mass Spectrometry," Elsevier, Amsterdam, 1963.

17. C. S. Barnes and J. L. Occolowitz, Austral. J. Chem., 1963, 16, 219.

18. K. Biemann, "Mass Spectrometry," p.140, McGraw-Hill, New York, 1962.

19. H. Budzikiewicz, C. Djerassi and D. H. Williams, "Interpretation of the Mass Spectra of Organic Compounds," p. 179., Holden-Day, San Francisco, 1964.

20. "Uncertified Mass Spectral Data," Spectrum No.1109, The Dow Chemical Company, Midland, Michigan.

21. E. Ritchie, W. C. Taylor and J. S. Shannon, Tetrahedron Letters, 1964, 1437.

22. J. D. McCollum and S. Meyerson, J. Amer. Chem. Soc. 1959, 18, 4116.

23. H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, ed., p.508, Academic Press, New York, 1963.

24. Reference 18, p.122.

25. A. Bolleter, K. Eiter and H. Schmid, Helv.Chim. Acta, 1951, 34, 186.

26. Reference 20, Spectrum No.1035.

27. Reference 20, Spectrum No.2437.

28. Reference 18, p.111.

29. N. S. Wulfson, V. I. Zaretskii and V. G. Zyakoon, Dokl. Acad. Nauk. SSSR, 1964, 155, 1104.

30. R. H. Shapiro and C. Djerassi, J. Amer. Chem. Soc., 1965, 87, 955.

31. D. M. Clugston and D. B. Maclean, Canad. J. Chem., 1965, 43, 2516.

32. E.L. Eliel, J. D. McCollum, S. Meyerson and P. N. Rylander, J. Amer. Chem. Soc., 1961, 83, 2481.

EXPERIMENTAL.

The mass spectra were determined with an A.E.I. Ltd. M.S.9 mass spectrometer using a direct inlet system. The ionizing voltage was 70eV and the source temperature was maintained at 200°C.

The mass spectra are tabulated overleaf.

Mass Spectrum of Chromone.

M/e	% Abund.	M/e	% Abund.
26	3.9	63	25.8
27	1.1	64	20.3
28	16.6	65	1.1
29	1.9	69	3.7
32	2.6	73	1.8
37	3.7	74	8.1
38	9.2	75	5.7
39	7.4	76	4.2
41	0.9	77	1.7
42	1.5	89	10.5
43	0.9	90	12.9
44	9.6	91	1.3
45	5.5	92	44.3
49	1.3	93	2.6
50	15.3	118	52.6
51	5.5	119	5.5
53	5.9	120	27.3
59	5.5	121	1.7
61	3.7	146	100.0 M
62	8.6	147	9.4

Mass Spectrum of 2-Methylchromone.

M/e	% Abund.	M/e	% Abund.
26	1.0	66	8.5
27	2.2	67	11.7
28	14.2	69	1.5
32	4.2	89	1.3
37	2.1	91	1.0
38	8.4	92	38.5
39	16.7	93	2.5
40	1.2	94	8.2
41	1.0	101	1.0
42	1.0	102	2.5
43	6.7	103	1.7
44	15.1	120	51.8
50	8.4	121	6.9
51	9.7	131	23.4
52	1.7	132	26.1
53	2.8	133	2.2
61	1.3	160	100.0 M
62	5.0	161	11.7
63	18.1		
64	16.7		
65	4.9		

Mass Spectrum of 2-Methyl-5,7-dihydroxychromone.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
36	2.1	65	1.9	121	2.1
37	1.4	66	2.1	122	0.9
38	3.7	67	4.2	123	4.7
39	14.0	68	1.1	124	14.0
40	2.3	69	19.8	125	0.9
41	4.4	70	0.9	135	2.3
42	4.2	73	1.9	136	2.1
43	14.0	74	1.4	148	1.9
44	1.6	75	0.9	149	0.9
50	5.8	76	0.9	150	0.9
51	5.6	77	2.3	152	14.0
52	1.9	78	2.6	153	2.3
53	4.4	79	2.1	159	0.9
54	1.4	80	0.9	160	1.2
55	4.7	81	0.9	163	11.6
56	1.2	82	4.0	164	16.0
57	2.3	83	0.9	165	1.4
59	1.6	95	1.6	191	1.9
60	1.4	96	7.0	192	100.0 M
62	1.9	108	1.2	193	11.6
63	2.3	111	2.6		

Mass Spectrum of 2-Methyl-5-hydroxy-7-methoxychromone.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	15.3	69	16.1	107	3.4	163	14.6
40	9.5	71	1.3	108	4.4	164	1.5
41	5.8	74	2.8	109	1.5	166	1.8
42	1.5	75	1.6	110	3.9	175	1.0
43	16.1	77	4.1	111	0.9	176	25.0
44	11.1	78	2.6	119	1.3	177	39.7
50	4.5	79	6.3	121	1.5	178	8.8
51	9.1	80	1.5	122	1.3	179	1.0
52	2.9	81	2.3	123	9.5	191	1.2
53	5.8	83	1.5	124	1.0	205	14.6
54	1.9	85	3.2	134	1.3	206	100.0 M
55	3.7	89	2.6	135	4.8	207	12.4
57	2.9	90	1.5	136	2.5	208	1.3
59	1.5	91	6.3	137	3.4		
62	4.2	92	3.1	138	5.7		
63	3.9	93	1.6	147	1.2		
64	2.2	95	10.1	148	14.6		
65	2.5	97	1.5	149	5.8		
66	2.9	103	1.5	150	0.9		
67	5.8	105	2.0	161	1.0		
68	1.5	106	1.5	162	0.9		

Mass Spectrum of Rubrofusarin.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	3.1	79	1.2	131	1.0	187	1.0
41	2.3	86	1.6	132	1.2	189	4.1
43	4.9	87	2.1	133	1.9	190	1.0
44	2.5	88	1.2	136	4.5	200	2.7
45	1.0	89	1.9	145	1.0	201	3.3
50	1.4	90	1.0	146	1.0	202	1.2
51	2.1	91	1.4	147	3.7	203	1.4
53	1.4	92	1.4	148	1.2	213	3.3
55	1.9	95	1.0	149	1.0	214	2.9
57	1.6	97	1.0	156	1.0	215	1.9
60	1.0	98	1.0	157	1.0	216	2.1
62	1.2	99	1.2	158	1.0	217	1.0
63	2.7	100	1.0	159	1.0	228	1.2
64	1.0	100.5	2.1	160	1.2	229	12.7
65	1.2	101	1.4	161	1.0	230	2.1
67	2.1	102	1.2	171	3.1	231	1.0
69	2.7	105	1.4	172	1.6	242	12.3
73	1.4	107	2.5	173	1.9	243	31.5
74	1.6	115	2.1	174	1.0	244	4.9
75	2.3	116	1.0	175	2.3	271	3.7
76	1.9	119	1.2	176	3.3	272	100.0 M
77	2.5	121	2.5	177	1.2	273	17.5
78	1.0	122	3.3	185	1.0	274	2.3

Mass Spectrum of 2-Methyl-5-hydroxy-7-allyloxychromone.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	44.8	69	40.9	96	2.1	133	4.5	178	5.4
40	9.1	70	1.5	97	1.5	134	2.1	185	1.5
41	100.0	71	1.5	102	2.1	135	4.2	186	1.8
42	4.5	74	2.1	103	1.8	136	3.9	187	2.1
43	51.5	75	2.7	105	7.0	137	2.1	188	1.5
44	9.1	76	1.8	106	18.2	145	1.5	189	25.8
50	8.8	77	9.1	107	10.6	146	1.5	190	9.4
51	18.5	78	10.6	108	4.5	147	4.8	191	8.5
52	5.2	79	17.6	109	1.5	148	11.5	192	32.4
53	11.5	80	2.1	110	1.2	149	5.2	193	3.3
54	4.5	81	3.0	111	1.8	150	6.4	203	23.9
55	10.9	82	1.5	115	2.4	151	3.6	204	52.1
56	1.5	83	1.8	117	1.2	152	2.4	205	17.9
57	3.0	85	20.9	118	2.4	161	18.2	206	8.5
60	0.9	86	1.2	119	3.3	162	6.1	214	1.5
61	1.2	87	1.8	120	3.0	163	46.7	215	9.1
62	7.6	89	2.4	121	3.6	164	12.1	216	2.1
63	9.1	90	3.0	122	21.2	165	2.1	217	80.0
64	3.0	91	9.1	123	44.8	173	1.2	218	9.7
65	6.4	92	3.3	124	8.8	174	1.5	2219	1.5
66	8.5	93	6.1	130	1.2	175	14.5	231	18.2
67	13.3	94	1.8	131	1.2	176	13.6	232	78.8 M
68	3.0	95	6.7	132	1.2	177	45.5	233	9.1
								234	1.2

Mass Spectrum of Peucenin.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	6.8	89	1.1	164	1.0	231	5.0
40	1.3	91	2.4	165	3.1	241	4.5
41	6.3	92	1.1	175	1.0	242	1.1
43	8.4	93	4.1	176	1.9	243	8.4
44	1.1	95	2.6	177	3.6	244	2.3
50	2.1	102	1.5	189	2.9	245	25.3
51	3.4	103	1.6	192	7.9	246	4.2
52	1.3	105	1.3	193	1.9	258	1.3
53	2.8	107	1.1	201	2.6	259	4.2
55	6.5	115	7.8	203	2.1	260	41.6 M
63	1.9	120	1.1	204	2.4	261	7.9
64	1.0	121	1.3	205	100.0	262	1.0
65	2.9	122	2.4	206	13.6		
67	4.9	123	6.3	207	1.6		
69	10.2	124	1.1	216	1.6		
77	3.7	137	1.6	217	82.2		
78	1.1	147	1.0	218	7.9		
79	2.1	148	1.0	219	3.6		
81	1.6	149	1.6	227	2.4		
85	3.6	151	2.1	229	2.6		
87	1.0	161	1.5	230	2.4		

Mass Spectrum of Allopeucenin.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	12.1	71	1.6	115	3.5	193	1.1
40	3.0	75	1.1	116	1.1	201	1.1
41	13.4	77	4.4	119	1.1	203	1.6
42	2.2	78	1.9	120	1.1	204	3.0
43	1912	79	3.6	121	1.6	205	100.0
44	9.6	80	1.6	122	1.6	206	17.3
50	2.2	81	2.7	123	5.8	207	2.5
51	4.4	83	1.6	124	1.1	217	29.3
52	2.2	85	2.5	133	1.1	218	5.5
53	5.2	89	1.1	135	1.1	219	2.2
54	1.1	91	6.0	136	1.6	227	0.8
55	11.0	92	2.2	137	1.6	229	0.8
56	3.0	93	3.8	147	1.4	230	0.8
57	3.0	94	1.1	148	1.4	231	3.0
58	3.5	95	2.5	149	1.6	241	1.6
63	3.3	96	1.1	151	1.9	243	3.6
64	2.2	99	1.4	165	2.7	244	1.1
65	3.8	101	1.4	173	1.4	245	12.9
66	1.9	103	1.4	175	2.5	246	2.5
67	5.5	105	2.2	176	5.8	259	1.6
68	2.5	107	1.6	177	2.5	260	31.2 M
69	11.2	108	1.6	189	1.6	261	6.6
70	1.1	109	1.9	192	3.0	262	1.1

Mass Spectrum of Isopeucenin.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	14.4	69	11.3	99	4.3	136	1.2	207	3.4
40	4.1	71	1.4	100	1.0	137	1.4	217	37.7
41	16.1	73	1.2	101	1.4	147	1.4	218	9.6
42	2.4	74	1.2	102	1.4	148	3.6	219	2.4
43	14.9	75	1.4	103	1.9	149	1.7	227	1.0
44	14.9	76	1.2	104	1.0	151	1.9	229	1.0
45	1.7	77	5.5	105	2.4	161	1.4	230	1.0
50	2.6	78	2.6	106	1.2	163	1.2	231	3.4
51	6.5	79	4.3	107	2.2	165	2.6	232	1.0
52	3.1	80	1.9	108	2.4	173	4.6	241	2.2
53	6.0	81	2.6	109	1.9	175	3.1	243	4.8
54	1.7	83	1.7	115	5.3	176	9.1	244	1.7
55	12.5	85	3.6	116	1.2	177	3.6	245	12.5
56	4.3	86	1.4	119	1.4	189	1.7	246	3.4
57	2.4	87	1.2	120	1.4	192	5.8	259	2.4
62	1.2	89	2.2	121	1.9	193	1.9	260	52.1 M
63	4.1	90	1.2	122	2.4	201	1.9	261	14.4
64	2.4	91	13.9	123	5.5	202	4.1	262	2.2
65	5.8	92	4.1	124	1.2	203	4.8		
66	2.9	93	5.3	130	1.0	204	25.4		
67	6.5	94	1.4	133	1.7	205	100.0		
68	1.9	95	2.6	135	1.2	206	23.0		

Mass Spectrum of Dihydropeucenin.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	3.0	103	0.8	229	1.1		
41	5.4	105	0.8	233	0.8		
43	3.3	109	1.0	245	1.2		
44	1.9	123	9.1	247	1.7		
51	1.2	124	0.8	262	16.0 M		
53	1.1	137	2.1	263	2.3		
55	6.8	151	2.7				
57	1.9	165	4.4				
65	1.2	176	1.0				
67	1.9	177	3.1				
69	6.6	178	0.9				
77	1.6	192	2.1				
79	1.1	193	1.3				
81	1.6	205	74.3				
83	1.1	206	100				
85	1.6	207	12.7				
91	1.4	208	1.6				
92	1.6	217	3.3				
95	1.4	219	14.3				
97	0.9	220	1.9				

Mass Spectrum of Dihydropeucenin-7-methyl ether.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	9.3	68	1.5	93	2.6	135	1.8	202	5.9
40	2.8	69	6.6	94	1.2	136	1.1	203	3.0
41	15.2	70	2.5	95	5.3	137	1.4	204	2.5
42	3.5	71	4.4	96	1.6	145	1.3	205	3.4
43	14.1	73	1.8	97	4.1	147	1.3	206	2.3
44	5.1	74	1.1	101	1.9	148	3.6	207	1.2
50	1.8	75	2.5	103	1.2	149	8.0	216	1.4
51	4.5	76	1.3	105	2.6	150	1.8	217	6.8
52	2.2	77	5.3	107	1.8	151	1.1	218	1.8
53	3.8	78	1.6	108	1.6	156	1.5	219	86.7
54	1.5	79	3.3	109	3.0	161	2.9	220	100.0
55	9.6	80	1.6	110	1.8	163	1.7	221	13.2
56	4.5	81	6.1	111	2.5	175	1.6	222	1.6
57	9.4	82	2.0	115	2.0	176	3.8	231	2.2
58	4.2	83	4.3	117	1.1	177	2.2	232	15.1
60	1.5	84	1.3	119	1.5	178	0.8	233	2.1
63	2.0	85	2.8	121	9.1	179	1.5	243	1.3
664	1.2	86	11.7	122	1.8	189	22.4	245	1.9
65	3.6	89	1.8	123	2.5	190	8.1	261	1.8
66	1.2	91	4.5	125	1.6	191	6.1	276	21.0 M
67	4.8	92	1.6	133	1.5	192	0.9	277	3.8

Mass Spectrum of Dihydroheteropeucenin.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	2.9	177	1.5		
41	2.9	191	0.7		
43	2.9	192	2.0		
51	1.2	205	100		
53	1.3	206	12.4		
55	2.1	233	0.6		
63	0.8	262	17.5 M		
65	1.3	263	2.8		
67	1.2				
69	4.2				
77	1.1				
79	1.3				
81	1.1				
93	1.1				
99	0.9				
123	0.9				
136	0.9				
137	1.4				
165	15.8				
166	1.2				
176	0.6				

Mass Spectrum of Dihydroheteropeucenin-7-methyl ether.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	3.5	121	4.4				
41	4.3	136	1.9				
43	4.2	149	4.3				
51	1.8	161	1.1				
52	1.2	176	2.9				
53	1.2	177	1.1				
55	1.5	179	2.8				
63	1.1	189	8.2				
64	0.8	190	1.2				
65	2.4	206	1.5				
67	1.6	217	0.8				
69	3.9	219	100				
77	1.9	220	13.8				
79	1.6	221	1.6				
80	0.8	261	0.2				
85	1.0	276	22.3 M				
91	1.3	277	3.8				
93	1.7						
105	0.8						
107	o.9						
108	1.4						

Mass Spectrum of 2-Methyl-5-methoxy-6-formyl-7-hydroxychromone.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
36	2.8	65	5.2	102	1.4	135	2.0	187	1.6
37	3.2	66	5.8	103	7.6	136	14.2	188	6.2
38	6.4	67	11.6	104	2.0	137	3.6	189	10.4
39	21.0	68	1.4	105	2.8	145	4.4	190	2.8
40	2.2	69	38.0	106	1.4	146	1.8	191	3.2
41	4.6	70	1.6	107	2.0	147	9.4	192	8.0
42	3.8	74	4.0	108	10.4	148	24.4	193	1.6
43	28.4	75	2.6	109	1.8	149	4.6	203	14.0
44	8.0	76	2.4	110	1.6	150	1.4	204	3.4
50	8.4	77	7.8	111	1.4	151	2.4	205	50.4
51	12.0	78	3.4	117	1.4	152	1.4	206	100.0
52	6.0	79	5.0	118	1.0	159	2.4	207	14.2
53	11.6	80	5.6	119	2.6	160	39.0	208	2.0
54	2.6	81	1.8	120	3.6	161	6.0	215	1.2
55	6.6	85	4.0	121	2.4	162	1.8	216	8.6
56	1.0	89	2.4	122	1.4	163	3.4	217	8.0
57	2.4	90	2.6	123	6.2	164	2.0	218	1.8
59	2.4	91	5.6	124	1.8	165	1.8	219	13.6
60	1.6	92	3.6	125	2.6	175	4.6	220	1.8
61	2.8	93	5.2	131	2.4	176	13.6	233	10.0
62	6.8	94	2.8	132	4.2	177	29.2	234	24.0 M
63	10.0	95	6.8	133	2.8	178	3.4	235	3.2
64	3.6	96	1.0	134	2.0	179	1.6		

Mass Spectrum of 2-Methyl-3-acetyl-5,7-dihydroxychromone.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	19.3	75	1.2	137	1.9	218	0.9
40	1.8	77	2.8	152	16.1	219	100.0
41	5.3	78	2.6	153	77.9	220	11.2
42	4.0	79	2.6	154	6.1	221	1.2
43	49.0	83	1.2	155	0.9	233	3.7
44	3.0	89	1.2	160	1.1	234	86.1 M
50	5.3	91	1.4	163	4.9	235	11.4
51	7.5	93	1.2	164	1.9	236	1.2
52	1.8	95	1.6	177	2.3		
53	5.1	96	5.3	178	0.9		
54	1.4	97	1.1	187	0.9		
55	6.5	103	1.8	188	5.6		
62	2.3	107	5.9	189	1.2		
63	4.0	108	1.8	191	1.9		
64	1.2	109	1.8	192	13.1		
65	3.5	111	2.6	193	1.2		
66	49.0	116	2.8	205	3.5		
67	3.3	123	4.2	206	1.4		
68	27.0	124	9.6	215	1.2		
69	1.1	125	1.2	216	26.3		
74	1.2	136	1.8	217	5.1		

Mass Spectrum of 2-Methyl-3-acetyl-5-hydroxy-7-acetoxychromone.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
36	1.9	69	14.7	134	1.1	217	9.2
38	1.5	74	1.1	135	1.3	218	1.3
39	9.6	75	1.1	136	1.3	219	100.0
40	1.1	76	0.8	145	0.8	220	12.8
41	3.0	77	1.9	147	0.8	221	1.5
42	8.9	78	1.9	148	1.1	233	4.5
43	87.6	79	1.9	149	0.8	234	57.6
44	8.5	83	1.9	152	6.8	235	6.8
50	2.8	85	1.5	153	32.1	276	46.4 M
51	4.5	89	1.1	154	2.1	277	6.6
52	1.3	90	0.8	160	1.1		
53	2.3	91	1.3	162	0.8		
54	0.8	92	0.8	163	3.2		
55	3.0	93	0.8	164	1.1		
60	1.7	95	1.3	187	0.8		
62	1.7	96	2.1	188	2.8		
63	3.0	108	1.1	191	1.3		
64	0.8	109	1.1	192	10.9		
65	1.7	110	0.8	193	1.3		
66	2.6	111	1.1	205	4.7		
67	29.4	123	6.8	206	4.7		
68	1.5	124	6.2	216	46.8		

Mass Spectrum of 5-Norvisnagin.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
38	1.1	80	1.0	188	1.8
39	2.9	91	1.1	216	100.0 M
41	1.0	92	3.3	217	13.0
43	3.3	103	1.2	218	1.5
44	1.6	108	4.1		
50	2.3	119	1.0		
51	4.4	120	9.6		
52	1.0	121	1.0		
53	1.8	131	1.5		
62	1.2	132	2.9		
63	2.9	135	3.3		
64	1.8	145	1.0		
65	1.0	147	1.0		
66	1.0	148	7.1		
67	1.2	149	1.1		
69	2.7	159	1.1		
74	1.8	160	6.8		
75	1.9	161	1.0		
76	1.2	176	21.6		
77	1.8	177	4.2		
79	2.2	187	7.5		

Mass Spectrum of Norisovisnagin.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
38	1.6	76	1.7	145	2.0
39	4.6	77	3.7	147	1.1
41	1.1	78	2.3	148	14.5
42	0.9	79	13.4	149	1.9
43	6.2	86	1.1	150	0.9
44	2.5	87	1.1	159	0.9
50	2.5	89	1.1	160	1.1
51	3.5	91	1.1	176	62.8
52	1.7	92	3.7	177	10.0
53	2.5	93	0.9	178	1.1
55	0.9	94	4.9	187	19.2
60	0.9	102	0.9	188	20.0
62	1.9	103	1.2	189	2.3
63	5.2	119	1.7	216	100.0 M
64	2.3	120	12.3	217	13.8
65	1.5	121	1.4	218	1.7
66	1.5	131	1.4		
67	1.7	132	1.2		
69	7.8	134	2.5		
74	3.4	135	12.0		
75	4.01	136	0.9		

Mass Spectrum of Khellinol.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
37	1.2	123	1.2		
38	4.1	163	18.2		
41	0.9	164	1.5		
43	2.4	175	0.9		
44	2.2	176	1.1		
50	1.1	177	0.9		
51	1.7	187	0.9		
52	1.2	191	8.8		
62	0.9	192	1.1		
63	1.2	202	0.9		
66	1.4	203	1.1		
67	3.0	205	1.2		
69	2.3	217	1.4		
75	0.9	221	1.2		
77	1.2	230	1.4		
79	1.4	231	100.0		
91	1.1	232	13.3		
94	0.9	233	1.7		
96	3.2	246	37.9 M		
107	1.1	247	5.8		
119	1.1				

Mass Spectrum of Visnagin.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
37	1.8	68	1.1	103	3.1	146	1.1	202	11.4
38	3.6	69	6.7	104	4.2	147	8.2	203	1.6
39	12.7	72	2.5	105	1.7	148	1.1	212	2.5
40	2.2	73	1.6	107	2.2	149	1.1	213	6.9
41	2.7	74	7.8	115	11.6	155	1.1	214	1.3
42	1.5	75	10.0	116	3.1	156	1.1	215	1.1
43	25.2	76	7.6	117	2.2	159	2.0	216	2.5
44	7.6	77	5.3	118	1.1	160	33.4	219	1.8
50	9.1	78	2.0	119	4.9	161	7.1	227	3.1
51	21.8	79	4.7	120	1.1	162	1.6	228	1.1
52	2.4	80	1.8	127	1.1	171	4.7	229	26.7
53	5.6	85	1.8	128	2.9	172	3.3	230	100.0 M
55	1.8	86	3.1	129	1.3	173	2.2	231	14.3
56	1.1	87	6.9	130	1.3	174	2.0	232	1.8
57	1.8	88	2.2	131	2.0	175	2.5		
58	1.6	89	3.3	132	12.0	176	1.3		
61	1.8	90	1.3	133	6.9	184	47.9		
62	6.7	91	2.2	134	2.9	185	6.9		
63	9.4	92	1.1	135	1.6	186	2.2		
64	1.8	93	1.1	136	1.1	187	3.3		
65	2.0	100	4.4	143	1.1	196	1.3		
66	1.8	101	2.2	144	2.2	200	6.0		
67	8.9	102	2.7	145	4.4	201	80.0		

Mass Spectrum of Khellol.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
37	1.8	83	3.8	123	3.2	173	3.2	229	4.1
38	2.8	86	2.5	129	3.2	174	1.3	230	1.8
41	1.5	87	5.3	130	1.8	175	2.3	231	1.0
43	1.8	88	2.7	131	6.0	176	1.8	232	1.0
50	1.8	89	3.8	132	11.3	185	1.3	243	1.3
51	3.3	90	1.7	133	5.0	186	3.3	244	5.0
55	5.5	91	4.2	134	3.8	187	14.6	245	25.3
57	1.2	92	1.3	135	1.7	188	2.5	246	100.0 M
61	1.7	93	1.3	142	1.3	189	3.3	247	14.8
62	1.8	100	1.7	143	3.0	190	1.7	248	1.8
63	2.6	101	3.3	144	4.0	191	2.5		
64	1.0	102	2.8	145	4.5	198	2.3		
65	2.0	103	4.0	146	1.5	199	2.6		
66	1.7	104	3.2	147	11.6	200	20.3		
67	1.3	105	2.2	148	1.3	201	5.0		
69	5.8	107	1.8	150	1.2	202	2.5		
73	1.8	108	1.3	159	6.2	211	1.3		
74	2.2	109	1.2	160	17.8	215	6.8		
75	3.1	115	6.7	161	10.0	216	5.8		
76	2.4	116	6.5	162	1.8	217	58.4		
77	2.0	117	2.3	170	1.8	218	9.3		
80	1.5	118	2.0	171	23.3	219	1.3		
81	1.2	119	4.8	172	3.3	228	4.0		

Mass Spectrum of Khellin.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
37	1.5	75	4.2	106	3.5	151	1.2	206	0.9
38	4.9	76	2.3	109	2.4	152	2.7	214	3.3
39	8.2	77	9.1	115	1.7	159	1.7	215	6.4
40	2.2	78	4.7	116	1.4	160	2.0	216	77.7
41	1.1	79	2.7	117	1.5	161	3.9	217	44.8
43	8.3	80	1.1	118	3.8	162	3.8	218	6.1
44	2.7	81	4.2	119	5.9	163	1.8	219	1.1
50	3.2	83	2.3	120	1.4	171	1.2	227	7.9
51	5.5	86	1.5	121	2.7	173	3.3	228	2.1
52	1.8	87	3.2	122	1.7	174	2.6	229	1.2
53	3.5	88	1.2	123	1.5	175	12.9	230	2.9
55	1.5	89	3.2	130	5.3	176	1.8	231	37.9
61	2.3	90	4.9	131	1.7	177	24.1	232	6.1
62	4.7	91	4.1	132	1.2	178	2.4	233	1.1
63	5.2	92	4.1	133	2.4	187	2.1	243	2.1
64	1.2	93	2.9	134	5.8	188	1.1	244	2.1
65	3.0	94	7.0	143	2.1	189	27.3	245	97.0
66	9.1	95	4.6	145	1.8	190	4.2	246	14.4
67	6.1	101	3.3	146	1.7	191	1.7	247	2.0
68	2.0	102	3.2	147	13.6	201	3.1	259	4.5
69	2.3	103	1.7	148	1.7	202	7.3	260	100.0 M
73	1.8	104	1.2	149	3.5	203	1.7	261	15.8
74	3.5	105	12.1	150	2.3	205	5.1	262	2.3

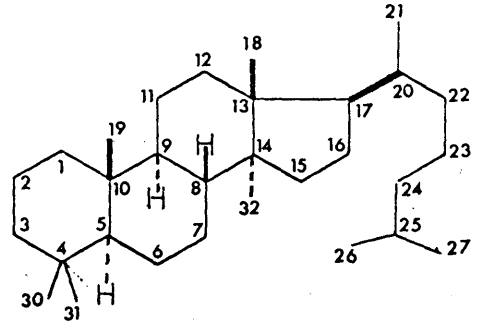
Mass Spectrum of Ammiol.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
37	1.5	67	4.8	101	3.5	136	3.0	176	2.0	221	2.3
38	2.0	69	7.3	102	1.3	137	1.0	177	13.6	230	3.5
39	9.1	70	1.3	103	2.3	138	1.8	178	1.8	231	9.9
40	1.3	71	1.8	104	1.8	143	2.0	186	1.8	232	41.4
41	5.8	73	2.8	105	10.1	144	1.0	187	5.3	233	19.4
42	2.8	74	3.8	106	2.8	145	3.5	188	1.5	234	6.1
43	11.4	75	5.6	107	1.8	146	1.8	189	3.8	243	5.6
44	20.2	76	2.8	109	2.3	147	10.1	190	1.8	244	1.8
45	4.0	77	6.6	115	2.8	148	2.0	191	2.8	245	4.6
50	4.0	78	2.8	116	2.5	149	5.1	192	4.6	246	2.8
51	6.3	79	2.5	117	2.0	150	3.5	201	5.6	247	35.4
52	1.5	81	3.8	118	2.5	151	1.5	202	3.8	248	5.3
53	5.3	83	7.3	119	5.3	152	1.0	203	15.4	259	3.9
55	8.8	86	1.5	120	1.5	153	4.3	204	2.9	260	2.8
56	2.0	87	3.8	121	2.3	159	3.8	205	18.9	261	100.0
57	3.8	88	2.0	122	1.5	160	2.3	206	3.3	262	15.1
59	1.5	89	4.0	123	2.3	161	3.0	207	1.3	263	2.3
60	2.0	90	3.8	124	1.8	162	3.8	214	1.3	274	2.3
61	2.3	91	4.0	130	1.0	163	3.0	215	3.3	275	4.6
62	5.6	92	2.8	131	3.0	164	2.0	216	5.3	276	89.1 M
63	6.3	93	2.5	132	1.5	171	1.8	217	5.3	277	13.1
64	1.5	94	5.6	133	3.0	173	10.6	218	2.9	278	2.0
65	3.0	95	6.6	134	5.0	174	2.5	219	8.3		
66	8.1	96	1.0	135	1.8	175	7.6	220	1.3		

Mass Spectrum of Isovisnagin.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
38	1.0	91	1.7	172	1.0
39	3.2	92	1.0	175	6.2
41	1.5	101	3.2	176	1.5
43	6.4	102	1.2	186	1.0
44	3.2	103	1.2	187	30.4
50	1.7	104	1.0	188	4.0
51	2.0	111	1.0	190	30.4
53	1.7	115	1.0	191	5.0
55	1.5	119	5.4	201	3.2
57	1.5	120	1.0	202	4.0
62	1.7	131	2.0	230	100.0 M
63	3.7	132	2.0	231	15.1
65	1.0	133	1.0	232	2.0
67	1.2	145	1.2		
69	4.0	147	11.4		
74	3.0	148	1.2		
75	5.4	149	1.2		
76	2.0	159	2.0		
77	2.4	160	1.5		
78	1.0	161	1.2		
79	1.2	162	5.0		

FIGURE I.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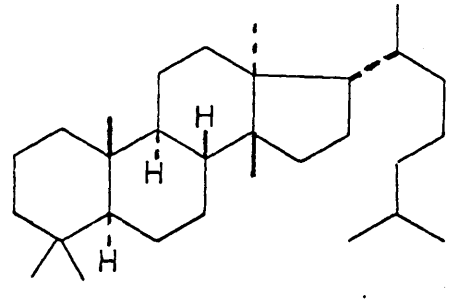


II

CHAPTER 3.

THE MASS SPECTRA OF TETRACYCLIC TRITERPENES.

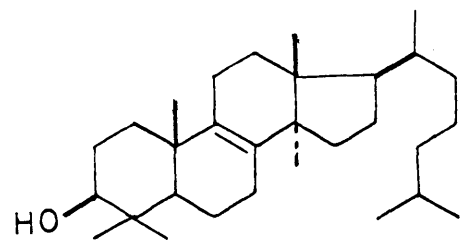
Introduction.

The triterpenes form a group of natural products which are considered to be derived by various cyclizations of squalene. The triterpenes, therefore, contain about thirty carbon atoms, and can be divided into the two main groups of tetracyclic and pentacyclic triterpenes. Although the tetracyclic triterpenes are closely related to steroids, in that both classes of compounds contain the perhydrocyclopentanophenanthrene skeleton, it is only in recent years that many of the structural problems associated with the tetracyclic triterpenes have been solved.

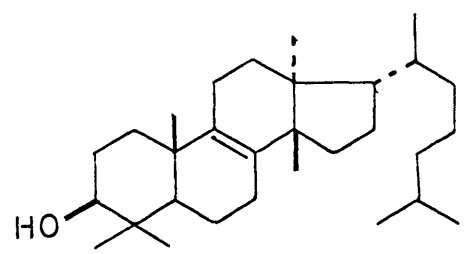
The present study is mainly concerned with the sub-groups of tetracyclic compounds that are related to lanostane (I, Fig.I) and euphane (II, Fig.I). Other compounds in these groups may be derived by modification of the rings and side chains by various oxygen containing functions and carbon-carbon double bonds.

The system of numbering and naming tetracyclic triterpenes is based upon the nomenclature rules for steroids, and is illustrated in Fig.I for lanostane. Substituents that are above the plane of the rings, i.e., cis to the C-19 methyl group are described as β; while those below the plane of the rings, i.e., trans to the C-19 methyl

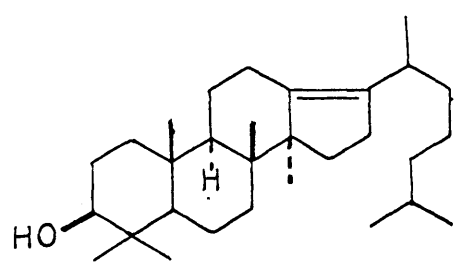
FIGURE II.



III



IV



V

are α. In the diagrammatic representation of such compounds, substituents that are β are attached to the ring by a thick line, those that are α by a broken line. Many of the compounds examined in this work have been named as derivatives of the acetates of lanostenol (III, Fig.II) and euphenol (IV, Fig.II).

The three fused cyclohexane rings of lanostane can adopt a chair: chair: chair conformation, whereas the rings of euphane must adopt a chair: chair:boat conformation. The energy difference between the chair and boat forms of cyclohexane has been estimated as 5.5 kcal./mole,[1] and it is accepted that, because of this energy difference, compounds which contain cyclohexane rings will exist in chair conformations if possible.

It is to be expected, therefore, that compounds with an all chair conformation will be thermodynamically more stable than compounds which are forced to adopt a boat conformation in one of the rings. Thus it is found that euphenol, on treatment with acid,[2,3] rearranges to iso-euphenol (V, Fig.II) the rings of which can exist in the chair conformation. The driving force for this rearrangement has been attributed[3] to the lessening of conformational strain. No corresponding rearrangement is known in the lanostenol series of compounds as such a rearrangement would lead to a conformationally unfavourable structure.[3]

It has been shown[4] that certain features of the mass spectra of cis - trans isomers can be related to their thermodynamic stabilities. Thus, it is a general rule that the abundance of the molecular ion of a cis isomer is smaller than that of the corresponding trans isomer, which usually parallels the relative stabilities of the compounds.[4] However, some exceptions are known; for example, the abundance of the molecular ion of cis - hexahydroindane is smaller than that of trans - hexahydroindane,[5] although the cis isomer is the thermodynamically more stable.[6]

It might be expected, therefore, that a similar effect would be observed in the mass spectra of the lanostane and euphane types of compounds, even although they are not cis - trans isomers.

The mass spectra of the tetracyclic triterpenes were determined with a two-fold objective; firstly, to examine the fragmentation of such compounds, and secondly, to investigate the possibility of relating any differences in their mass spectra with conformational effects.

Discussion.

The mass spectra of euph-8-enyl acetate and lanost-8-enyl acetate are characterized by a lack of specific fragmentation of the tetracyclic ring system. The only important ions in their spectra are the molecular ion, the $(M-CH_3)^+$ ion, and the ion formed by the loss of

acetic acid from the $(M-CH_3)^+$ ion.

The mass spectra of steroids which have a C-17 side chain contain an abundant ion corresponding to the loss of the side chain plus 42 mass units,[7] and the evidence available at present indicates that this fission proceeds with the loss of the C-15, C-16 and C-17 carbon atoms.[8] It is a reasonable assumption that, as the strain associated with the crowding at the C/D ring junction would be relieved, such fragmentation would be an important process in the mass spectra of lanostenyl acetate and euphenyl acetate. However, it is found that no ion corresponding to cleavage through ring D is formed.

The abundance of the molecular ion of lanostenyl acetate is 2.2% Σ_{39}, whilst that of euphenyl acetate is 1.7% Σ_{39}, in agreement with their expected thermodynamic stabilities. Loss of a methyl radical from C-18, C-19 or C-32 would result in stabilization of the positive charge by the Δ^8 double bond in the $(M-CH_3)^+$ ions. The abundance of the $(M-CH_3)^+$ ion of the more congested isomer, euphenyl acetate, is 7.5% Σ_{39}, the corresponding value for lanostenyl acetate being 7.2% Σ_{39}.

As it is known that euphenyl acetate rearranges to the more stable iso-euphenyl acetate, it is to be expected that the molecular ion of iso-euphenyl acetate will be more abundant than that of its isomer. The mass spectrum of iso-euphenyl acetate is in good agreement with

this prediction, the abundance of the molecular ion amounting to 5.0% Σ_{39}. The loss of a methyl radical is a much less probable process, the abundance of the $(M-CH_3)^+$ ion being 0.2% Σ_{39}. In spite of the fact that it is formed by a vinylic fission, the ion corresponding to the loss of the C-17 side chain, m/e 357, is of major importance (2.5% Σ_{39}) in the mass spectrum of iso-euphenyl acetate. Subsequent decomposition of m/e 357 with loss of acetic acid yields m/e 297 (m^* calculated for $357^+ \rightarrow 297^+$ = 271.2; observed 271.2).

Cleavage of the bonds in ring C that are allylic to the 13(17) double bond and concomitant transfer of a hydrogen atom, results in the formation of the ions m/e 263, containing ring A, and m/e 207, containing ring D. Fission of the 8:14 and 9:11 bonds, i.e., at the B/C ring junction yields the ions m/e 249 and m/e 220 for the ring A and ring D containing products respectively. Metastable ions of m/e 156.7 and m/e 143.5 corresponding to the transitions

$$263^+ \longrightarrow 203^+ + 60 \quad (m^* \text{ calculated} = 156.7)$$

and

$$249^+ \longrightarrow 189^+ + 60 \quad (m^* \text{ calculated} = 143.4)$$

confirm that the ions of mass 263 and 249 do contain ring A.

Three compounds with a Δ^7 double bond were available for study, namely, lanost-7-enyl acetate, 9β-euph-7-enyl acetate and 9α-euph-7-enyl acetate (dihydrobutyrospermyl acetate). The mass spectra of lanost-7-enyl acetate and 9α-euph-7-enyl acetate are very

similar to each other and to the spectra of euph-8-enyl and lanost-8-enyl acetates. The abundances of the molecular ions are 1.8 and 1.9% Σ_{39} for the euphene and lanostene compounds respectively. However some steric influence on the fragmentation of these compounds is evident from the abundance of the $(M-CH_3)^+$ ion, which is 9.0% Σ_{39} for 9α-euph-7-enyl acetate and 5.7% Σ_{39} for lanost-7-enyl acetate.

Retro-Diels-Alder decomposition, a reaction which is a prominent feature of the mass spectra of certain pentacyclic[9] and tetracyclic[10] triterpenes, yields the charged diene, m/e 288, of very low abundance in both spectra.

A comparison between the two derivatives of euphenol is possible as the 9α compound, dihydrobutyrospermyl acetate, has a boat form in ring C, while the 9β isomer adopts an all chair conformation. Thus, in agreement with the expected thermodynamic stabilities of these compounds, it is found that the abundance of the molecular ion of 9β-euph-7-enyl acetate is 3.3% Σ_{39}, which is greater than that (1.8% Σ_{39}) that of dihydrobutyrospermyl acetate. The abundances of the $(M-CH_3)^+$ and $(M-CH_3-CH_3CO_2H)^+$ ions are smaller, in the spectrum of the 9β compound, than the abundances of the corresponding ions in the spectrum of the 9α isomer; however, at lower masses the reverse situation occurs. Thus abundant ions are observed at m/e's 357, 315, 397, 288, 270 and 255 in the mass spectrum of 9β-euph-7-enyl acetate.

The ions of mass 357 and 315 arise by loss of the side chain and by loss of the side chain plus 42 mass units respectively. Each of these ions can eliminate a molecule of acetic acid, m/e 357 forming m/e 297 (m^* calculated for $357^+ \longrightarrow 297^+$ = 247.0; observed 247.0), and m/e 315 forming m/e 255 (m^* calculated for $315^+ \longrightarrow 255^+$ = 206.4; observed 206 - 207).

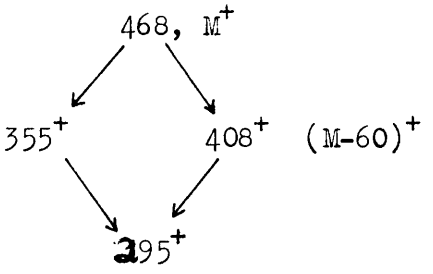
The ion at m/e 270 arises from decomposition, with loss of acetic acid, of m/e 330 which is formed by fission of the 13:17 and 15:16 bonds, a cleavage previously noted in the mass spectra of C-17 substituted steroids.[11]

The mass spectra of lanost-9(11)-enyl acetate and euph-9(11)-enyl acetate are very similar to each other and to the spectra of the isomeric compounds containing a C-7(8) or C-8(9) double bond. Thus loss of a methyl radical and loss of acetic acid from the $(M-CH_3)^+$ ion are the only important features in the spectra of these compounds. No ion corresponding to the monoene or diene produced by retro-Diels-Alder fragmentation is observed in the spectra of either of the $\Delta^{9(11)}$ isomers.

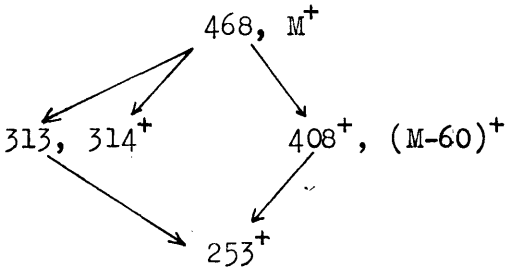
The additional stability conferred on the molecular ion by the presence of a conjugated diene is evident from the abundance ($9.7\% \Sigma_{39}$) of the molecular ion of eupha-7,9(11)-dienyl acetate. Identification of metastable ion transitions (Table I) confirms that

the four fragmentation schemes shown below are possible for eupha-7,9(11)-dienyl acetate.

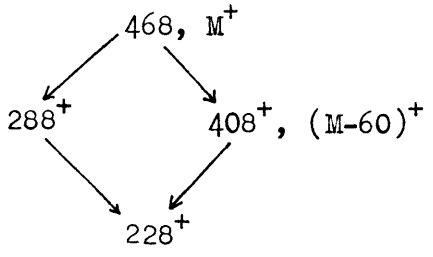
(1)



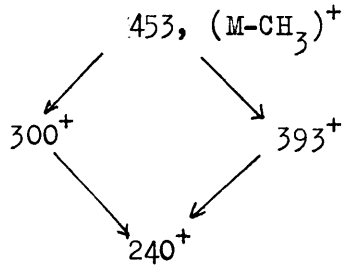
(2)



(3)



(4)



Scheme (1) involves loss of the C-17 side chain, whilst (2)

TABLE I.

	Transition	Observed m*	Calculated m*
Scheme (1)	$468^+ \rightarrow 408^+ + 60$	355.9	355.7
	$468^+ \rightarrow 355^+ + 113$	258.9	258.9
	$355^+ \rightarrow 295^+ + 60$	241.5	241.5
Scheme (2)	$468^+ \rightarrow 313^+ + 155$	209.5	209.3
	$468^+ \rightarrow 314^+ + 154$	210.9	210.7
	$313^+ \rightarrow 253^+ + 60$	204.5	204.5
	$408^+ \rightarrow 253^+ + 155$	157.0	156.9
Scheme (3)	$468^+ \rightarrow 288^+ + 180$	177.3	177.3
	$288^+ \rightarrow 228^+ + 60$	180.6	180.6
Scheme (4)	$453^+ \rightarrow 300^+ + 153$	199.0	198.8
	$300^+ \rightarrow 240^+ + 60$	192.1	192.0

corresponds to the loss of the side chain plus 41 (m/e 314) and 42 mass units (m/e 313).

The ion of mass 288 in scheme (3) must contain ring A as it subsequently decomposes with the loss of acetic acid, and, therefore, must be formed by cleavage of (a) the 11:12, 13:14 and 15:16 bonds; or (b) the 12:13, 13:14 and 14:15 bonds; or (c) the 8:14, 13:14 and 13:17 bonds. Each of these processes (a $\longrightarrow$ c) requires the transfer of a hydrogen atom to the product ion. Of the possibilities (b) seems the most likely as it involves cleavage of bonds which are allylic to the double bonds. Similarly, fragmentation across rings C and D has been noted in the mass spectra of compounds related to the Δ^7 pentacyclic triterpene, bauerene, and of compounds derived from the $\Delta^{9(11)}$ triterpene arborene.[9]

The ion of mass 300 in scheme (4) is formed by loss of the C-17 side chain plus 40 mass units from the $(M-CH_3)^+$ ion.

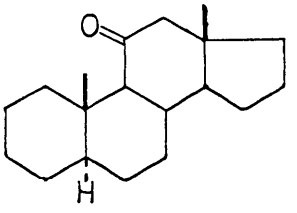
The mass spectrum of lanost-7-en-3-one is almost identical to that of 9β-euph-7-en-3-one. The major differences occur in the abundances of the molecular and $(M-CH_3)^+$ ions. Although both compounds can adopt an all chair (or quasi-chair) conformation, it is found that the molecular ion of 9β-euph-7-en-3-one is more stable than that of its isomer, the respective abundances being 2.6% Σ_{39} and 1.4% Σ_{39}. This result is in good agreement with the relative

stabilities of lanost-7-enyl acetate and 9β-euph-7-enyl acetate. Thus the ratio of the abundance of the molecular ion of 9β-euph-7-enyl acetate to that of lanost-7-enyl acetate is 1.7/1; the corresponding ratio for 9β-euph-7-en-3-one and lanost-7-en-3-one is 1.8/1. This quantitative agreement may be rather fortuitous, but it does demonstrate that the compounds derived from Δ^7-euphene are the more stable to electron bombardment.

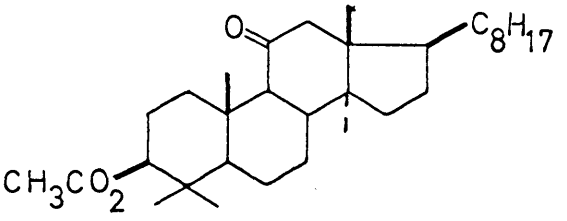
Release of steric crowding on fragmentation would account for the differences in the abundance of the $(M-CH_3)^+$ ions. The abundance of this ion in the spectrum of the less stable isomer (lanost-7-en-3-one) is 6.2% Σ_{39}, that of 9β-euph-7-en-3-one is 2.8% Σ_{39}.

At lower masses both spectra contain peaks at m/e 313, 286, 271 and 245. Loss of the C-17 side chain is responsible for the formation of m/e 313. "Steroid-type" fragmentation with loss of the side chain plus 42 mass units[7] yields the ion of m/e 271. Precise mass determination confirmed that the compositions of the ions m/e 286 and m/e 245 are $C_{20}H_{30}O$ and $C_{17}H_{25}O$ respectively. Hence both ions contain ring A. The ion of mass 286 can be readily derived by fission of the 13:17 and 15:16 bonds of ring D. As the ion m/e 245 contains ring A, it must be formed by fragmentation across rings C and D. Cleavage of the 12:13, 13:14 and 14:15 bonds, a process suggested to occur in the mass spectrum of eupha-7,9(11)-dienyl acetate, results in the formation

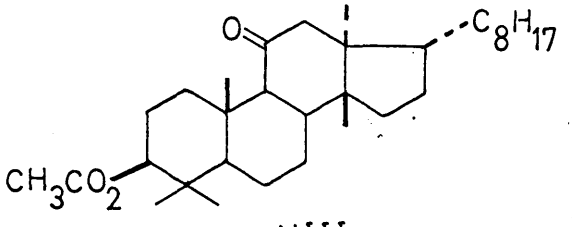
FIGURE III.



VI



VII



VIII

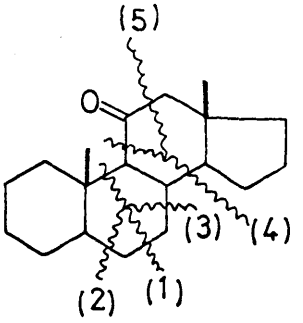
of an ion of mass 245 and composition $C_{17}H_{25}O$.

It has been shown[12] that the main features of the mass spectrum of 5 α-androstan-11-one (VI, Fig.III) can be rationalized in terms of charge localization on the carbonyl group followed by cleavage of the bonds α or β to the carbonyl group. If the same processes occur in the mass spectrum of an 11-keto tetracyclic triterpene it is possible to predict, by calculation of the appropriate mass shift, the ions which should appear in the spectrum of, e.g., 11-ketolanostanyl acetate (VII, Fig.III). A comparison of the predicted and observed ions is given in Fig.IV.

From Fig.IV it is seen that with one exception every process which results in the formation of an ion in the mass spectrum of androstan-11-one is also responsible for the formation of an ion in the spectrum (Fig.Va) of 11-ketolanostanyl acetate. That the observed ions do, in fact, have the correct elemental composition was confirmed by high resolution mass spectrometry.

Although there is a good qualitative agreement between the predicted and observed ions, it can be seen that several processes are less important even on a rough quantitative basis. This is not entirely surprising as it was found that about 50% of the hydrogen transferred in the formation of the ions, m/e 164, 151 and 177, in the spectrum of androstan-11-one originate from C-4.[12] The absence of

FIGURE IV.



	Androstan-11-one		11-Ketolanostanyl acetate	
Fission	ion observed		ion expected	ion observed
(1)	164 (100%)		290	290 (13%)
(2)-H	177	(65%)	303	303 (58%)
(5)-H	177		263	263 (72%)
(3)+H	151 (30%)		277	277 (4%)
(4)-H(A+B)	149 (40%)		235	-----
(4) (C+D)	124 (30%)		250	248 (6%)

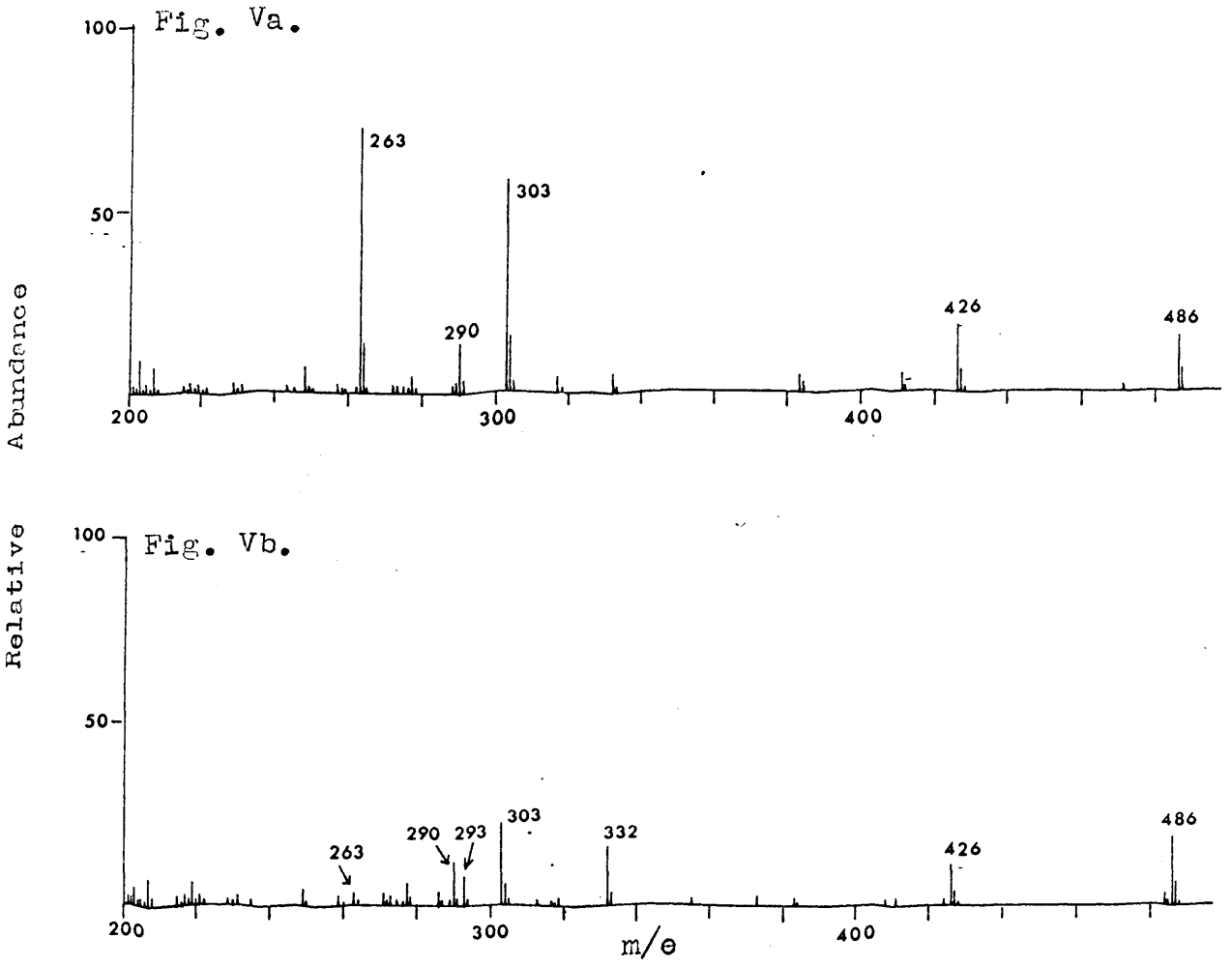


Fig.Va: Mass Spectrum of 11-Ketolanostanyl acetate

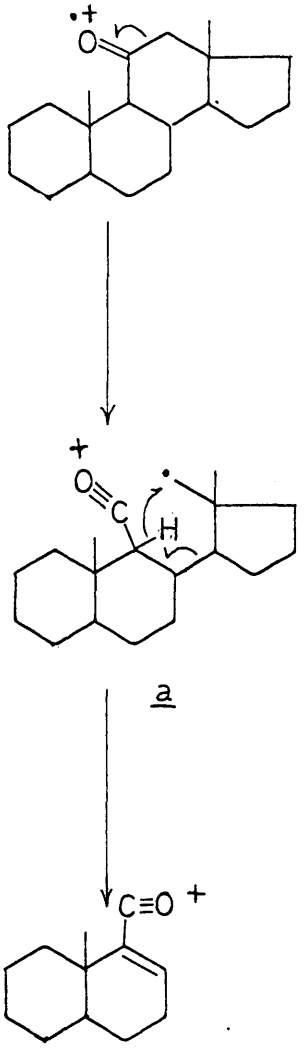
Fig.Vb: Mass Spectrum of 11-Ketoeuphanyl acetate

hydrogen atoms on C-4 would then explain the reduced importance in the mass spectrum of 11-ketolanostanyl acetate of the ion m/e 290 which corresponds to the ion m/e 164 in that of androstan-11-one. This argument, however, should apply equally well to the formation of the ions of mass 277 and 303 in the spectrum of 11-ketolanostanyl acetate. The fact that the fission which gives rise to the ion m/e 303 is of equal, rather than smaller, prominence means that factors other than the availability of hydrogen atoms must be taken into consideration. For example, the increased abundance of m/e 263 and 303 can be attributed to the release of steric crowding of the molecule which accompanies their formation.

The mass spectrum (Fig.Vb) of 11-ketoeuphanyl acetate (VIII, Fig.III) shows some interesting differences from that of the isomeric lanostane compound. The most remarkable difference is the almost complete absence of the ion of m/e 263 in the spectrum of 11-ketoeuphanyl acetate. It has been shown that the formation of the corresponding ion in the spectrum of androstan-11-one, m/e 177, can be explained on the basis of the initial fission of the 11:12 bond; migration of the C-9 hydrogen atom via a six-membered transition state to C-12; and subsequent homolysis of the 8:14 linkage (Fig.VI).[12]

Recent studies with deuterium labelled 11-,[12] 12-,[13] 15-[14] and 16-keto steroids[15] have indicated that the McLafferty rearrangement[16]

FIGURE VI.



a

m/e 177

of ketones will only take place if the interatomic distance between the carbonyl group and the itinerant hydrogen is less than 1.8Å.

It is, therefore, a reasonable assumption that, if the mechanism shown in Fig.VI can be applied to the formation of the ion m/e 263 in the spectrum of 11-ketolanostanyl acetate, the C-9 hydrogen atom and the C-12 carbon atom must attain a minimum separation of approximately 2 Å. The interatomic distance between the C-9 hydrogen and the C-12 carbon atom is approximately 3 Å in the intact molecule. Hence, if this distance is maintained after initial homolysis of the 11:12 bond, rotation about the 8:14 bond is required for the centres involved in the hydrogen transfer reaction to approach each other by about 2 Å. However, Dreiding models show that rotation about the 8:14 bond of the ion, from 11-ketoeuphanyl acetate, corresponding to a (Fig.VI) produces overlap of the C-18 and C-7 hydrogen atoms before this separation can be attained. Thus transfer of the C-9 hydrogen atom and the subsequent formation of the ion m/e 263 may be prevented.

It is also of interest that, when the spectrum of 11-ketoeuphanyl acetate was determined under high resolving power conditions, the ion of mass 277 was found to be composed of two different species which were present in equal amounts. One species corresponded to the expected fragment, $C_{19}H_{33}O$, while the other corresponded to $C_{17}H_{25}O_3$. On the other hand, this ion in the spectrum of 11-ketolanostanyl

acetate was found to be composed of the $C_{19}H_{33}O$ species only. The $C_{17}H_{25}O_3$ fragment may be readily formed by fission of the 12:13 and 8:14 bonds and concomitant transfer of a hydrogen atom. The driving force for this cleavage can be attributed to the release of the strain at the C/D ring junction which accompanies the formation of the $C_{17}H_{25}O_3$ ion.

In addition, the mass spectrum of 11-ketoeuphanyl acetate contains an ion of mass 293. No ion of this mass is observed in the spectrum of the corresponding compound derived from lanostane. Precise mass measurement showed that the composition of m/e 293 is $C_{18}H_{19}O_3$, and that it, therefore, contains ring A. It may be derived by fission of the 11:12, 13:14 and 14:15 bonds, i.e., across rings C and D, thus demonstrating that an unfavourable fragmentation can be produced by steric effects.

Although it is expected that 11-ketoeuphanyl acetate will be the thermodynamically less stable isomer because of the chair:chair:boat conformation it is forced to adopt, the abundance of its molecular ion was found to be greater than that of 11-ketolanostanyl acetate. The respective values are $1.4\% \Sigma_{39}$ and $0.9\% \Sigma_{39}$.

The mass spectrum of 3,11-diketolanostane fully confirms the behaviour to electron impact of an 11-ketolanostane derivative. Thus the ions of m/e 303, 290 and 277 which are present in the spectrum of

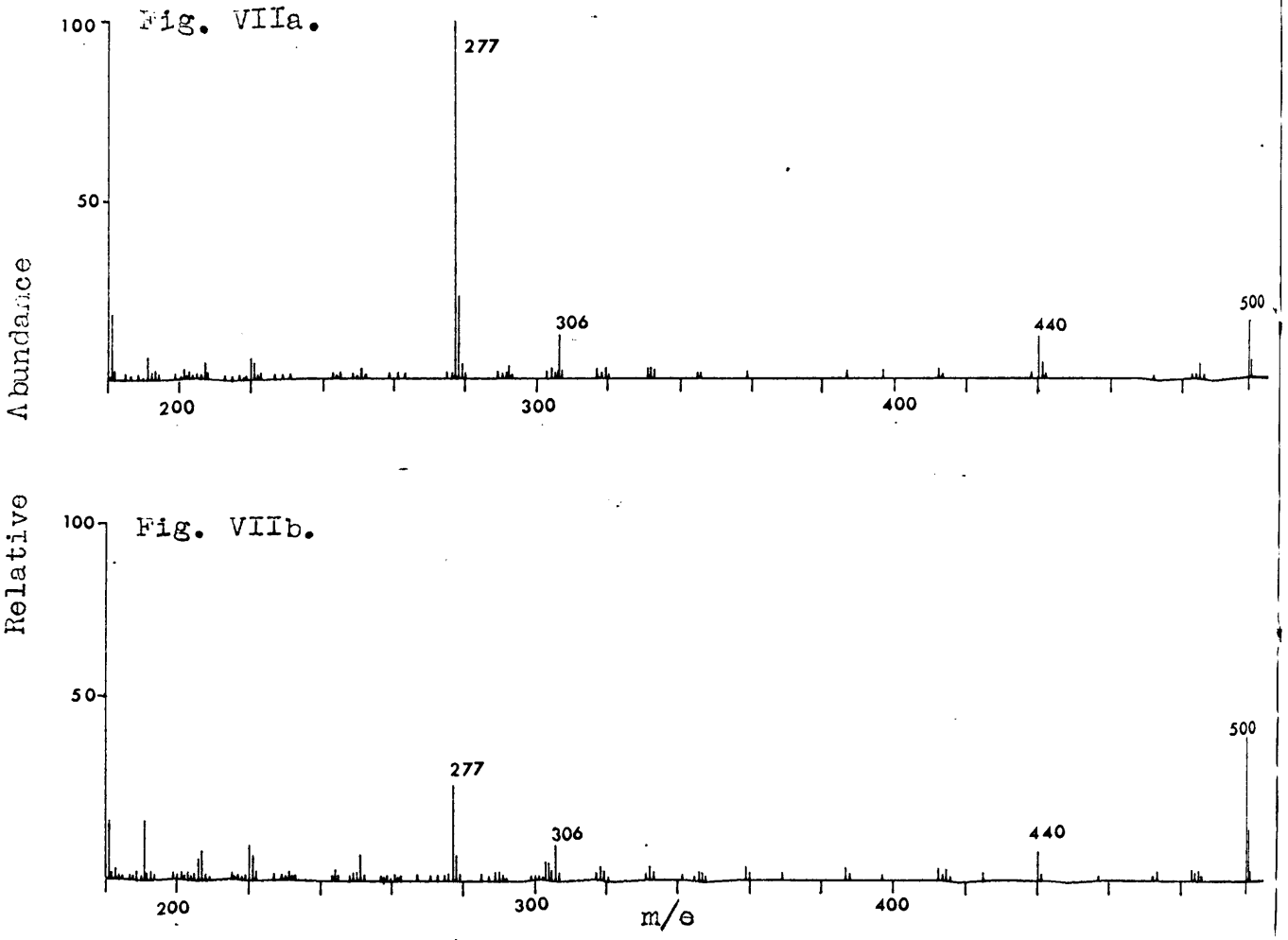


Fig.VIIa: Mass Spectrum of 7,11-Diketoeuphanyl acetate

Fig.VIIb: Mass Spectrum of 7,11-Diketolanostanyl acetate

11-ketolanostanyl acetate are also observed in that of 3,11-diketolanostane; whereas the ion of mass 263 in the spectrum of 11-ketolanostanyl acetate is shifted by 44 mass units to m/e 219 in the spectrum of the diketo compound. In other words the fragmentation of the molecule is still directed by the 11-keto function. However, one new mode of fragmentation is observed in the spectrum of 3,11-diketolanostane. An abundant ion at m/e 414 corresponding to $(M-28)^+$ was proved, by the use of high resolution mass spectrometry, to be formed by the loss of a molecule of carbon monoxide.

In contrast to the behaviour of 11-ketolanostanyl acetate and 11-ketoeuphanyl acetate, it is found that the abundances of the molecular ions of 7,11-diketolanostanyl acetate and 7,11-diketoeuphanyl acetate, which are $2.8\% \Sigma_{39}$ and $1.2\% \Sigma_{39}$ respectively, are in agreement with the expected relative stabilities of the compounds. It might be expected that the mass spectra of the diketo derivatives will exhibit enhanced fragmentation of ring B as the additional carbonyl group at C-7 provides extra sites where favourable cleavages may take place.

Thus, although the ion of m/e 277, which is the most abundant ion in the spectrum (Fig.VIIa) of 7,11-diketoeuphanyl acetate and which is also an important ion in that (Fig.VIIb) of 7,11-diketolanostanyl acetate, could be formed by a process analogous to that resulting in the formation of m/e 263 in the spectrum of 11-ketolanostanyl acetate,

it is found that the composition of m/e 277 is $C_{19}H_{30}O$. Therefore the ion of mass 277 is formed by cleavage of the 9:10 and 7:8 bonds of ring B and concomitant transfer of a hydrogen atom. The alternative mode of formation of the ion m/e 277 by fission of the 11:12 and 8:14 linkages could have been excluded for 7,11-diketoeuphanyl acetate without the use of high resolution mass spectrometry as this process only occurs to a very small extent in the mass spectrum of 11-ketoeuphanyl acetate.

The ion of mass 306 which is present in both spectra is also formed by fission through ring B. Thus it arises by cleavage of the 9:10 and 6:7 bonds, the positive charge remaining with the ring D portion of the molecule.

Another ion which is common to the spectrum of 7,11-diketolanostanyl acetate and to that of the isomeric euphane derivative is m/e 251. Cleavage of the 9:11 and 8:14 linkages results in the formation of two species each of mass 250, but differing in chemical composition. The composition of the fragment containing ring A is $C_{15}H_{22}O_3$, whereas that of the portion containing ring D is $C_{17}H_{30}O$. Thus it is possible that the ion m/e 251 consists of two species each arising from fission at the B/C ring junction accompanied by the transfer of a hydrogen atom. Precise mass measurement confirmed that both species are formed and that 90% of the abundance of the ion m/e 251 is contributed by the $C_{15}H_{23}O_3$ ion. A metastable ion at m/e 145.3 in the mass spectrum of

7,11-diketolanostanyl acetate shows that m/e 251 can decompose with the loss of acetic acid from the $C_{15}H_{23}O_3$ species (m^* calculated for $251^+ \rightarrow 191^+$ = 145.3; observed 145.3).

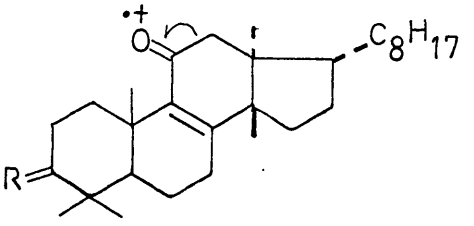
As many of the major fragmentation processes of an 11-keto triterpene take place by initial cleavage of the 9:10 bond, it can be predicted that these fragmentations would be suppressed by the presence of a Δ^8 double bond, as in addition to producing unfavourable vinylic cleavages, hydrogen atoms which can take part in rearrangement reactions are no longer present.

Observation of the shifts in mass of the ions in the spectra of 11-ketoeuph-8-enyl acetate (IX, Fig.VIII) and 3,11-diketoeuph-8-ene (X, Fig.VIII) allows structural assignments to be made for some of the ions. Thus, the ions observed at m/e 332, 303 and 277 in the spectrum of 11-ketoeuphenyl acetate are shifted by 44 units to lower mass values in the spectrum of 3,11-diketoeuphene, i.e., to m/e's 288, 259 and 233. Hence each of these ions contains ring A.

As the ion of mass 332 in the spectrum of 11-ketoeuphenyl acetate contains ring A the neutral fragment must contain the elements of the side chain plus 39 mass units. The simplest way to extract the 39 mass units would be from ring D, although the usual fragmentation of ring D involves loss of the side chain plus 42 mass units.

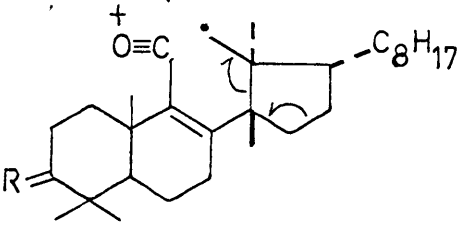
The origin of the ions of m/e 303 and m/e 259 in the spectra of

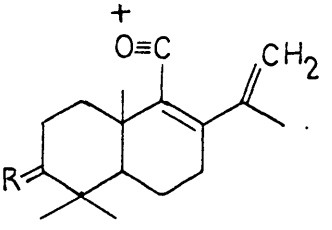
FIGURE VIII.



IX, R = $CH_3CO_2(H)$

X, R = O





m/e 303, R = $CH_3CO_2(H)$

m/e 259, R = O

11-ketoeuphenyl acetate and 3,11-diketoeuph-8-ene respectively can be readily interpreted in terms of charge localization on the 11-keto group, followed by homolysis of the 11:12, 13:14 and 15:16 bonds (Fig.VIII).

The remaining process common to both spectra involves cleavage of the 8:14 and 12:13 linkages accompanied by the transfer of a hydrogen atom to the charge bearing product. This fission gives rise to the ions m/e 277 and 233 in the spectra of 11-ketoeuphenyl acetate and 3,11-diketoeuphene respectively.

It is thus seen that, as expected, the main features of the mass spectra of 11-ketoeuphenyl acetate and 3,11-diketoeuph-8-ene are fragmentations of ring D and not of ring B.

The mass spectrum of 3,11-diketoeuphene contains an ion, m/e 412, which was shown by high resolution mass spectrometry to correspond to $(M-CO)^+$. A metastable ion at m/e 285.5 confirms that the ion of mass 412 can fragment with the loss of 69 mass units (m^* calculated for $412^+ \rightarrow 343^+ = 285.5$), which was proved to be C_5H_9 by exact mass measurement. Thus the ion of m/e 343 corresponds formally to the loss of the four carbon atoms of ring A, although it is formed by a two-step process. Loss of the carbon atoms of ring A which occurs in the mass spectra of coprostan-3-one[11] and 5α-androstan-3-one[17] is known to be a process that is extremely sensitive to slight structural changes.

For example, neither cholestan-3-one[11] nor 4,4-dimethyl-5α-androstan-3-one[18] exhibit this fragmentation when subject to electron impact.

The two ions of greatest abundance in the mass spectra of 7-ketoeuph-8-enyl acetate and 3,7-diketoeuph-8-ene are the molecular ion and the $(M-CH_3)^+$ ion. However, many of the low abundance fragment ions can be assigned structures by the appropriate mass shift in the two spectra. Thus, the ions of mass 327, 313, 285, 271, 259 and 234 in the spectrum of 3,11-diketoeuphene appear at m/e's 371, 357, 329, 315, 303 and 278 in that of 7-ketoeuphenyl acetate respectively.

Loss of the side chain and of the side chain plus 42 mass units from the molecular ion is responsible for the formation of the ions m/e 327 and 285 in the spectrum of the diketone.

Elimination of the side chain less one hydrogen atom from the $(M-CH_3)^+$ ion yields m/e 313, while expulsion of the side chain plus 41 mass units from the $(M-CH_3)^+$ ion yields m/e 271 in the spectrum of 3,11-diketoeuph-8-ene.

The remaining fissions common to both spectra also involve cleavage at the C/D ring junction. Thus the ion m/e 257 can arise by initial homolysis of the allylically activated 11:12 bond with subsequent collapse of the 13:14 and 15:16 bonds. The most probable mode of formation of m/e 234 is by fragmentation of the 12:13 and 8:14 linkages and concomitant transfer of two hydrogen atoms to the ring A/B portion of the molecule.

Conclusions.

The mass spectra of the tetracyclic triterpenes have shown that the presence of a Δ^7, Δ^8 or $\Delta^{9(11)}$ double bond is not sufficient to produce specific fission of the tetracyclic ring system of these compounds. However, it is found that those compounds which contain a carbonyl group in rings B or C undergo cleavage through the rings when subject to electron bombardment. Thus the mass spectra of such derivatives may be of more use in the determination of structural features.

In addition it was found that, with one exception, the compounds which are derived from lanostane are more stable to electron impact than the corresponding compounds derived from euphane, a result which could have been predicted from consideration of the conformations of the rings of the compounds.

REFERENCES.

1. W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger and W. N. Hubbard, J. Amer. Chem. Soc., 1960, 82, 1255.

2. D. Arigoni, R. Viterbo, M. Dunnenberger, O. Jeger and L. Ruzicka, Helv. Chim. Acta, 1954, 37, 2306.

3. D. H. R. Barton, J. F. McGhie, M. K. Pradhan and S. A. Knight, J. Chem. Soc., 1955, 876.

4. P. Natalis in "Mass Spectrometry," R. I. Reed, ed., pp. 379 - 414 and references cited therein, Academic Press, London, 1965.

5. P. Natalis, Nature, 1963, 200, 881.

6. E. L. Eliel, "Stereochemistry of Carbon Compounds," p.276, McGraw-Hill, New York, 1962.

7. R. I. Reed, J. Chem. Soc., 1958, 3432; S. S. Friedland, G. H. Lane, Jr., R. T. Longman, K. E. Train and M. J. O'Neal, Jr., Analyt. Chem., 1959, 31, 169; R. Ryhage and E. Stenhagen, J. Lipid Res., 1960, 1, 361; H. J. M. Fitches in "Advances in Mass Spectrometry," Vol. 2, R. M. Elliot, ed., p. 428, Pergamon Press, London, 1962.

8. H. Budzikiewicz, C. Djerassi and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 2, p.94, Holden-Day Inc., San Francisco, 1964.

9. H. Budzikiewicz, J. M. Wilson and C. Djerassi, J. Amer. Chem. Soc., 1963, 85, 3688.

10. H. E. Audier and B. C. Das, Tetrahedron Letters, 1965, 2205.

11. H. Budzikiewicz and C. Djerassi, J. Amer. Chem. Soc., 1962, 84, 1430.

12. D. H. Williams, J. M. Wilson, H. Budzikiewicz and C. Djerassi, J. Amer. Chem. Soc., 1963, 85, 2091.

13. C. Djerassi and L. Tokes, J. Amer. Chem. Soc., 1966, 88, 536.

14. C. Djerassi, G. von Mutzenbecher, J. Fajkos, D. H. Williams and H. Budzikiewicz, J. Amer. Chem. Soc., 1965, 87, 817.

15. C. Beard, J. M. Wilson, H. Budzikiewicz and C. Djerassi, J. Amer. Chem. Soc., 1964, 86, 269.

16. F. W. McLafferty, Analyt. Chem., 1959, 31, 82.

17. R. H. Shapiro, D. H. Williams, H. Budzikiewicz and C. Djerassi, J. Amer. Chem. Soc., 1964, 86, 2837.

18. R. H. Shapiro and C. Djerassi, Tetrahedron, 1964, 20, 1987.

EXPERIMENTAL.

The mass spectra were determined using an A. E. I. M. S. 9 double-focusing mass spectrometer. The source temperature was maintained at 200°C and the energy of the electron beam was 70eV. A direct inlet system was used to introduce the samples.

The mass spectra of the compounds examined are tabulated overleaf.

The author gratefully acknowledges the generous gift of samples from Dr. W. Lawrie.

MASS SPECTRUM OF LANOST-8-ENYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	1.7	85	3.0	122	3.2	149	6.9	177	2.3
41	27.6	91	6.8	123	9.8	150	1.5	179	1.8
42	1.2	92	1.1	124	1.2	151	2.2	183	1.9
43	45.6	93	11.0	125	2.6	155	1.8	184	0.8
44	1.4	94	2.1	128	1.2	156	1.4	185	5.0
53	1.4	95	24.8	129	2.6	157	5.4	186	1.9
55	22.2	96	10.9	130	1.4	158	1.9	187	11.0
56	1.5	97	1.0	131	7.2	159	12.3	188	2.6
57	17.8	105	12.4	132	2.2	160	3.2	189	8.3
58	0.7	106	2.1	133	12.1	161	15.2	190	1.5
67	6.9	107	15.0	134	3.7	162	2.6	191	1.9
69	30.0	108	2.5	135	14.7	163	5.5	193	3.3
70	1.9	109	15.6	136	4.3	164	1.1	197	1.8
71	9.7	110	1.7	137	4.3	165	1.8	198	0.8
72	0.7	111	7.2	141	1.2	169	2.1	199	4.1
77	1.8	112	0.7	142	1.4	170	1.1	200.	1.2
79	5.7	115	1.0	143	4.4	171	5.7	201	6.9
80	0.8	117	3.0	144	1.8	172	1.9	202	1.7
81	12.4	118	1.1	145	11.0	173	9.9	203	3.7
82	1.6	119	17.9	146	2.6	174	2.5	204	0.8
83	15.7	120	3.3	147	11.2	175	8.4	205	2.9
84	1.1	121	15.9	148	2.2	176	1.5	206	1.0

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
207	2.5	240	4.1	272	1.4	301	4.8	393	3.7
211	1.9	241	10.3	273	10.8	302	1.5	394	1.5
212	1.1	242	2.5	274	4.3	303	1.7	395	88.9
213	5.9	243	5.7	275	8.3	311	1.1	396	28.9
214	4.0	244	1.2	276	2.1	313	3.5	397	5.3
215	11.0	245	1.7	281	1.8	314	1.4	408	1.1
216	2.1	247	1.9	282	1.0	315	3.0	409	1.4
217	1.7	253	4.6	283	4.3	316	1.1	410	1.9
219	3.9	254	1.5	284	1.1	325	1.7	411	1.8
220	1.1	255	6.8	285	1.7	327	1.2	413	1.1
221	1.7	256	1.5	286	1.4	329	1.1	453	2.5
225	2.1	257	3.5	287	2.9	330	1.1	454	1.4
226	1.1	258	1.0	288	1.9	337	1.2	455	100
227	11.2	259	4.1	289	3.9	339	1.5	456	34.7
228	2.9	260	1.4	290	1.1	341	1.9	457	6.6
229	10.8	261	2.5	295	1.7	342	1.0	468	10.9
230	2.2	267	1.4	297	3.0	343	2.3	469	4.4
231	1.4	269	2.5	298	1.1	355	1.2	470	29.9 M
233	2.1	270	1.5	299	3.0	357	1.0	471	10.8
239	2.3	271	2.5	300	1.5	379	1.0	472	1.9

MASS SPECTRUM OF EUPH-8-ENYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	2.5	83	22.1	119	23.5	146	2.9	174	2.7
41	24.7	84	1.8	120	4.1	147	14.0	175	10.1
42	1.9	85	4.4	121	20.9	148	2.6	176	1.6
43	48.6	91	10.7	122	4.2	149	8.0	177	3.0
44	2.6	92	1.8	123	12.6	150	1.5	179	1.8
45	1.8	93	17.3	124	1.5	151	2.9	183	1.9
53	2.3	94	4.5	125	3.7	155	1.8	185	5.5
55	34.2	95	41.0	128	1.4	156	1.3	186	2.1
56	2.8	96	4.0	129	3.5	157	6.2	187	12.9
57	26.3	97	14.9	130	1.6	158	2.1	186	3.1
58	1.1	98	1.2	131	9.6	159	14.1	189	12.2
67	11.0	105	18.3	132	2.1	160	3.2	190	2.0
68	1.4	106	3.1	133	14.4	161	15.4	191	2.3
69	44.0	107	21.9	134	3.1	162	2.6	193	3.2
70	3.0	108	3.4	135	15.4	163	5.6	197	1.7
71	14.2	109	22.6	136	3.3	164	1.3	199	4.1
72	1.1	110	2.3	137	5.3	165	1.9	200	1.3
77	3.2	111	10.0	141	1.3	169	2.0	201	8.6
79	9.7	112	1.1	142	1.4	170	1.1	202	1.9
80	1.4	115	1 .3	143	5.4	171	5.9	203	5.3
81	20.2	117	4.0	144	2.0	172	2.1	204	1.3
82	2.9	118	1.5	145	13.3	173	12.2	205	3.0

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
206	4.7	230	1.9	266	1.0	297	2.9	342	1.0
207	1.3	231	1.4	267	1.3	299	2.9	343	2.4
211	1.3	233	2.6	269	2.6	301	4.2	357	1.9
213	5.4	239	1.8	271	2.1	302	1.1	395	92.0
214	3.2	241	10.0	273	7.3	303	1.1	396	29.5
215	11.5	242	2.1	274	2.6	311	1.1	397	6.5
216	2.2	243	5.1	275	3.3	313	1.5	410	1.8
217	1.8	244	1.1	281	2.4	315	2.3	411	1.6
219	3.5	245	1.8	282	1.o	325	1.3	413	1.0
220	2.0	247	2.1	283	4.0	327	1.2	455	100
221	2.1	255	5.4	284	1.1	328	1.1	456	34.0
225	1.5	256	1.3	285	1.5	329	1.1	457	6.7
227	11.0	257	2.8	287	2.4	337	2.5	470	23.0 M
228	2.6	259	3.1	288	1.1	339	1.1	471	8.3
229	10.0	261	1.8	289	3.0	341	2.9	472	1.4

MASS SPECTRUM OF ISOEUPHENYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	2.1	82	24.1	120	8.0	148	9.9	190	16.1
41	27.5	83	22.9	121	39.2	149	23.0	191	15.8
42	1.8	84	1.8	122	32.6	150	8.0	192	2.8
43	64.2	85	4.1	123	46.8	151	15.3	193	3.0
44	2.1	91	17.7	124	8.3	152	2.1	201	5.0
53	3.2	92	3.2	125	8.7	153	1.1	202	4.2
55	36.9	93	43.6	128	1.6	159	7.1	203	37.2
56	2.8	94	25.2	129	1.6	160	2.8	204	16.3
57	22.5	95	99.5	131	5.9	161	32.1	205	13.3
58	1.0	96	9.4	132	1.8	162	5.5	206	28.2
65	1.6	97	15.1	133	20.9	163	12.4	207	45.9
67	18.1	98	1.6	134	7.6	164	3.9	208	27.3
68	3.2	105	20.9	135	40.6	165	2.5	209	3.7
69	76.1	106	5.7	136	18.6	173	6.4	215	2.8
70	5.0	107	45.9	137	20.9	174	2.1	217	1.3
71	11.9	108	11.2	138	3.7	175	15.6	218	1.6
72	1.1	109	46.8	139	1.8	176	3.0	219	3.4
77	7.3	110	5.5	143	1.6	177	5.7	220	49.3
78	1.1	111	20.6	144	1.0	178	1.4	221	16.1
79	22.9	112	2.1	145	6.9	187	8.7	227	1.8
80	3.2	117	3.0	146	2.3	186	2.8	229	1.4
81	57.3	119	25.2	147	25.2	189	37.2	231	13.1

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
232	2.8	250	2.1	297	25.7	358	14.0	411	3.2
233	3.0	257	1.1	298	6.4	359	2.1	412	1.0
241	1.0	259	1.8	299	1.8	385	1.6	427	1.1
243	1.0	262	2.8	315	1.0	386	2.3	455	4.8
245	1.8	263	5.7	325	1.4	395	2.8	456	1.8
246	1.8	264	3.4	326	1.0	396	1.0	470	100.0 M
247	1.4	271	1.0	356	1.3	409	1.1	471	36.2
249	9.6	273	1.6	357	54.4	410	3.2	472	6.7

MASS SPECTRUM OF LANOST-7-ENYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	1.1	91	9.3	124	1.7	150	1.9	179	2.1
41	14.9	92	3.2	125	2.5	151	2.9	183	1.4
42	1.2	93	14.0	127	1.7	153	1.1	185	4.8
43	38.9	94	4.1	128	1.1	155	1.4	186	1.8
44	1.3	95	29.2	129	2.7	156	1.1	187	11.4
53	1.5	96	3.5	130	1.3	157	5.1	188	2.9
55	22.1	97	9.3	131	8.9	158	1.8	189	7.1
56	1.9	98	1.0	132	3.3	159	12.4	190	1.5
57	18.4	105	17.2	133	20.5	160	3.6	191	2.5
67	7.9	106	4.0	134	8.3	161	14.4	193	3.0
68	1.2	107	20.0	135	27.4	162	2.8	197	1.3
69	27.3	108	3.7	136	5.4	163	6.4	199	3.8
70	2.0	109	17.9	137	5.9	164	1.1	200	1.4
71	10.4	110	2.0	139	1.5	165	2.3	201	6.4
77	2.3	111	6.2	142	1.3	169	1.6	202	3.1
79	7.8	117	4.4	143	4.4	171	5.5	203	5.2
80	1.5	118	1.8	144	1.9	172	2.0	204	1.3
81	17.0	119	20.2	145	12.0	173	15.4	205	2.5
82	2.8	120	5.9	146	3.3	174	3.1	206	1.7
83	14.3	121	17.9	147	15.4	175	15.7	207	2.4
84	1.1	122	5.8	148	6.1	176	2.4	211	1.5
85	3.3	123	13.4	149	11.1	177	3.0	213	5.9

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
214	2.5	241	7.2	269	5.6	297	4.9	357	1.5
215	6.8	242	1.8	270	12.6	298	1.3	367	1.0
216	1.5	243	5.4	271	5.3	299	2.3	393	1.5
217	2.2	244	1.2	272	1.3	301	3.2	395	100
219	3.3	245	2.3	273	10.7	302	1.1	396	32.3
220	1.1	246	2.0	274	3.4	303	1.7	397	5.8
221	1.7	247	2.8	275	4.2	311	1.5	410	4.3
225	1.2	253	2.4	276	1.1	313	2.0	411	2.2
227	7.9	254	1.0	281	1.4	315	5.3	413	1.5
228	2.3	255	20.2	283	4.7	316	2.4	455	74.9
229	12.4	256	4.7	284	1.2	325	2.1	456	26.0
230	2.6	257	4.1	285	1.9	327	1.5	457	4. 9
231	2.1	259	10.2	287	2.9	329	4.2	468	4.6
233	3.5	260	3.1	288	7.3	330	3.7	469	1.8
239	1.4	261	3.7	289	6.2	339	1.2	470	24.5 M
240	2.2	262	2.8	290	1.3	341	1.9	471	8.8
						343	2.2	472	1.7

MASS SPECTRUM OF DIHYDROBUTYROSPERMYL ACETATE

M/e	% Abund.	M/e	% abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	1.0	85	2.8	124	1.3	157	3.6	189	9.9
41	12.9	91	8.7	125	2.4	158	1.3	190	1.8
42	1.0	92	2.4	127	1.1	159	10.3	191	2.4
43	31.5	93	13.0	129	2.0	160	2.4	193	2.7
44	1.0	94	4.3	130	1.1	161	12.1	199	2.7
53	1.3	95	32.8	131	6.6	162	2.4	201	6.4
55	21.2	96	3.9	132	2.2	163	5.0	202	2.6
56	1.7	97	9.6	133	15.0	164	1.0	203	5.9
57	16.9	105	15.5	134	5.8	165	1.7	204	1.4
67	7.4	106	3.5	135	18.7	169	1.0	205	2.6
68	1.1	107	18.6	136	3.7	171	3.9	206	3.3
69	26.4	108	3.3	137	4.5	172	1.3	207	4.0
70	1.7	109	18.4	139	1.4	173	10.0	208	1.1
71	10.1	110	1.8	143	3.1	174	2.4	213	3.8
72	1.0	111	6.9	144	1.3	175	13.9	214	1.9
77	2.1	117	3.4	145	8.9	176	2.1	215	7.6
79	7.2	118	1.3	146	2.2	177	2.6	216	1.6
80	1.1	119	16.9	147	12.2	179	1.7	217	1.9
81	16.2	120	4.7	148	3.8	185	3.4	218	1.4
82	2.6	121	15.3	149	7.4	186	1.3	219	3.4
83	13.6	122	4.7	150	1.3	187	10.7	220	1.8
84	1.0	123	10.5	151	2.5	188	2.5	221	3.0

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
227	7.8	246	1.3	273	9.4	301	3.4	395	82.2
228	2.0	247	2.8	274	3.1	303	1.0	396	26.5
229	8.0	255	6.6	275	3.4	311	1.0	397	5.0
230	1.5	256	1.5	281	1.4	313	1.1	410	1.7
231	1.4	257	3.4	283	4.7	315	2.1	411	1.2
233	2.7	259	6.8	284	1.1	323	1.3	413	1.1
239	1.0	260	2.0	285	1.4	325	1.3	455	100
241	7.0	261	3.2	287	2.0	329	1.7	456	34.4
242	1.7	262	2.4	288	3.3	341	2.3	457	6.2
243	4.9	269	3.4	289	2.9	343	2.1	468	1.6
244	1.0	270	1.1	297	3.6	344	1.0	470	19.9 M
245	1.6	271	1.8	298	1.0	357	2.0	471	7.2
				299	2.2	393	1.0	472	1.3

Mass Spectrum of 9β-Euph-7-enyl acetate.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	4.4	78	2.0	110	7.2	136	17.4	165	3.7
41	48.1	79	24.9	111	14.8	137	12.7	171	9.1
42	4.0	80	5.8	112	2.1	138	2.9	172	4.4
43	100.0	81	58.4	113	2.9	143	8.5	173	31.7
44	3.3	82	14.5	117	8.4	144	4.0	174	9.1
53	5.1	83	40.2	118	3.9	145	25.9	175	34.4
54	1.2	84	3.8	119	46.0	146	7.6	176	6.2
55	70.4	85	10.0	120	14.9	147	34.4	177	6.9
56	6.5	91	21.9	121	47.4	148	15.4	178	1.8
57	58.1	92	13.0	122	40.6	149	25.5	179	3.4
58	2.5	93	39.5	123	31.9	150	5.4	180	5.1
59	1.1	94	15.1	124	5.3	151	6.2	181	1.5
60	1.1	95	75.6	125	6.8	155	2.3	185	8.6
65	2.2	96	10.9	127	3.3	156	1.8	186	3.6
66	1.0	97	21.4	128	2.3	157	10.3	187	20.3
67	26.9	98	2.3	129	5.2	158	4.3	188	7.4
68	5.2	99	2.9	130	3.2	159	28.0	189	14.3
69	84.2	105	43.1	131	18.8	160	7.5	190	3.3
70	6.7	106	12.0	132	8.7	161	26.0	191	6.0
71	31.6	107	52.2	133	42.9	162	6.5	192	2.9
72	2.5	108	13.8	134	22.6	163	11.4	193	7.4
77	7.6	109	45.6	135	75.9	164	2.7	199	9.1

Over.

Mass Spectrum of 9 β -Euph-7-enyl acetate (Cont'd.).

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
200	4.1	230	8.0	269	4.4	314	1.9	385	2.2
201	21.0	231	4.4	270	22.8	315	17.9	393	2.5
202	8.3	233	5.9	271	7.9	316	12.5	394	1.1
203	17.3	234	2.3	272	2.0	317	3.5	395	82.1
204	4.2	239	2.2	273	16.0	325	3.5	396	26.0
205	5.6	240	2.4	274	7.8	326	1.2	397	5.0
206	28.2	241	11.2	275	14.1	327	2.1	410	20.0
207	12.8	242	3.6	276	8.0	329	2.1	411	8.5
208	3.2	243	6.6	277	3.4	330	5.6	412	2.1
213	13.4	244	1.5	283	4.3	331	1.5	455	89.0
214	6.0	245	3.2	287	5.5	339	1.7	456	30.2
215	15.2	246	3.9	288	21.4	341	2.8	457	5.4
216	11.9	247	4.7	289	15.9	343	2.9	470	100.0 M
217	18.4	248	2.2	290	4.7	344	1.6	471	35.8
218	4.2	255	29.3	297	32.8	353	1.8	472	6.5
219	5.8	256	7.5	298	8.6	355	2.2		
220	14.7	257	6.9	299	3.6	356	1.3		
221	8.3	259	5.1	301	5.5	357	17.1		
227	17.6	260	2.9	302	4.4	358	5.9		
228	9.1	261	5.4	303	2.2	367	2.2		
229	32.9	262	2.5	313	2.4	369	1.8		

MASS SPECTRUM OF LANOST-9 (11)-ENYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	2.0	83	18.4	120	8.8	145	13.6	173	11.7
41	20.9	84	1.9	121	24.2	146	4.6	174	3.4
42	1.7	85	4.5	122	6.7	147	14.6	175	19.0
43	47.0	91	11.4	123	14.3	148	4.6	176	4.9
44	1.7	92	2.3	124	1.8	149	10.8	177	3.8
45	1.2	93	19.1	125	3.5	150	3.0	179	2.2
53	2.1	94	23.2	127	1.6	151	1.2	183	1.1
55	31.0	95	41.1	128	1.2	153	1.1	185	4.2
56	2.6	96	4.9	129	2.7	155	1.2	186	1.6
57	22.9	97	11.5	130	1.4	156	1.0	187	10.7
58	1.1	98	1.1	131	10.1	157	5.2	188	4.0
67	12.0	99	1.1	132	4.7	158	2.1	189	9.5
68	1.8	105	21.1	133	17.8	159	15.0	190	2.6
69	37.6	106	5.7	134	7.9	160	3.7	191	2.6
70	2.8	107	4.8	135	20.9	161	19.5	193	7.6
71	12.2	108	7.3	136	8.0	162	3.9	195	1.2
72	1.0	109	26.2	137	6.7	163	6.8	197	1.2
77	3.3	110	7.9	138	1.1	164	1.2	199	3.5
79	9.8	115	1.2	139	1.0	165	2.3	200	1.0
80	1.8	117	4.5	142	1.1	169	1.5	201	7.4
81	22.3	118	2.1	143	4.3	171	5.4	202	2.2
82	12.4	119	27.4	144	2.0	172	2.1	203	5.2

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
204	1.2	230	2.0	261	3.1	298	1.1	353	1.0
205	2.6	231	1.8	269	2.3	299	2.9	357	2.4
206	1.2	233	2.1	270	1.9	301	4.4	358	1.0
207	3.0	239	1.8	271	2.3	302	1.6	367	1.0
211	1.1	241	7.3	272	3.0	303	1.5	395	87.1
213	5.4	242	1.8	273	10.5	313	1.6	396	28.1
214	2.8	243	4.7	274	7.5	315	3.3	397	5.7
215	10.0	244	1.2	275	9.0	317	6.0	409	1.0
216	2.5	245	1.4	276	2.7	318	3.4	310	3.3
217	1.9	247	1.9	281	1.5	325	1.2	411	2.2
219	4.0	248	5.7	283	3.4	327	1.3	412	1.2
220	1.3	249	1.4	285	1.5	330	1.1	413	1.6
221	3.0	255	7.0	286	1.2	332	2.5	455	100
225	1.2	256	1.7	287	3.3	337	1.0	456	37.9
227	7.6	257	5.4	288	4.2	341	2.5	457	7.2
228	2.6	258	1.4	289	6.5	342	1.1	470	36.3 M
229	9.2	259	4.8	290	1.6	343	2.1	471	13.9
		260	1.8	297	4.7	344	1.0	472	4.0

MASS SPECTRUM OF 8α-EUPH-9 (11)-ENYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	1.6	84	1.7	120	5.6	148	3.2	177	2.8
41	17.2	85	4.2	121	18.3	149	7.9	179	1.6
42	1.4	91	9.2	122	4.5	150	1.5	183	1.3
43	36.1	92	1.9	123	11.7	151	2.6	185	3.6
44	1.4	93	14.8	124	1.5	155	1.3	186	1.4
53	1.7	94	16.9	125	3.3	156	1.0	187	10.4
55	26.0	95	34.2	128	1.1	157	4.8	188	2.6
56	2.5	96	3.6	129	2.7	158	1.8	189	10.0
57	19.6	97	11.2	130	1.3	159	12.2	190	2.0
58	1.0	98	1.1	131	8.6	160	3.1	191	2.2
67	9.5	103	1.0	132	3.8	161	13.7	193	3.6
68	1.4	105	17.0	133	14.9	162	2.5	197	1.1
69	31.6	106	4.2	134	4.9	163	4.9	199	2.8
70	2.6	107	19.6	135	15.2	164	0.9	200	0.9
71	10.7	108	4.1	136	3.6	165	1.9	201	7.0
72	1.0	109	17.7	137	4.8	169	1.3	202	1.8
77	2.8	110	1.9	142	1.2	171	4.6	203	4.9
79	8.0	111	7.4	143	3.8	172	1.6	204	1.4
80	1.5	112	0.8	144	1.8	173	10.1	205	2.7
81	17.5	117	3.8	145	11.7	174	2.7	206	1.6
82	9.2	118	1.6	146	3.6	175	12.7	207	4.5
83	17.9	119	21.7	147	12.2	176	2.7	208	1.2

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
211	1.1	231	1.5	260	1.0	288	2.7	393	1.4
213	5.9	233	2.3	261	2.0	289	2.8	395	80.1
214	2.8	239	1.4	269	2.3	297	3.1	396	25.0
215	9.9	240	1.3	270	1.4	299	2.2	397	4.9
216	2.0	241	7.9	271	2.0	301	3.8	410	1.7
217	1.6	242	1.8	272	0.9	302	1.1	411	1.2
219	3.5	243	4.7	273	7.6	303	1.1	413	0.9
220	1.2	246	1.4	274	3.4	313	1.7	455	100
221	2.2	247	2.2	275	3.9	315	2.5	456	34.7
225	1.0	253	1.3	276	1.0	325	1.1	457	5.7
227	9.3	255	5.8	281	1.3	327	1.0	468	3.5
228	2.7	256	1.5	283	3.4	339	1.0	469	1.6
229	8.8	257	2.7	285	1.3	341	1.9	470	19.8 M
230	1.8	259	3.2	287	2.6	343	1.8	471	7.7
						357	2.0	472	1.3

MASS SPECTRUM OF EUPHA-7, 9 (11)-DIENYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	1.0	94	1.3	130	1.8	159	11.3	191	1.0
41	11.4	95	14.9	131	9.2	160	2.6	193	2.3
42	1.0	96	1.7	132	6.1	161	4.0	195	2.2
43	31.4	97	5.3	133	9.0	163	1.2	196	1.3
44	1.0	105	8.4	134	3.4	167	1.6	197	5.1
53	1.9	106	2.9	135	5.8	168	1.3	198	1.8
55	16.0	107	9.9	136	1.0	169	6.8	199	6.3
56	1.4	108	2.0	137	1.5	170	3.3	200	2.0
57	12.6	109	7.8	141	2.3	171	12.5	201	4.8
67	4.6	110	1.0	142	3.2	172	4.1	202	1.5
69	19.6	111	3.0	143	9.2	173	9.7	203	1.5
70	1.4	115	1.2	144	3.1	174	2.1	205	1.1
71	6.6	117	3.0	145	13.1	175	2.0	207	1.0
77	1.4	118	1.5	146	4.9	181	1.9	209	1.8
79	2.5	119	11.0	147	5.8	182	1.4	210	1.1
81	6.1	120	2.7	148	1.3	183	6.2	211	5.7
82	1.6	121	6.5	149	2.1	184	2.4	212	1.8
83	6.8	122	1.9	154	1.0	185	9.1	213	11.2
85	1.7	123	4.7	155	5.0	186	3.9	214	2.8
91	3.5	125	1.1	156	3.8	187	7.2	215	1.9
92	1.0	128	2.1	157	12.7	188	1.7	219	1.0
93	6.4	129	4.4	158	4.0	189	1.6	223	1.5

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
224	1.0	253	21.3	281	2.4	313	19.9	383	2.4
225	8.0	254	8.8	285	1.0	314	7.6	393	23.3
226	2.9	255	3.9	286	5.3	315	2.6	394	10.7
227	9.7	256	1.0	287	4.1	316	1.5	395	2.8
228	5.2	257	2.7	288	19.9	323	2.3	408	6.2
229	2.9	265	1.0	289	4.6	325	1.4	409	4.6
237	1.3	267	2.0	295	10.6	327	1.1	410	1.4
238	1.0	268	1.1	296	2.8	328	2.4	425	1.0
239	11.6	269	1.3	297	1.9	339	5.8	453	17.2
240	24.9	271	1.8	299	2.3	340	2.0	454	5.9
241	12.2	273	6.5	300	6.5	341	1.4	455	1.3
242	3.1	274	1.6	301	7.2	355	6.4	468	100.0 M
243	1.1	279	1.7	302	3.1	356	2.4	469	34.0
				311	1.2	365	1.4	470	6.7

MASS SPECTRUM OF LANOST-7-EN-3-ONE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	9.9	70	56.5	98	3.6	122	6.3	147	10.6
40	8.0	71	7.5	99	1.8	123	16.5	148	3.5
41	69.2	72	23.3	100	2.2	124	4.5	149	8.2
42	8.6	73	15.1	101	2.1	125	7.3	150	2.2
43	81.7	74	2.7	103	1.4	126	2.8	151	5.4
44	13.2	77	7.4	104	1.0	129	4.1	152	2.3
45	4.5	78	2.1	105	23.5	130	2.2	155	1.7
50	2.1	79	16.9	106	6.1	131	9.4	156	1.7
51	2.1	80	4.0	107	20.8	132	4.3	157	4.2
52	1.1	81	38.1	108	5.2	133	17.5	158	1.6
53	7.8	82	6.6	109	22.0	134	5.8	159	8.2
54	5.3	83	30.2	110	5.2	135	12.4	160	2.9
55	77.6	84	3.5	111	9.6	136	4.2	161	9.1
56	11.2	85	6.1	112	1.8	137	7.1	162	1.7
57	53.7	86	1.8	113	1.0	138	3.4	163	7.3
58	2.1	91	17.5	115	2.0	139	3.9	164	1.8
59	25.5	92	4.5	116	1.1	140	1.3	165	3.6
60	4.2	93	20.3	117	5.7	142	1.8	166	1.0
66	3.2	94	7.2	118	1.6	143	4.8	169	1.2
67	1.9	95	43.4	119	20.2	144	1.9	171	4.0
68	28.2	96	9.9	120	6.1	145	9.6	172	1.3
69	6.1	97	19.4	121	18.1	146	3.1	173	5.6

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
174	1.8	195	2.1	227	1.6	259	10.0	300	1.0
175	6.8	199	3.2	228	1.2	260	2.5	315	4.5
176	1.5	200	2.1	229	2.8	261	2.9	316	1.3
177	3.5	201	4.7	230	1.0	269	1.7	321	1.0
178	1.0	202	1.3	231	3.9	271	21.4	323	5.2
179	4.4	203	4.0	232	1.1	272	6.3	324	1.8
180	1.3	204	3.1	233	1.7	273	7.4	325	1.0
181	3.2	205	1.0	241	1.1	274	1.6	335	2.4
182	1.4	206	1.8	243	6.6	275	1.6	337	1.2
187	4.4	213	1.8	244	3.1	281	3.5	393	2.8
188	2.3	215	3.7	245	15.8	282	1.0	409	1.7
189	12.7	216	1.6	246	2.5	283	1.3	411	100.0
190	3.1	217	2.0	247	1.4	285	8.4	412	33.4
191	4.6	218	3.1	253	1.4	286	8.8	413	5.2
192	1.4	219	3.4	255	1.4	287	2.7	424	2.5
193	2.5	220	2.7	256	1.2	288	2.0	426	22.8 M
194	1.0	221	1.3	257	7.8	297	2.1	427	6.9
				258	2.9	299	4.0	428	1.3

MASS SPECTRUM OF 9 β - EUPH-7-EN-3-ONE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	5.7	71	22.1	107	24.0	132	3.6	161	7.1
40	4.2	72	1.2	108	6.9	133	19.4	162	1.5
41	65.1	77	7.2	109	20.9	134	7.8	163	6.2
42	6.7	78	1.8	110	5.0	135	19.4	164	1.0
43	100.0	79	17.6	111	6.8	136	4.5	165	1.6
44	5.4	80	4.0	112	1.2	137	5.0	169	1.2
45	1.2	81	36.5	115	2.2	138	1.7	171	2.7
50	1.3	82	8.2	116	1.2	139	4.1	172	1.4
51	1.5	83	23.4	117	4.5	143	3.2	173	5.8
53	7.5	84	2.7	118	1.5	144	1.9	174	2.2
54	2.1	85	3.8	119	19.3	145	9.3	175	8.3
55	65.7	91	18.1	120	6.2	146	3.7	176	1.5
56	9.8	92	6.2	121	19.3	147	13.2	177	3.1
57	56.2	93	21.5	122	10.6	148	4.1	178	1.0
58	2.0	94	9.3	123	14.1	149	8.3	179	1.3
59	1.4	95	40.6	124	1.9	150	1.7	180	1.7
65	2.4	96	9.1	125	6.2	151	2.8	185	1.7
66	1.0	97	10.6	126	1.4	152	1.1	186	1.4
67	23.5	98	1.0	127	1.4	157	4.2	187	7.9
68	4.5	99	1.3	129	2.5	158	2.0	188	1.9
69	45.6	105	23.1	130	1.2	159	8.3	189	5.2
70	4.5	106	5.6	131	8.1	160	3.2	190	1.0

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
191	2.7	207	4.2	230	1.0	259	3.2	297	1.2
192	1.3	208	1.0	231	1.8	260	1.0	299	1.2
193	2.7	213	1.0	232	2.9	261	1.0	313	12.0
194	1.3	215	2.7	233	3.5	271	14.7	314	2.7
199	1.4	216	1.4	234	1.2	272	5.8	327	1.4
200	1.1	217	4.2	243	3.6	273	3.7	341	2.5
201	3.5	218	2.1	244	2.9	274	1.3	411	24.8
202	1.3	219	4.0	245	12.4	275	2.8	412	6.9
203	2.7	220	3.3	246	3.2	285	1.4	413	1.3
204	2.1	221	1.3	247	1.0	286	4.9	424	1.0
205	2.4	227	1.7	257	2.7	287	1.9	426	35.0 M
206	4.6	229	2.5	258	2.0	288	1.5	427	11.2
								428	1.9

MASS SPECTRUM OF 11-KETOLANOSTANYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	5.6	70	8.1	106	4.6	134	7.5	165	1.9
40	3.1	71	7.0	107	27.3	135	22.8	166	1.1
41	52.7	77	4.9	108	31.8	136	17.1	171	1.1
42	4.8	78	1.5	109	8.2	137	17.1	173	3.0
43	100	79	17.3	110	6.7	138	3.7	174	1.9
44	5.6	80	4.7	111	1.1	139	2.9	175	13.4
45	3.6	81	43.5	112	1.1	143	4.1	176	7.1
50	1.4	82	31.7	117	1.9	144	2.9	177	4.8
51	1.2	83	28.4	118	1.3	145	8.4	178	1.1
53	6.9	84	4.1	119	15.4	146	3.9	179	1.1
54	5.7	85	4.1	120	6.8	147	8.9	185	1.1
55	65.4	86	1.2	121	30.1	148	7.9	187	1.9
56	9.2	91	12.3	122	13.2	149	4.1	188	1.1
57	51.1	92	2.8	123	19.0	150	2.0	189	3.4
58	1.9	93	27.7	124	4.5	151	1.1	190	1.9
59	11.4	94	15.6	125	2.6	157	1.1	191	3.2
60	3.2	95	68.3	126	1.1	159	3.9	192	1.4
65	1.9	96	11.1	127	1.4	160	3.3	193	2.6
66	1.5	97	11.9	128	1.1	161	9.2	194	1.3
67	28.9	98	2.0	131	3.1	162	3.0	199	1.1
68	8.4	99	1.1	132	2.6	163	6.9	201	2.3
69	79.5	105	15.9	133	14.2	164	1.9	202	1.4

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
203	8.7	220	2.0	259	1.0	286	1.7	333	1.1
204	1.9	221	1.1	262	1.3	287	1.1	383	3.8
205	1.6	229	2.5	263	72.3	289	2.4	384	2.7
206	1.1	230	1.3	264	12.8	290	13.0	411	3.7
207	5.6	231	1.5	265	1.9	291	2.8	412	1.9
208	1.7	243	1.1	271	2.4	303	58.2	426	17.9
215	1.6	245	1.1	272	2.1	304	14.7	427	7.4
216	1.4	248	6.4	275	1.2	305	3.1	428	1.9
217	1.8	249	1.9	276	1.2	317	4.1	471	1.4
218	1.1	250	1.2	277	3.6	318	1.8	486	15.3 M
219	2.4	257	1.9	278	1.0	319	1.1	487	6.1
		258	1.2	281	1.1	332	4.1	488	1.3

MASS SPECTRUM OF 11-KETOEUPHANYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	6.6	70	5.9	107	22.0	136	13.2	173	2.7
40	2.1	71	16.7	108	9.1	137	14.7	174	1.6
41	62.7	72	1.9	109	32.8	138	2.7	175	12.4
42	6.8	77	4.0	110	11.9	139	2.0	176	4.1
43	100	78	1.2	111	5.6	143	1.0	177	5.2
44	8.6	79	13.9	112	1.1	145	4.1	178	1.1
45	3.6	80	3.8	113	1.2	146	1.7	185	1.4
50	1.4	81	38.1	117	1.6	147	5.8	186	1.0
51	1.2	82	25.4	118	1.0	148	2.7	187	2.3
53	5.4	83	20.6	119	11.8	149	7.1	188	1.0
54	2.6	84	3.0	120	5.0	150	4.0	189	2.6
55	52.3	85	3.4	121	22.4	151	1.8	190	1.4
56	6.8	91	9.2	122	8.7	152	1.1	191	2.0
57	42.7	92	2.0	123	15.2	157	1.0	192	1.1
58	2.4	93	23.1	124	2.6	159	4.2	193	4.7
59	1.6	94	24.5	125	3.1	160	2.2	194	1.1
60	1.3	95	68.2	129	1.4	161	7.9	199	1.1
65	2.2	96	10.7	131	2.8	162	3.6	201	1.6
66	1.4	97	9.9	132	1.2	163	5.7	202	1.6
67	24.0	98	1.4	133	10.1	164	1.3	203	3.8
68	7.2	105	10.7	134	4.8	165	2.1	204	1.1
69	72.3	106	3.8	135	20.4	171	1.2	205	1.1

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
206	1.2	231	1.9	272	1.3	295	1.4	384	1.1
207	6.9	233	1.1	273	1.5	303	21.6	411	2.6
208	2.9	235	1.1	275	1.2	304	5.1	412	1.4
215	2.1	241	2.4	276	1.0	305	1.3	424	1.2
216	1.0	242	1.0	277	4.6	313	1.4	426	10.4
217	1.7	243	1.3	278	1.1	317	1.2	427	4.0
218	1.8	245	1.3	286	3.4	318	1.1	428	1.0
219	6.3	249	3.7	287	1.1	319	2.2	468	1.1
220	1.8	250	1.7	289	1.1	332	13.1	471	1.4
221	3.0	259	2.0	290	11.5	333	2.9	484	3.6
222	1.9	263	3.4	291	3.1	355	1.5	485	2.1
229	1.1	264	1.1	293	7.0	373	1.7	486	18.3 M
230	1.1	271	2.5	294	1.3	374	1.1	487	6.2
						383	2.3	488	1.1

MASS SPECTRUM OF 7, 11 - DIKETOLANOSTANYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	6.4	70	4.9	107	30.8	138	3.2	173	2.6
40	3.8	71	20.0	108	15.2	143	1.1	174	1.0
41	59.6	72	2.1	109	30.1	145	3.9	175	4.1
42	6.0	77	4.5	110	6.8	146	1.0	176	1.1
43	100	78	1.3	111	5.0	147	6.9	177	2.9
44	5.8	79	13.2	112	1.2	148	2.1	178	1.8
45	1.7	80	6.8	117	2.1	149	8.4	179	2.0
50	1.1	81	30.9	119	12.1	150	3.4	181	4.1
51	1.1	82	9.8	120	6.7	151	3.5	182	1.1
53	5.6	83	21.2	121	34.5	153	1.3	183	1.3
54	2.4	84	1.3	122	16.0	157	1.1	185	1.0
55	59.4	85	3.0	123	18.1	158	1.0	187	2.1
56	5.8	91	11.2	124	3.8	159	3.1	188	1.1
57	51.0	92	3.2	125	3.0	160	1.4	189	2.8
58	2.3	93	24.9	129	1.1	161	4.2	190	1.0
59	1.2	94	8.5	131	2.8	162	2.3	191	15.7
60	1.0	95	44.7	132	1.2	163	9.7	192	1.7
65	2.3	96	10.3	133	7.8	164	3.8	193	2.9
66	1.0	97	10.7	134	3.0	165	3.0	194	1.1
67	23.6	98	1.4	135	19.5	166	1.4	199	1.1
68	6.1	105	12.0	136	13.1	167	1.0	201	1.3
69	64.8	106	3.7	137	2.6	171	1.0	203	1.8

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
204	1.0	232	1.0	271	1.0	307	1.8	388	1.2
205	1.8	233	1.3	275	1.3	317	1.1	413	2.7
206	4.6	243	1.2	276	1.6	318	2.8	414	1.2
207	8.0	244	2.0	277	24.5	319	2.1	415	3.0
208	1.6	245	1.2	278	6.8	320	1.3	416	1.3
209	1.0	248	1.1	279	2.7	331	1.3	425	2.0
215	1.0	249	1.8	289	2.4	332	3.4	440	7.3
217	1.0	250	1.4	290	2.1	333	1.0	441	2.1
218	1.0	251	6.4	291	2.2	341	1.0	472	2.0
219	1.9	252	1.4	292	1.3	345	1.1	483	3.4
220	10.4	257	1.3	301	1.4	346	1.9	484	1.5
221	7.1	259	1.5	302	1.1	347	1.9	485	3.2
222	2.5	261	1.3	303	4.5	348	1.2	486	1.4
227	0.9	262	1.0	304	4.8	359	3.2	500	39.4 M
229	0.9	263	1.3	305	2.6	360	2.1	501	14.2
231	2.1	267	1.0	306	8.7	387	2.6	502	3.1

MASS SPECTRUM OF 7, 11-DIKETOEUPHANYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
39	5.8	70	3.6	107	20.7	146	1.2	176	1.8
40	4.0	71	14.2	108	9.1	147	5.6	177	2.0
41	52.3	72	1.4	109	22.0	148	1.6	178	1.1
42	4.8	75	4.8	110	4.6	149	6.3	179	1.2
43	85.4	76	1.2	111	4.0	150	1.9	181	18.5
44	3.6	77	9.9	117	1.8	151	2.9	182	2.8
45	2.1	78	4.8	119	8.2	152	1.4	185	1.1
50	1.4	79	23.7	120	15.9	153	1.0	187	1.1
51	1.3	80	8.0	121	30.8	157	1.2	189	2.3
53	5.2	81	15.2	122	12.4	158	1.0	190	1.0
54	2.1	82	2.1	123	3.4	159	2.4	191	5.7
55	45.7	83	2.3	124	3.0	160	1.2	192	1.1
56	4.6	91	9.4	131	2.4	161	4.1	193	3.1
57	37.9	92	3.9	132	1.0	162	1.7	194	1.0
58	2.4	93	21.3	133	6.2	163	14.5	199	1.1
59	1.3	94	6.2	134	3.1	164	4.4	201	1.4
60	1.3	95	35.1	135	15.6	165	3.8	203	1.6
65	1.7	96	6.7	136	43.7	166	1.0	205	1.1
66	1.2	97	8.8	137	13.2	171	1.0	206	1.1
67	20.0	98	1.3	138	1.8	173	2.5	207	3.7
68	5.4	105	9.1	139	1.9	174	1.1	208	1.0
69	48.7	106	4.0	145	3.6	175	2.5	213	1.1

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
215	1.4	243	1.0	279	3.6	318	1.1	415	1.0
216	1.0	244	0.9	280	1.0	319	2.1	422	1.7
217	1.3	245	1.0	289	1.1	320	1.0	423	1.1
218	1.1	249	1.0	290	1.1	331	1.0	425	1.0
219	1.2	250	0.8	291	1.1	332	1.0	438	1.1
220	4.5	251	1.9	292	1.7	333	1.0	440	10.7
221	3.5	259	1.0	293	1.0	345	1.4	441	1.0
222	1.0	261	1.1	303	2.0	346	0.8	457	1.3
223	1.0	263	1.0	304	2.7	359	1.0	472	1.0
227	1.1	275	1.1	305	2.4	387	1.0	485	3.8
229	1.1	276	1.1	306	11.8	397	1.1	486	1.3
231	1.1	277	100.0	307	2.8	412	1.6	500	14.9 M
233	1.1	278	22.6	317	1.8	413	1.0	501	4.8
								502	1.3

MASS SPECTRUM OF 11-KETOEUPH-8-ENYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
53	1.1	95	15.9	134	2.5	169	1.3	202	1.7
55	23.0	96	2.1	135	10.6	171	2.8	203	14.0
56	3.0	97	4.2	136	2.2	172	1.1	204	2.1
57	15.2	105	7.6	137	3.2	173	5.5	207	1.1
60	1.1	106	1.5	143	2.2	174	1.9	211	1.1
67	6.1	107	9.3	144	1.1	175	5.5	213	2.2
68	1.5	108	2.5	145	5.3	176	1.3	215	3.6
69	24.7	109	8.9	146	1.5	177	3.6	216	2.2
70	2.2	110	1.1	147	5.9	179	1.7	217	7.8
71	6.6	111	1.7	148	2.1	183	1.3	218	1.7
77	2.2	117	1.9	149	4.4	184	3.0	219	1.5
79	4.4	119	8.5	150	1.1	185	1.1	225	1.1
80	1.1	120	2.1	151	1.1	186	3.8	227	2.3
81	10.2	121	9.9	155	1.1	187	1.7	228	1.1
82	2.1	122	5.9	157	2.8	188	7.0	229	1.7
83	8.5	123	7.0	158	1.3	189	1.5	231	1.1
84	1.1	124	1.1	159	5.3	190	1.5	233	1.3
85	1.7	128	1.3	160	1.7	192	2.1	241	1.9
91	5.5	129	1.9	161	5.9	197	1.1	243	2.3
92	1.1	131	3.6	162	1.3	199	2.2	255	1.7
93	7.2	132	1.3	163	2.2	200	1.1	257	1.1
94	1.7	133	7.0	164	1.1	201	6.7	261	3.6

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
263	2.8	303	7.0	332	19.0	396	1.7	431	1.7
269	4.9	304	3.8	333	4.2	409	8.5	432	1.9
270	1.3	311	1.0	342	1.1	410	3.2	468	2.3
271	1.1	316	1.5	346	1.0	422	1.3	469	4.4
272	1.1	317	1.5	355	1.5	423	1.1	470	2.1
277	43.3	318	1.1	371	2.1	424	27.5	482	2.3
278	8.5	327	1.1	372	1.5	425	10.2	483	1.7
279	1.1	328	1.1	381	1.7	426	3.2	484	100.0 M
288	1.1	329	1.5	382	1.0	427	1.3	485	36.8
289	1.1	330	1.1	395	4.2	430	1.9	486	6.8

MASS SPECTRUM OF 3, 11-DIKETOEUPH-8-ENE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
53	3.3	92	1.6	124	1.4	149	8.0	179	1.8
55	75.9	93	9.6	125	3.1	150	1.6	183	1.6
56	4.1	94	2.5	126	1.0	151	1.6	185	2.9
57	28.4	95	19.0	128	1.8	155	1.4	186	1.2
58	1.2	96	2.9	129	2.7	156	1.0	187	4.9
59	1.4	97	5.7	130	1.4	157	3.5	188	2.0
65	1.6	105	11.7	131	4.7	158	1.6	189	5.5
67	12.3	106	2.0	132	1.2	159	6.1	190	1.6
68	1.8	107	12.3	133	7.6	160	2.0	191	2.5
69	35.2	108	2.2	134	2.2	161	9.4	193	1.8
70	2.9	109	11.4	135	13.3	162	2.4	197	1.4
71	11.8	110	1.6	136	2.4	163	3.3	199	2.5
77	4.3	111	2.5	137	3.5	164	1.0	200	1.0
78	1.0	115	1.8	138	1.2	165	1.0	201	3.8
79	7.8	116	1.0	141	1.0	169	1.4	202	1.4
80	1.4	117	3.3	142	1.4	171	3.3	203	2.9
81	15.3	118	1.0	143	3.1	172	1.4	204	1.4
82	2.2	119	12.1	144	1.6	173	5.9	205	3.9
83	12.1	120	2.0	145	6.9	174	2.2	207	1.4
84	1.2	121	8.0	146	1.8	175	6.3	211	1.0
85	1.6	122	2.0	147	7.4	176	1.8	213	2.2
91	9.8	123	6.3	148	2.0	177	4.5	214	1.0

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
215	4.1	235	1.8	274	1.0	329	3.9	397	4.1
216	1.2	239	1.0	285	5.9	330	1.6	398	1.6
217	9.2	241	1.8	286	3.3	342	3.5	407	1.2
218	2.0	243	2.5	287	2.0	343	70.4	411	8.3
219	9.6	244	1.2	288	17.2	344	19.6	412	32.9
220	1.6	245	1.8	289	3.9	345	2.5	413	10.0
225	1.0	255	1.2	290	1.0	354	1.8	414	1.6
227	1.8	257	2.2	299	1.2	355	3.9	425	8.6
229	3.1	259	13.5	300	1.0	356	1.8	426	3.1
230	1.2	260	4.1	301	1.4	357	1.0	438	1.6
231	2.4	269	1.2	311	1.2	369	1.8	439	1.7
232	1.6	271	2.0	313	1.6	370	1.0	440	100 M
233	94.9	272	2.7	327	5.1	383	1.2	441	34.0
234	15.8	273	2.4	328	2.5	385	1.2	442	5.9

MASS SPECTRUM OF 7-KETOEUPH-8-ENYL ACETATE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
53	2.5	94	2.2	131	4.5	159	7.0	197	1.3
55	29.7	95	22.1	132	1.1	160	1.9	199	2.5
56	3.2	96	2.5	133	8.5	161	8.1	201	3.4
57	25.0	97	5.3	134	2.1	162	1.7	202	1.1
58	1.0	105	10.6	135	12.7	163	3.4	203	3.0
65	1.1	106	1.7	136	1.7	164	1.1	205	1.1
67	8.0	107	12.9	137	2.5	169	1.3	206	1.1
68	1.5	108	2.1	141	1.0	171	2.5	207	10.6
69	30.7	109	8.7	142	1.1	172	1.1	208	1.7
70	2.5	110	1.3	143	2.5	173	6.6	211	1.3
71	8.9	111	2.8	144	1.3	174	1.7	213	2.1
77	2.8	117	2.3	145	5.7	175	10.2	214	1.1
79	6.9	119	10.6	146	1.7	176	1.7	215	2.1
80	1.0	120	1.7	147	9.1	177	1.3	217	1.3
81	11.5	121	19.1	148	2.1	183	1.3	225	1.0
82	1.7	122	3.0	149	6.6	185	2.8	227	2.3
83	10.8	123	5.7	150	1.1	186	1.1	228	1.1
84	1.0	124	1.0	151	1.1	187	4.2	229	4.9
85	1.5	125	1.1	155	1.1	188	1.3	230	1.1
91	7.2	128	1.1	156	1.0	189	5.3	231	1.0
92	1.5	129	1.9	157	3.0	190	1.1	241	1.5
93	12.5	130	1.1	158	1.1	191	1.1	242	1.0

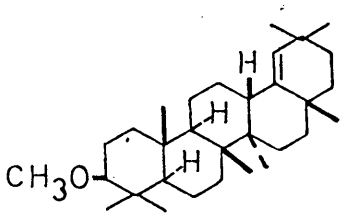
M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
243	6.8	271	1.0	302	1.9	330	1.5	424	1.0
244	1.3	273	1.5	303	3.4	331	1.0	425	1.1
247	1.1	278	7.6	304	1.5	344	1.1	427	1.1
255	2.3	279	1.5	305	1.1	355	1.1	441	1.5
256	1.1	287	2.3	311	1.1	357	4.5	469	100.0
257	1.3	288	1.7	315	4.2	358	1.1	470	36.0
259	1.1	289	1.3	316	3.6	371	10.8	471	6.4
261	1.1	297	1.1	317	1.8	372	3.0	484	91.2 M
269	1.3	301	1.3	329	3.6	391	1.1	485	31.8
						399	1.1	486	5.9

MASS SPECTRUM OF 3, 7-DIKETOEUPH-8-ENE

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
50	2.4	79	8.1	111	1.3	141	1.8	169	1.6
51	2.3	80	1.9	115	2.4	142	1.8	170	1.0
52	1.3	81	13.5	116	1.3	143	2.9	171	2.9
53	5.8	82	3.4	117	3.2	144	1.5	172	1.5
54	2.3	83	13.5	118	1.1	145	6.8	173	6.5
55	45.4	84	2.4	119	9.2	146	1.9	174	1.9
56	7.8	85	3.6	120	2.4	147	8.1	175	7.6
57	33.4	91	11.0	121	23.5	148	2.1	176	1.6
58	1.6	92	2.1	122	3.7	149	6.5	179	1.6
59	1.8	93	14.4	123	7.3	150	1.3	183	1.5
60	4.9	94	6.6	124	1.5	151	1.9	185	2.9
65	3.4	95	22.7	125	4.4	155	1.6	186	1.1
66	5.2	96	4.1	128	2.8	156	1.3	187	3.6
67	13.6	97	7.5	129	3.1	157	3.1	188	2.3
68	2.9	98	1.6	130	1.6	158	1.6	189	3.9
69	34.2	99	1.3	131	4.9	159	6.5	190	1.1
70	4.9	105	10.0	132	1.5	160	2.1	191	1.1
71	13.1	106	2.1	133	7.9	161	6.5	193	1.0
73	1.8	107	10.0	134	2.4	162	1.9	195	1.0
74	2.4	108	2.8	135	14.9	163	3.6	197	1.3
77	5.5	109	11.3	136	2.3	164	1.0	199	2.1
78	2.0	110	2.1	137	4.5	165	1.9	201	2.9

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
202	1.1	229	1.5	261	1.3	303	1.0	397	1.5
203	1.8	231	1.0	269	1.0	309	1.0	398	1.0
205	1.1	233	1.0	271	7.9	311	1.9	411	1.1
206	1.5	234	6.8	272	6.5	313	7.6	412	1.3
207	13.3	235	1.8	273	3.2	314	1.9	423	1.9
208	2.6	241	1.1	274	1.1	325	1.9	424	1.8
211	1.1	243	1.3	285	4.5	326	1.5	425	92.3
213	1.6	245	4.1	286	2.1	327	18.3	426	30.3
215	1.6	246	1.1	287	2.6	328	4.5	427	5.5
217	1.5	255	1.0	288	1.6	329	1.1	438	2.9
219	1.1	257	2.1	299	1.5	339	1.0	439	2.3
221	1.0	258	2.8	300	2.1	341	1.0	440	100.0 M
227	1.5	259	10.0	301	1.3	355	1.6	441	33.2
		260	2.8	302	1.6	356	1.0	442	7.0

FIGURE I.



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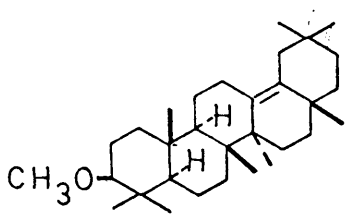

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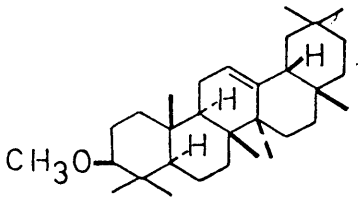

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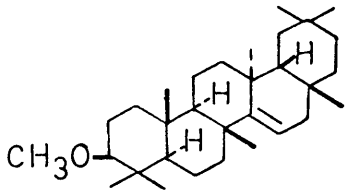

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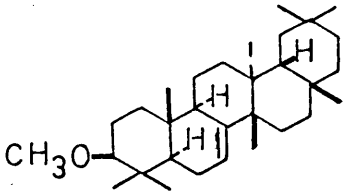

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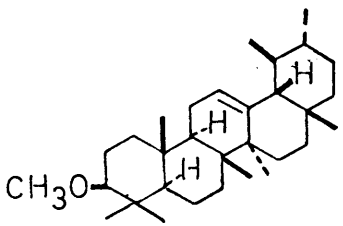
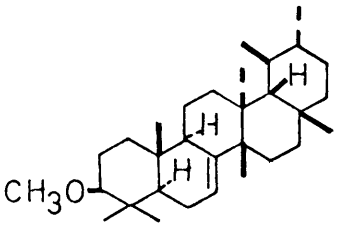
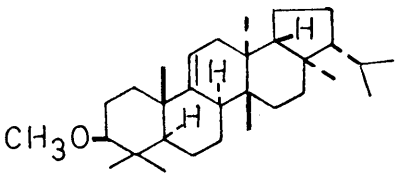


VI



VII



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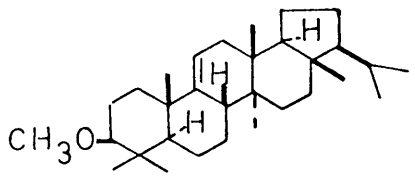


IX

CHAPTER 4.

STRUCTURE DETERMINATION OF SOME PENTACYCLIC AND TETRACYCLIC TRITERPENES.

A) Pentacyclic Triterpenes.

Extensive studies of the mass spectra of pentacyclic triterpenes by Djerassi and his co-workers[1,2] showed that, in many cases, the mass spectrum is characteristic of a given compound in this class. This is especially true if the triterpene contains a carbon-carbon double bond which is found to direct the fission along specific paths, other functional groups, e.g., carbonyl, hydroxyl and carbomethoxyl having, in general, little influence on the fragmentation of the molecule. For example, the most important cleavage of Δ^{12} oleanenes and ursenes can best be described as a retro-Diels-Alder reaction involving the 12:13 double bond, the positive charge remaining with the diene produced. From the mass of the molecular ion and the mass of the ion produced by this reaction, it is possible to position substituents in the ring A,B or ring D,E portion of the molecule.

Therefore it seemed probable that mass spectrometry could provide a ready means of identification of pentacyclic triterpenes isolated from natural sources, and, indeed, several recent identifications by this method have been described.[3]

Triterpenes from Saccharum Officinarum L and Cortaderia Toetoe Zotov.

During the course of an investigation[4] of the constituents of the leaf wax of Cuban sugar cane (Saccharum officinarum L) it was found that the material isolated, which was preliminarily designated as Substance W, was in all probability a mixture of triterpene methyl ethers. When Substance W was subject to gas liquid chromatographic analysis[5] it was resolved into two major and one minor component. Therefore, in order to facilitate the identification of these ethers, it was necessary to determine the relative retention times of selected authentic triterpene methyl ethers.

Thus it was found that none of the stationary phases employed (0.5% Apiezon L, 1.5% SE-30, 1.5% QF-1, 1% CDMS) gave any clear distinction between germanicol methyl ether (I,Fig.I), δ-amyrin methyl ether (II,Fig.I), β-amyrin methyl ether (III,Fig.I), taraxerol methyl ether (IV,Fig.I), and multiflorenol methyl ether (V,Fig.I), i.e., the compounds derived from the oleanane or friedo rearranged oleanane skeleton. Nevertheless, it was possible to distinguish these ethers (I-V, Fig.I) from any of the compounds α-amyrin methyl ether (VI, Fig.I), bauerenol methyl ether (VII, Fig.I), arundoin (VIII, Fig.I) and cylindrin (IX, Fig.I).

A comparison of the gas liquid chromatographic data of substance

W with that of the authentic methyl ethers suggested that Substance W contained arundoin and one or more of the oleanane group as the major, and bauerenol methyl ether as the minor component.

As it was known that the pentacyclic nucleus fragments, under electron bombardment, in a way determined by the position of the double bond, Substance W was subject to preparative gas liquid chromatography and mass spectrometric analysis. Although it was not possible to isolate the minor component on account of its very low abundance in the mixture, both major components were successfully isolated. Thus, by comparison with the mass spectra of authentic samples, it was established that one was arundoin (VIII, Fig.I) and that the other was taraxerol methyl ether (IV, Fig.I).

From the work of Djerassi and his associates,[1,2] it is possible to predict the cracking patterns of taraxerol methyl ether and arundoin. Table I shows that the mass spectra of taraxerol methyl ether and arundoin, as determined in the present work, are in excellent agreement with the predicted spectra. However, in addition to the ions predicted to be present (series A), the mass spectra of these two compounds contain a further series of ions (series B). Observation of the appropriate metastable ions showed that this extra series of ions is derived, by the loss of methanol, from ions of series A which contain the methoxyl group. The mass spectra of

TABLE I

Major Peaks In The Mass Spectra Of Triterpene Methyl Ethers

Compound	Predicted* Mass Spectral Peaks	Observed Mass Spectral Peaks (Relative Ion Abundances Given as %age of Base Peak = 100)		Metastable Peaks For Loss of Methanol From Ion Of Series A To Corresponding Ion Of Series B	
		Series A Corresponding To Predicted Ions	Series B Arising By Loss Of Methanol	Observed	Calculated
Arundoin (VIII) (Heated Inlet System)	m/e 440 (Parent) 425 (h) 355 (l) 287 (m) 273 (b) 261 (l)	m/e 440 (15%) 425 (60%) 365 (14%) 355 (1%) 287 (8%) 273 (58%) 261 (5%)	m/e 408 (16%) 393 (100%) 332 (4%) 323 (3%) 255 (31%) 241 (76%) 229 (14%)	378.3 363.4 294.0 226.5 212.8 201.0	378.3 363.4 293.9 226.6 212.8 200.9
Arundoin (VIII) (Direct Inlet System)	m/e 440 (Parent) 425 (h) 355 (l) 287 (m) 273 (b) 261 (l)	m/e 440 (48%) 425 (100%) 355 (1%) 287 (10%) 273 (100%) 261 (9%)	m/e 393 (50%) 323 (4%) 255 (26%) 241 (80%) 229 (19%)	 363.4 294.0 226.5 212.8 201.0	 363.4 293.9 226.6 212.8 200.9
Taraxerol Methyl Ether (IV) (Direct Inlet System)	m/e 440 (Parent) 425 (l) 316 (m) 301 (m) 218 (m) 204 (b) 189 (m)	m/e 440 (14%) 425 (8%) 316 (33%) 301 (29%) 218 (28%) 204 (100%) 189 (26%)	m/e 393 (6%) 284 (15%) 269 (20%)	 363.4 255.2 240.4	 363.4 255.2 240.4
Bauerenol Methyl Ether(VII) (Direct Inlet System)	m/e 440 (Parent) 425 (m) 287 (l) 273 (l) 261 (b) 234 (l) 205 (m)	m/e 440 (46%) 425 (32%) 287 (6%) 273 (20%) 261 (100%) 234 (8%) 205 (24%)	m/e 393 (21%) 255 (10%) 241 (18%) 229 (77%) 202 (8%)	 363.4 226.6 212.8 201.0 ?	 363.4 226.6 212.8 200.9 174.4
b-Amyrin Methyl Ether (III) (Direct Inlet System)	m/e 440 (Parent) 425 (l) 222 (l) 221 (l) 218 (b) 205 (l) 203 (m) 189 (m) 133 (l)	m/e 440 (7%) 425 (2%) 222 (3%) 221 (7%) 218 (100%) 205 (3%) 203 (36%) 189 (14%) 133 (10%)	m/e 408 (1%) 393 (1%) 190 (15%) 189	378.5 363.4 162.6 161.6	378.3 363.4 162.6 161.6
a-Amyrin Methyl Ether (VI) (Direct Inlet System)	m/e 440 (Parent) 425 (l) 222 (l) 221 (l) 218 (b) 205 (l) 203 (m) 189 (m) 133 (l)	m/e 440 (4%) 425 (1%) 222 (5%) 221 (11%) 218 (100%) 205 (2%) 203 (14%) 189 (14%) 133 (8%)	m/e 408 (1%) 393 190 (10%) 189	378.5 363.4 162.6 161.6	378.3 363.4 162.6 161.6
Cylindrin (IX) (Direct Inlet System)	m/e 440 (Parent) 425 (h) 355 (l) 287 (m) 273 (b) 261 (l)	m/e 440 (70%) 425 (100%) 355 (9%) 287 (16%) 273 (87%) 261 (10%)	m/e 393 (61%) 323 (13%) 255 (30%) 241 (52%) 229 (22%)	 363.4 294.0 226.6 212.8 201.0	 363.4 293.9 226.6 212.8 200.9

*Calculated from fragmentation patterns established by H. Budzikiewicz, J.M. Wilson and C. Djerassi.[2]

l = low intensity

m = medium intensity

h = high intensity

b = base peak

bauerenol methyl ether (VII, Fig.I), α- and β-amyrin methyl ethers (VI, III, Fig.I) and cylindrin methyl ether (IX, Fig.I) confirm that their mass spectra can be predicted from the published data, and that the loss of methanol is a general process of triterpene methyl ethers. The predicted ions, the observed ions and the observed metastable ions pertinent to this loss of methanol are shown in Table 1.

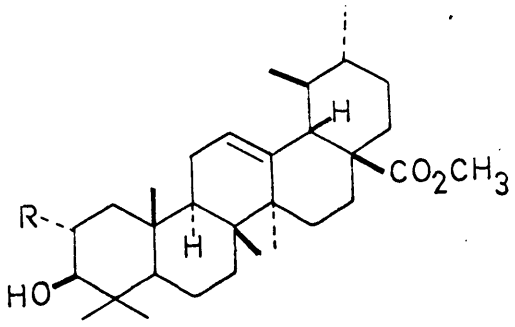
Although not the most favoured route of mass spectral fragmentation, a similar loss of methanol occurs with simple methyl ethers, as is apparent from the data tabulated by McLafferty.[6] Thus, in addition to providing a further illustration that the fragmentation of the pentacyclic triterpene nucleus is directed by a double bond rather than by any other functional group, the triterpene methyl ethers provide an example of a usually less important process gaining some prominence.

From the detailed studies of the gas liquid chromatographic behaviour of authentic triterpene methyl ethers it was likely that material isolated from the native New Zealand plant, Cortaderia toetoe, contained the methyl ether of α-amyrin; one or more of the methyl ethers of germanicol, δ-amyrin, β-amyrin, taraxerol or multiflorenol; and arundoin. The mass spectra of the fractions obtained from preparative gas liquid chromatography confirmed that α- and β-amyrin methyl ethers and arundoin are constituents of Cortaderia toetoe.

It is of interest that when the mass spectrum of arundoin was determined using a heated reservoir system, instead of the direct inlet system routinely employed, the ion, m/e 408, corresponding to the loss of methanol from the molecular ion became more pronounced. The increased abundance of the ion m/e 408 may be due to a thermal process prior to ionization, although a metastable peak at m/e 378.3 confirms that the ion m/e 408 is formed, in part at least, from the molecular ion. Furthermore, the ions of m/e's 393, 255 and 241, in the mass spectrum of arundoin obtained using the heated reservoir system, are more abundant than the ions from which they are derived through loss of methanol; whereas the reverse occurs in the mass spectrum obtained using the direct inlet system.

Also of interest is the appearance of an ion of mass 365 in the spectrum of arundoin determined employing the heated reservoir system. A metastable ion at m/e 326.5, corresponding to the transition $408^{+} \rightarrow 365^{+} + 43$, shows that this fission can be attributed to the loss of the isopropyl side chain from ring E. It has been established that the loss of the isopropyl side chain is a characteristic of those pentacyclic triterpenes which contain an isopropyl group,[2] and no explanation can be offered to account for the lack of this fission in the spectrum of arundoin obtained using the direct inlet system.

FIGURE II.



X, R=H

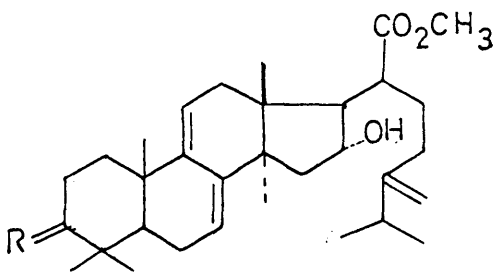
XI, R=OH

Triterpenes from Gaultheria Subcorymbosa and Chameanerion Augustifolium.

Ethanolic extraction of the twigs and leaves of the native New Zealand shrub Gaultheria subcorymbosa resulted in the isolation of a substance which showed widely differing melting points on crystallization from different solvents.[7] In addition, the melting point of the methyl ester derived from this substance was also dependent on the solvent used for crystallization. It was, therefore, possible that these different methyl ester fractions corresponded to different compounds. However, examination of the mass spectra of the methyl ester fractions not only revealed that the spectra were the same but also, by comparison with the published spectrum[1], identified the ester as methyl ursolate (X, Fig. II). The observed melting point differences may be explained by different crystalline forms or may be due to solvation effects.

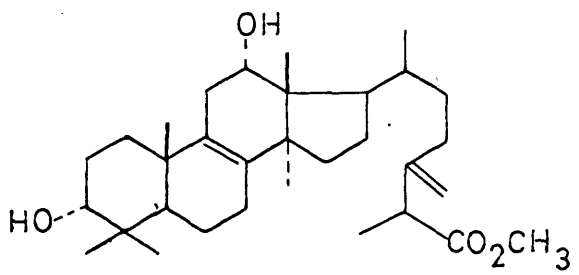
Ursolic acid, characterised as methyl acetyl ursolate, was shown to be a constituent of the leaves of the rose-bay willow-herb (Chamaenerion augustifolium)[8] by comparison with the mass spectrum of an authentic sample. In addition, the mass spectrum of a triterpene isolated from the same source contained abundant ions at m/e 486 ($C_{31}H_{50}O_4$), the molecular ion, at m/e 262, m/e 223 and m/e 203. The ions m/e 262 and 203 are consistent with a 12:13 double bond and a carbomethoxyl group at C-17 (m^* calculated for $262^+ \rightarrow 203^+ = 157.4$;

FIGURE III.



XII, R=O

XIII, R=OH(H)



XIV

observed 157.4). As the molecule contains four oxygen atoms the remaining two must be in rings A and B, in agreement with the presence of a peak at m/e 223 corresponding to the ring A, B portion of the molecule. A study of the other physical and chemical properties of this compound showed it to be methyl 2 α-hydroxyursolate (XI, Fig.II).[8]

(B) Tetracyclic Triterpenes.

In the course of an intensive examination of the fungi Daedalia quercina and Polyporus betulinus several metabolites of each fungus were isolated. The compounds isolated from Daedalia quercina were code-named D.Q.1, D.Q.4, D.Q.5 and D.Q.7; those from Polyporus betulinus were code-named P.B.1, P.B.2 and P.B.5. It is proposed to discuss the mass spectra of the compounds P.B.1, P.B.5, D.Q.4 and D.Q.5, and to describe the role played by mass spectrometry in the elucidation of the structures of the others. A description of the other physical and chemical properties of these compounds has been given elsewhere.[9]

The Compounds P.B.1, P.B.5, D.Q.4 and D.Q.5.

It was known[10] that Polyporus betulinus was a source of the polyporenic acids A and C and a comparison with authentic samples established that the compounds P.B.1 and P.B.5 were methyl polyporenate C (XII, Fig.III) and methyl polyporenate A (XIV, Fig.III) respectively. In a similar manner it was shown that the compound D.Q.4 was identical with methyl polyporenate C, and that the compound D.Q.5 was identical with methyl 7,11-dehydrotumulosate (XIII, Fig.III).

Although the mass spectra of methyl polyporenate C and the compounds P.B.1 and D.Q.4 exhibited an abundant ion at the expected molecular weight of 496, another molecular ion of mass 498 was present in all three spectra. The contaminant of molecular weight 498 was almost certainly the corresponding 8(9)-monoene, methyl 7,11-dihydropolyporenate C, and as it has been shown[11] that the mass spectra of such compounds do not contain abundant ions formed by fragmentation of the rings, the presence of the small amount of methyl 7,11-dihydropolyporenate C has been ignored in the interpretation of the mass spectrum of methyl polyporenate C. Similarly it was assumed that the small amount of methyl tumulosate, which was found to be present in the samples of the compound D.Q.5 and methyl dehydrotumulosate, makes little contribution to the intermediate mass region of the spectra of these compounds.

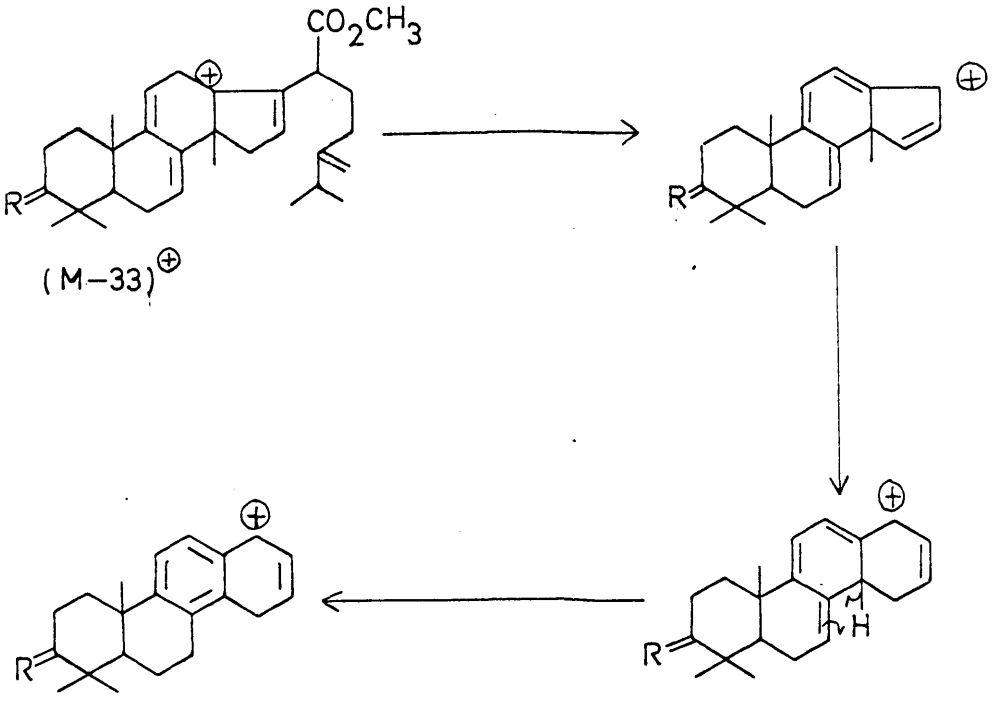
In the high mass region of the spectra of methyl polyporenate C and methyl dehydrotumulosate the main features are ions which correspond to the loss from the molecular ion of a methyl radical, a water molecule, and these combined. The abundance of the $(M-H_2O)^+$ ion in the spectrum of methyl dehydrotumulosate is not significantly greater than that of the corresponding ion in the spectrum of methyl polyporenate C, although methyl dehydrotumulosate contains two hydroxyl groups.

At lower masses, abundant ions are observed at m/e's 311, 295 and 271 in the spectrum of methyl dehydrotumulosate and at m/e's 309, 293 and 269 in that of methyl polyporenate C. Therefore these ions are formed by corresponding fissions and must contain the left-hand portion of both molecules. Thus the ions at m/e's 311 and 309 are formed by the loss of the C-17 side chain and a molecule of water. As both compounds exhibit this fragmentation, it is likely that the C-3 hydroxyl group is retained in the ion of mass 311 in the mass spectrum of methyl dehydrotumulosate. Although it is known[12] that the elimination of water, induced by electron impact, does not proceed by a 1:2 mechanism, the formation of a centre of unsaturation in ring D by the loss of a water molecule could well explain the high abundance of the ion subsequently formed by the loss of the side chain.

"Steroid-type" fission[13] through ring D with the loss of C-15, C-16 and C-17 and their substituents gives rise to the ions at m/e 271 and m/e 269 in the spectra of methyl dehydrotumulosate and methyl polyporenate C respectively.

The genesis of the remaining significant fission common to both spectra is less easy to explain. However, a metastable ion at m/e 185.2 shows that m/e 293, the ion formed by this fission, arises by cleavage of the ion m/e 463 (m^* calculated for $463^+ \rightarrow 293^+ = 185.4$) in the mass spectrum of methyl polyporenate C. In a similar way, the

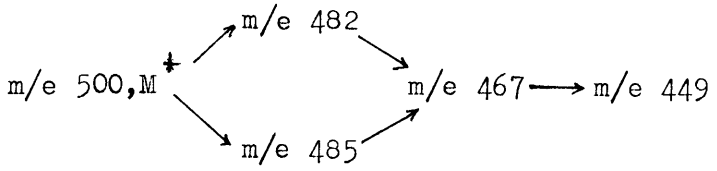
FIGURE IV.



XV, R=O m/e 293
R=OH(H) m/e 295

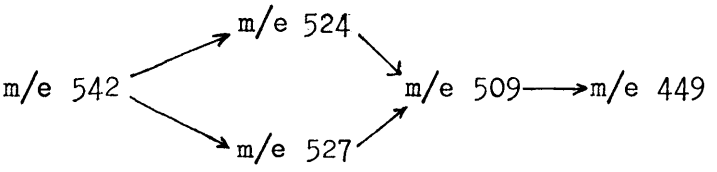
corresponding transition in the spectrum of methyl dehydrotumulosate gives rise to a metastable ion at m/e 187.5 (m^* calculated for $465^+ \rightarrow 295^+$ = 187.2). Thus this cleavage proceeds by the loss of the side chain plus one hydrogen atom from the $(M-33)^+$ ion. The driving force for this fission may be the aromatisation of rings C and D, and the ion formed can be represented by a structure such as XV (Fig.IV). In addition to the fragmentation paths described above, metastable ions at m/e 276.0 and 260.0 indicate that methyl dehydrotumulosate also breaks down by expelling a molecule of water from the ions m/e 311 and m/e 295 (m^* calculated for $311^+ \rightarrow 293^+$ = 276.0; m^* calculated for $295^+ \rightarrow 277^+$ = 260.1). No such losses are observed in the spectrum of methyl polyporenate C, thus confirming that the ions m/e 311 and 295 do contain ring A.

The mass spectrum of methyl polyporenate A (XIV, Fig.III) is characterised by fragmentations corresponding to the loss of the methyl and hydroxyl groups. Ions are observed at m/e 485 ($M-CH_3$), m/e 482 ($M-H_2O$), m/e 467 ($M-CH_3-H_2O$) and m/e 449 ($M-CH_3-H_2O-H_2O$). The only ion to which any significance could be attached at lower masses is m/e 313 which arises by the loss of the C-17 side chain from m/e 482. Observation of the appropriate metastable ions shows that the sequence of fragmentation is :-



Transition	Observed m*	Calculated m*
$500^+ \longrightarrow 482^+ + 18$	468.4	464.6
$500^+ \longrightarrow 485^+ + 15$	470.5	470.5
$467^+ \longrightarrow 449^+ + 18$	431.9	431.7

The behaviour of methyl 3-acetylpolyporenate A, under electron impact, is similar to that of methyl polyporenate A. Metastable ions present in the spectrum confirm that the molecular ion of methyl 3-acetylpolyporenate A, m/e 542, decomposes as shown :-



Transition	Observed m*	Calculated m*
$542^+ \longrightarrow 527^+ + 15$	512.4	512.4
$542^+ \longrightarrow 524^+ + 18$	506.8	506.6
$527^+ \longrightarrow 509^+ + 18$	491.8	491.6
$524^+ \longrightarrow 509^+ + 15$	493-494	494.4
$509^+ \longrightarrow 449^+ + 60$	396.1	396.1

From the above it is seen that the loss of acetic acid from the $(M-33)^+$ ion in the mass spectrum of methyl 3-acetylpolyporenate A

replaces the loss of water from the $(M-33)^+$ ion in the spectrum of methyl polyporenate A. This type of fragmentation of $\Delta^{8(9)}$ tetracyclic triterpenes, even although it does not involve a specific fission of the tetracyclic ring system, proved to be of great value in elucidating the structures of the other metabolites isolated.

The Compound P.B.2.

The compound P.B.2, when subject to electron bombardment, exhibited a molecular ion at m/e 600. Exact mass measurement of the molecular ion and of several of the abundant fragment ions was carried out. The results obtained are collected in Table II.

From Table II and observation of the corresponding metastable ions (Table III) the fragmentation pathways shown in Fig.V can be deduced.

The presence of abundant ions at m/e 467 and m/e 449, together with m/e 313 as the only significant fragment of lower mass suggested that the compound P.B.2 was a derivative of methyl polyporenate A. The fact that the ions of mass 500, 482, 467, 449 and 313 corresponded exactly in elemental composition to the corresponding ions in the spectrum of methyl polyporenate A was a further indication that this suggestion was correct. Moreover, the mass spectrum of the compound P.B.2. was similar to the spectrum of methyl 3-acetylpolyporenate A in that the elimination of a $C_4H_6O_4$ species from the $(M-33)^+$ ion replaces the loss of acetic acid from the $(M-33)^+$ ion in the mass spectrum of methyl 3-acetylpolyporenate A.

FIGURE V.

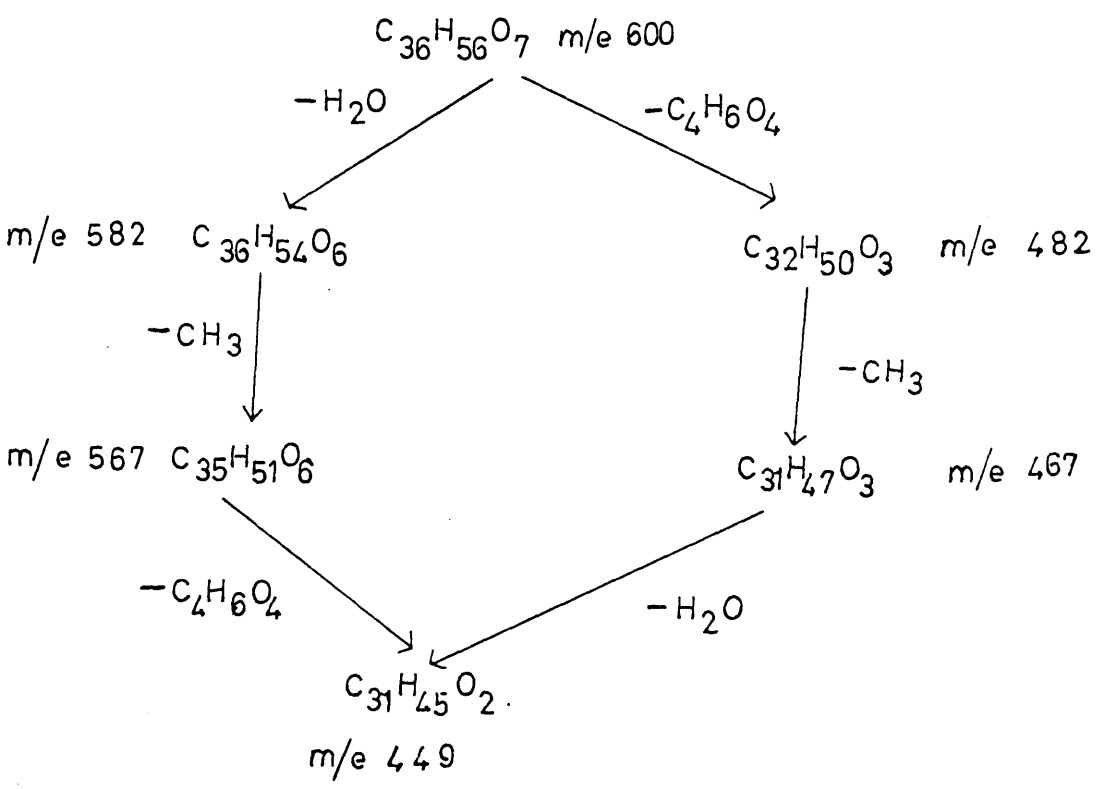

$C_{36}H_{56}O_7$ m/e 600
$-H_2O$
$-C_4H_6O_4$
m/e 582 $C_{36}H_{54}O_6$
$C_{32}H_{50}O_3$ m/e 482
$-CH_3$
$-CH_3$
m/e 567 $C_{35}H_{51}O_6$
$C_{31}H_{47}O_3$ m/e 467
$-C_4H_6O_4$
$-H_2O$
$C_{31}H_{45}O_2$
m/e 449

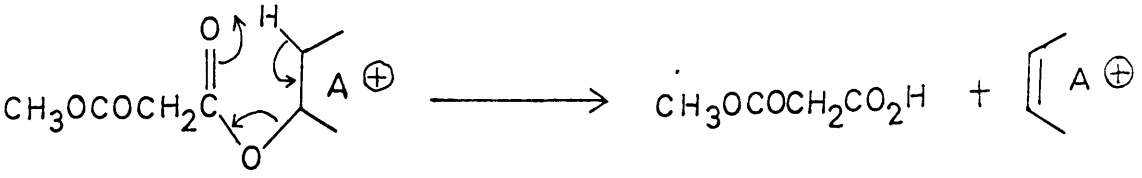
TABLE II

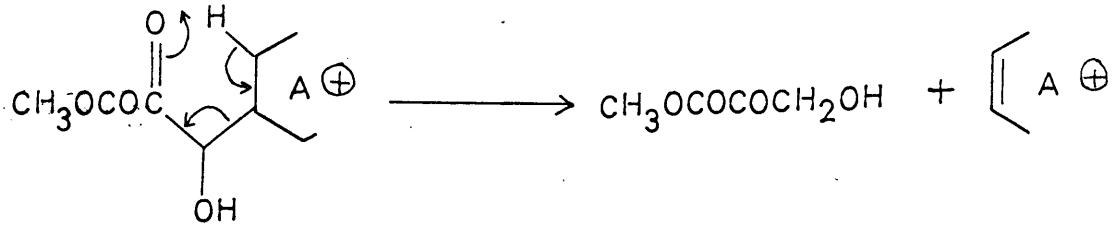
Nominal Mass	Observed Mass	Formula Assigned	Calculated Mass
600	600.4043	$C_{36}H_{56}O_7$	600.4026
567	567.3694	$C_{35}H_{51}O_6$	567.3685
500	500.3879	$C_{32}H_{52}O_4$	500.3865
482	482.3765	$C_{32}H_{50}O_3$	482.3760
467	467.3520	$C_{31}H_{47}O_3$	467.3525
449	449.3228	$C_{31}H_{45}O_2$	449.3419

TABLE III

Transition	Observed m*	Calculated m*
$600^+ \longrightarrow 582^+ + 18$	564.5	564.5
$600^+ \longrightarrow 482^+ + 118$	387.0	387.2
$567^+ \longrightarrow 449^+ + 118$	355.2	355.5
$467^+ \longrightarrow 449^+ + 18$	431.6	431.6

FIGURE VI.


O
H
A ⊕
CH3OCOCH2C
O
CH3OCOCH2CO2H
+
A ⊕


O
H
A ⊕
CH3OCOC
OH
CH3OCOCOCH2OH
+
A ⊕

Thus from a comparison of the mass spectra it seemed probable that the compound P.B.2 was basically methyl polyporenate A linked by the C-3 oxygen atom to a $C_4H_5O_3$ unit. Additional support for this theory was furnished by the infra-red (I.R.) and nuclear magnetic resonance (N.M.R.) spectral analyses which were consistent with the presence of two methoxycarbonyl, a secondary hydroxyl and an exomethylene group.[9]

The problem now focused on determining the nature of the $C_4H_6O_4$ species which the compound P.B.2 expelled under electron bombardment. As two methoxycarbonyl groups had been shown to be present, one of them must be contained in the $C_4H_6O_4$ fragment. The most plausible structures for $C_4H_6O_4$ are :-

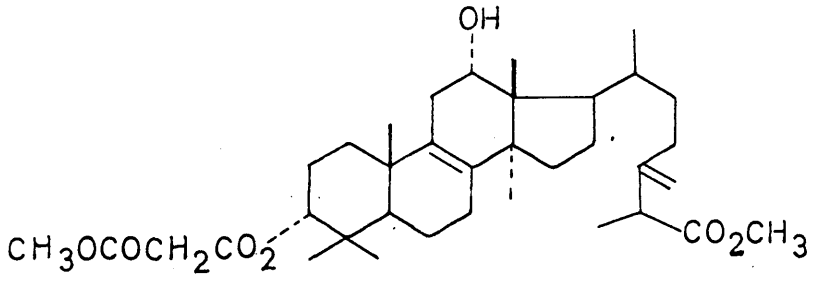
(1) $CH_3O.CO.O.CO.CH_3$ (2) $CH_3O.CO.O.CH_2CHO$

(2) $CH_3O.CO.CO.OCH_3$ (4) $CH_3O.CO.CH_2CO_2H$

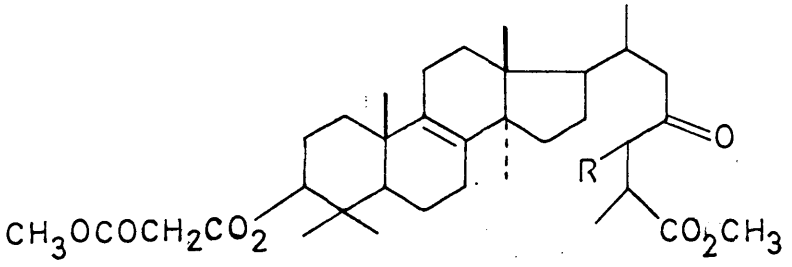
(5) $CH_3O.CO.CO.CH_2OH$

As structures (4) and (5) could be readily expelled (Fig.VI) by a McLafferty rearrangement[14], they were considered the most likely. Distinction between (4) and (5) was possible as only (4) could easily give rise to the ion of composition $C_{32}H_{52}O_4$ (m/e 500) observed in the spectrum of the compound P.B.2.

FIGURE VII.



XVI



XVII, R=CH_3

XVIII, R=CH_2CH_2OH

Thus the compound P.B.2 was probably a methoxycarbonylacetate of methyl polyporenate A.

Further proof of the structure was gained in the following way; the mass spectrum of the compound P.B.2A, obtained by treatment of the compound P.B.2 with methanolic sodium methoxide,[9] yielded a molecular weight of 500 and a precise mass determination showed a molecular formula of $C_{32}H_{52}O_4$ (calculated 500.3865; found 500.3854). The compositions of the ion m/e 313 was found to be $C_{22}H_{33}O$ (calculated 313.2531; found 313.2534). In addition the mass spectrum of the compound P.B.2A was identical, except for some differences in ion abundances, with that of methyl polyporenate A. It is known that the C-24 exomethylene double bond of methyl polyporenate A moves into conjugation with the C-26 methoxycarbonyl group under basic conditions, and an examination[9] of the other physical properties of the compound P.B.2A established its identity with methyl isopolyporenate A.

Thus the most likely structure for the compound P.B.2 was that of a methyl methoxycarbonylacetylpolyporenate A, and a comparison[9] with model compounds such as cholesteryl malonate confirmed that the compound P.B.2 was methyl 3-methoxycarbonylacetylpolyporenate A (XVI, Fig.VII).

The Compound D.Q.1.

The mass spectrum of the compound D.Q.1 showed a molecular weight of 600. The results of high resolution measurement of the molecular ion

and of several fragment ions are collected in Table IV. Identification of metastable ion transitions (Table V) lead to the fragmentation pathway shown in Fig.VIII for the compound D.Q.1.

It can be seen that, like the compound P.B.2, the compound D.Q.1 fragments with the loss of a $C_4H_6O_4$ entity. Hence the compound D.Q.1 probably contained a methoxycarbonylacetyl group also. Additional evidence as to the nature of the functional groups was available from the I.R. and N.M.R. spectra which were consistent with not only a methoxycarbonylacetyl function, but also with a further methoxycarbonyl group, and an aliphatic or six-membered alicyclic ketone.[9]

As four of the oxygen atoms present in the compound D.Q.1 were accounted for in the methoxycarbonylacetyl unit, the other methoxycarbonyl group and the ketone must be eliminated in the fragment of composition $C_8H_{14}O_3$. The $C_8H_{14}O_3$ fragment contains two double bond equivalents and, therefore, it is unlikely to be contained in a cyclic system. Probably it arises from a rearrangement process involving the carbonyl function.

The elemental compositions of several ions of lower mass enabled the structure of this portion of the molecule to be determined. It was noticed that abundant ions were present at m/e's 153, 143 and 115. Ions which arise by random fission of a triterpene nucleus are normally present at these masses, but are always weakly abundant.

FIGURE VIII.

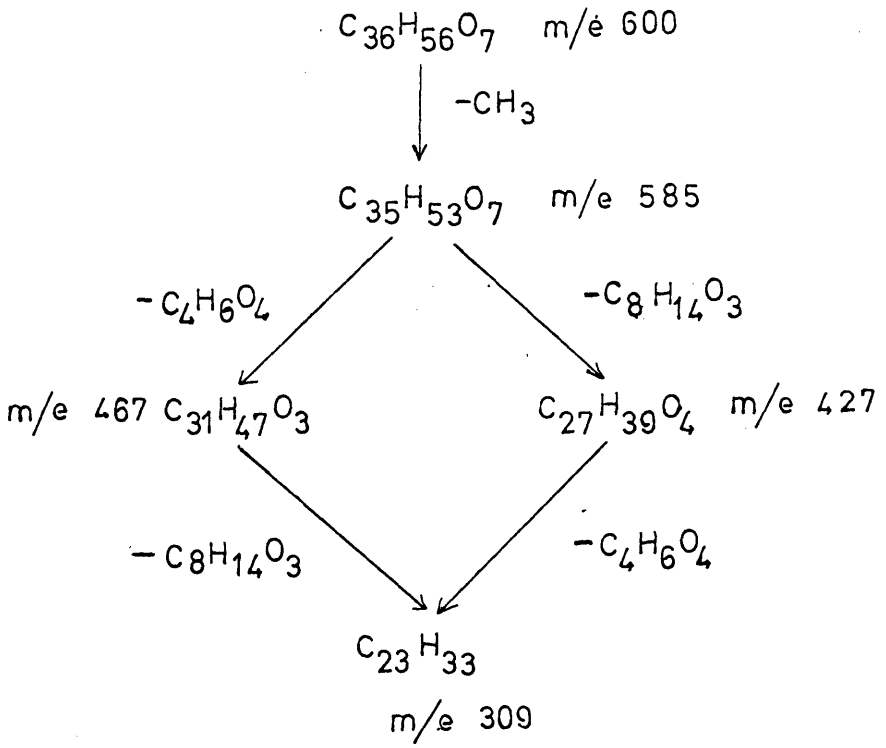

$C_{36}H_{56}O_7$ m/e 600
$-CH_3$
$C_{35}H_{53}O_7$ m/e 585
$-C_4H_6O_4$
$-C_8H_{14}O_3$
m/e 467 $C_{31}H_{47}O_3$
$C_{27}H_{39}O_4$ m/e 427
$-C_8H_{14}O_3$
$-C_4H_6O_4$
$C_{23}H_{33}$
m/e 309

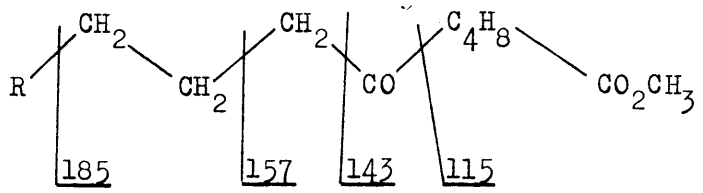
TABLE IV

Nominal Mass	Observed Mass	Formula Assigned	Calculated Mass
600	600.4010	$C_{36} H_{56} O_7$	600.4026
585	585.3792	$C_{35} H_{53} O_7$	585.3791
467	467.3530	$C_{31} H_{47} O_3$	467.3525
427	427.2857	$C_{27} H_{39} O_4$	427.2848
309	309.2578	$C_{23} H_{33}$	309.2582
185	185.1174	$C_{10} H_{17} O_3$	185.1178
153	153.0910	$C_9 H_{13} O_2$	153.0915
143	143.0705	$C_7 H_{11} O_3$	143.0708
115	115.0759	$C_6 H_{11} O_2$	115.0759

TABLE V

Transition	Observed m*	Calculated m*
$600^+ \longrightarrow 585^+ + 15$	570.4	570.4
$585^+ \longrightarrow 467^+ + 118$	373.0	372.8
$585^+ \longrightarrow 427^+ + 158$	311.7	311.6
$467^+ \longrightarrow 309^+ + 158$	204.5	204.6
$427^+ \longrightarrow 309^+ + 118$	223.5	223.6
$185^+ \longrightarrow 153^+ + 32$	126.5	126.5

The composition of the ion m/e 185 was also determined as a metastable ion at m/e 126.5 corresponding to the transition $185^{+} \rightarrow 153^{+} + 32$ was present in the spectrum. M/e 185 was found to be a doublet of composition $C_{10}H_{17}O_3$ and $C_{14}H_{17}$. Therefore there must be a further two carbon atoms in the chain containing the $C_8H_{14}O_3$ entity. The ions of mass 143 ($C_7H_{11}O_3$) and 115 ($C_6H_{11}O_2$) differ in composition by the elements of carbon monoxide, and thus could readily arise from fission on either side of the carbonyl group. A partial structure for this portion of the molecule would then be :-



Cleavage of the bond β to the carbonyl group with the migration of a hydrogen to the carbonyl oxygen atom i.e., a McLafferty rearrangement,[14] would explain the elimination of 158 mass units ($C_8H_{14}O_3$) in the mass spectrum of the compound D.Q.1. Fission of the carbon-carbon bond δ to the carbonyl suggested that this point might be a site of chain branching.

Little evidence is available for the nature of the $C_{22}H_{33}$ ion (m/e 309), but since the fungus Daedalia quercina had been shown to produce tetracyclic triterpenes it seemed a reasonable assumption that the compound D.Q.1 was also a tetracyclic triterpene. The aliphatic

carbon chain would thus form the C-17 side chain of the molecule.

Eight of the nine double bond equivalents of the compound D.Q.1 have now been accounted for, and spectroscopic evidence[9] points to the presence of an 8:9 double bond, in agreement with the lack of specific fragmentation of the ring system observed in the mass spectrum of the compound D.Q.1. Therefore the compound D.Q.1 most likely has the structure XVII (Fig.VII).

The Compound D.Q.7.

Exact mass measurement (Table VI) of the molecular ion, m/e 612, of the remaining metabolite of Daedalia quercina, that has been subject to mass spectrometric investigation, showed that the compound D.Q.7 had a molecular formula of $C_{37}H_{56}O_7$, i.e., the molecular formula is exactly one carbon atom more than that of the compound D.Q.1. The mass spectrum of the compound D.Q.7 shows the loss of 118 mass units characteristic of the methoxycarbonylacetyl group, and the peaks associated with fragmentation of the side chain are shifted 12 units to higher mass. Thus the neutral fragment of 158 units, eliminated in the mass spectrum of the compound D.Q.1, appeared as a loss of 170 units (Fig.IX) in the mass spectrum of the compound D.Q.7. Similarly the peaks at m/e's 185, 153, 143 and 115 in the spectrum of the compound D.Q.1 were replaced in that of the compound D.Q.7 by peaks at m/e's 197, 165, 155 and 127.

FIGURE IX.

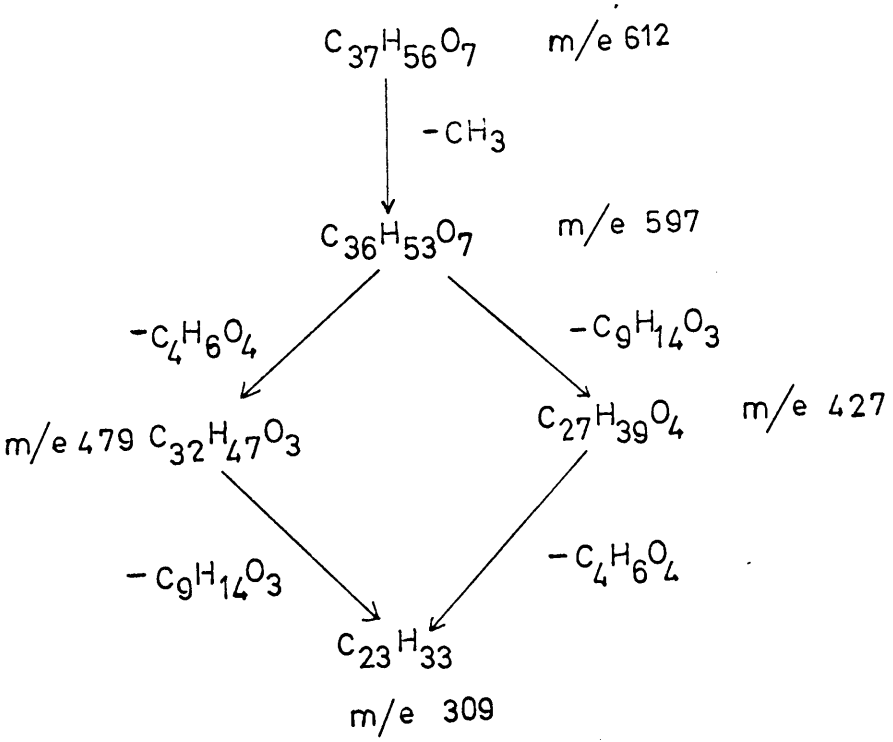

$C_{37}H_{56}O_7$ m/e 612
$-CH_3$
$C_{36}H_{53}O_7$ m/e 597
$-C_4H_6O_4$
$-C_9H_{14}O_3$
m/e 479 $C_{32}H_{47}O_3$
$C_{27}H_{39}O_4$ m/e 427
$-C_9H_{14}O_3$
$-C_4H_6O_4$
$C_{23}H_{33}$
m/e 309

TABLE VI

Nominal Mass	Observed Mass	Formula Assigned	Calculated Mass
612	612.4037	$C_{37} H_{56} O_7$	612.4026
597	597.3774	$C_{36} H_{53} O_7$	597.3791
479	479.3518	$C_{32} H_{47} O_3$	479.3525
427	427.2848	$C_{27} H_{39} O_4$	427.2848
309	309.2571	$C_{23} H_{33}$	309.2582
197	197.1153	$C_{11} H_{17} O_3$	197.1178

TABLE VII

Transition	Observed m*	Calculated m*
$612^+ \longrightarrow 597^+ + 15$	582.3	582.3
$597^+ \longrightarrow 479^+ + 118$	384.5	384.3
$597^+ \longrightarrow 427^+ + 170$	306.0	305.4
$479^+ \longrightarrow 309^+ + 170$	199.2	199.3
$427^+ \longrightarrow 309^+ + 118$	223.9	223.6
$197^+ \longrightarrow 165^+ + 32$	138.1	138.2

It was, therefore, concluded that the compounds D.Q.1 and D.Q.7 were structurally identical in rings A, B, C and D, and up to C-23, the carbon atom bearing the carbonyl group. The additional 12 mass units could then be accounted for by the presence of another carbon atom in the side chain together with a double bond or equivalent. However, the N.M.R and O.R.D. spectra of the compound D.Q.7 can only be explained by the presence of a $-CH_2-CH_2-O-$ group[9], and all the oxygen atoms of the observed molecular ion have been allocated. Hence the observed molecular ion must be derived from a more highly oxygenated species. It is thought that the ion m/e 612 represents a $(M-H_2O)^+$ ion, the structure of the compound D.Q.7 being that (XVIII) shown in Fig.VII.

REFERENCES.

1. C. Djerassi, H. Budzikiewicz and J. M. Wilson, Tetrahedron Letters, 1962, 263.

2. H. Budzikiewicz, J. M. Wilson and C. Djerassi, J. Amer. Chem. Soc., 1963, 85, 3688.

3. See for example, M. H. A. Elgamal, M. B. E. Fayez and G. Snatzke, Tetrahedron, 1965, 21, 2109; R. E. Taylor-Smith, ibid., 1965, 21, 3721; I. P. Varshney, K. M. Shamsuddin and R. E. Beyler, Tetrahedron Letters, 1965, 1187; R. O. Donchai and J. B. Thomson, ibid., 1965, 2223; B. Tursch, J. Leclercq and G. Chiurdoglu, ibid., 1965, 4161.

4. T. A. Bryce, M. Martin-Smith, G. Oaske, K. Schrieber and G. Subramanian, Tetrahedron, in the press.

5. The gas liquid chromatographic analyses were carried out at the University of Strathclyde.

6. F. W. McLafferty, Analyt. Chem., 1957, 29, 1782.

7. M. Alauddin, T. A. Bryce, E. Clayton, M. Martin-Smith and G. Subramanian, J. Chem. Soc., 1965, 4611.

8. A. T. Glen, W. Lawrie, J. McLean and M. El-Garby Younes, Chem. and Ind., 1965, 1908.

9. I. M. Campbell, Ph.D. Thesis, Glasgow, 1965; T. A. Bryce, I. M. Campbell and N. J. McCorkindale, Tetrahedron Letters, in the press.

10. L. C. Cross, C. G. Eliot, I. M. Heilbron and E. R. H. Jones, J. Chem. Soc., 1940, 632.

11. This volume, chapter 3.

12. P. Natalis, Bull. Chim. Soc. Belges, 1960, 69, 224; C. G. McDonald, J. S. Shannon, and G. Sudowdz, Tetrahedron Letters, 1963, 807; H. Budzikiewicz, Z. Pelah and C. Djerassi, Monatsh, 1964, 95, 158; J. Karliner, H. Budzikiewicz and C. Djerassi, J. Org. Chem., 1966, 31, 710.

13. R. I. Reed, J. Chem. Soc., 1958, 3432; S. S. Friedland, G. H. Lane, Jr., R. T. Longman, K. E. Train and M. J. O'Neal, Jr., Analyt. Chem., 1959, 31, 169; R. Ryhage and E. Stenhagen, J. Lipid Res., 1960, 1, 361; H. J. M. Fitches in "Advances in Mass Spectrometry", Vol. 2, R. M. Elliot, ed., Pergamon Press, London, 1962.

14. F. W. McLafferty, Analyt. Chem., 1959, 31, 82.

EXPERIMENTAL.

The mass spectra were determined using an A.E.I., M.S.9, double-focusing mass spectrometer. The samples were introduced by means of a direct inlet system.

The mass spectra of the compounds examined are tabulated overleaf.

Mass Spectrum of Methyl Polyporenate C.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
53	11	91	20	121	12	148	2
54	2	92	5	122	2	149	4
55	100	93	19	123	13	151	2
56	7	94	4	125	10	152	2
57	15	95	22	126	2	153	4
58	3	96	12	127	3	154	3
59	7	97	34	128	7	155	13
65	4	98	3	129	11	156	10
67	25	103	2	130	5	157	25
68	3	104	2	131	15	158	10
69	47	105	24	132	18	159	15
70	4	106	4	133	16	160	3
71	7	107	20	134	3	161	6
77	10	108	3	135	6	165	6
78	3	109	15	137	5	166	4
79	17	110	2	139	2	167	6
80	3	111	4	141	7	168	4
81	26	115	5	142	8	169	19
82	4	116	4	143	18	170	11
83	23	117	7	144	6	171	23
84	14	118	3	145	20	172	8
85	5	119	24	146	5	173	8
87	4	120	4	147	9	175	4

Over.

Mass Spectrum of Methyl Polyporenate C (Cont'd.).

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
177	2	208	4	243	4	284	2
178	3	209	10	244	2	293	75
179	5	210	3	245	3	294	20
180	3	211	7	251	4	295	32
181	11	212	3	252	2	296	7
182	5	213	6	253	5	307	5
183	15	215	2	254	2	308	20
184	6	221	4	255	20	309	66
185	12	222	3	256	5	310	20
186	3	223	9	257	4	311	10
187	5	224	3	265	4	312	3
193	6	225	5	267	3	317	2
194	3	226	2	268	23	319	3
195	11	227	7	269	39	322	2
196	5	229	3	270	21	463	22
197	10	231	2	271	10	464	6
198	3	235	3	272	10	478	8
199	6	237	5	273	2	479	4
201	4	238	2	279	2	480	4
203	3	239	3	280	-	481	7
205	2	241	4	281	3	482	2
207	6	242	3	283	4	496	7 M
						497	2
						498	2

Mass Spectrum of Methyl 7,11-dehydrotumulosate.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
50	7	81	48	111	14	137	7
51	10	82	11	112	2	138	3
52	3	83	33	115	4	139	3
53	13	84	6	116	3	141	5
54	5	85	7	117	8	142	6
55	100	86	2	118	3	143	14
56	13	87	5	119	23	144	5
57	25	91	21	120	5	145	19
59	6	92	4	121	19	146	4
65	5	93	27	122	15	147	9
66	3	94	6	123	16	148	3
67	36	95	46	124	4	149	9
68	8	96	14	125	6	150	4
69	68	97	26	128	5	151	4
70	10	98	3	129	8	153	3
71	14	99	2	130	4	154	2
73	2	105	34	131	13	155	8
74	3	106	5	132	18	156	6
77	24	107	24	133	16	157	17
78	4	108	6	134	3	158	8
79	22	109	31	135	12	159	18
80	5	110	6	136	3	160	4

Over.

Mass Spectrum of Methyl 7,11-dehydrotumulosate(Cont'd.).

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
161	7	193	3	231	2	310	9
162	2	194	2	235	3	311	29
163	6	195	6	236	2	312	8
167	4	196	8	237	4	313	3
168	3	197	3	238	2	463	3
169	12	198	6	239	4	464	2
170	7	201	4	251	2	465	10
171	19	202	2	253	6	466	3
172	6	203	3	254	2	480	10
173	8	207	3	255	3	481	3
174	2	209	7	257	3	483	5
175	4	210	3	259	3	484	2
177	4	211	7	270	6	498	5 M
179	4	212	2	271	8	499	2
181	5	213	4	272	11	500	2
182	3	217	3	273	5		
183	11	221	3	274	4		
184	6	222	2	277	13		
185	13	223	4	278	3		
186	4	224	2	293	4		
187	7	225	5	295	61		
189	4	227	4	296	15		
191	4	229	2	297	7		

MASS SPECTRUM OF METHYL POLYPORENATE A.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
50	3	77	13	108	9	134	7	159	20
51	3	78	4	109	53	135	32	160	6
52	2	79	28	110	7	136	6	161	16
53	19	80	5	111	8	137	11	162	4
54	5	81	69	112	2	138	2	163	6
55	96	82	9	113	8	139	3	164	2
56	11	83	24	115	5	141	8	165	4
57	26	84	5	116	3	142	4	167	4
58	2	85	19	117	8	143	11	168	3
59	29	88	7	118	3	144	4	169	10
60	2	91	27	119	30	145	19	170	4
65	5	92	5	120	8	146	5	171	11
66	2	93	37	121	36	147	18	172	4
67	49	94	7	122	9	148	5	173	14
68	8	95	46	123	16	149	11	174	4
69	87	96	7	124	2	150	3	175	10
70	7	97	10	125	3	151	4	176	3
71	15	98	2	129	8	153	4	177	5
72	2	99	4	130	4	155	5	178	2
73	7	105	33	131	17	156	4	179	7
74	2	106	7	132	4	157	13	180	2
75	2	107	44	133	22	158	5	181	4

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
182	2	205	3	241	4	295	2	395	2
183	5	207	2	242	2	297	3	407	2
184	2	209	3	243	3	299	2	409	4
185	9	211	4	253	4	311	3	410	2
186	4	212	2	255	4	312	2	411	2
187	11	213	6	257	4	313	11	412	3
188	4	214	3	259	2	314	4	449	32
189	7	215	5	260	2	321	3	450	11
190	2	217	4	261	2	324	2	451	5
191	3	223	3	262	2	326	2	467	100
195	2	225	5	263	2	327	2	468	35
197	5	226	4	265	2	328	2	469	10
198	3	227	5	267	2	329	3	470	3
199	7	228	2	269	2	330	2	482	12
200	3	229	5	271	3	331	3	483	4
201	9	230	2	273	2	338	4	484	2
202	3	231	3	279	3	340	2	485	3
203	4	239	5	281	3	341	2	500	29 M
204	2	240	2	293	2	342	2	501	10
						353	2	502	3

Mass Spectrum of Methyl 3-acetylpolyporenate A.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
50	13	76	2	109	54	138	3
51	16	77	31	110	10	141	4
52	4	78	22	111	17	142	2
53	12	79	43	112	2	143	6
54	5	80	71	117	5	144	2
55	100	81	14	118	2	145	12
56	14	82	36	119	23	146	3
57	40	83	55	120	5	147	12
58	2	84	14	121	27	148	4
59	15	91	19	122	27	149	13
60	4	92	4	123	22	150	4
61	2	93	29	124	5	151	6
65	4	94	7	125	7	155	3
66	3	95	56	129	4	157	9
67	46	96	13	130	2	158	3
68	10	97	23	131	8	159	12
69	84	98	4	132	2	160	3
70	11	99	3	133	16	161	12
71	18	105	42	134	5	162	3
73	3	106	6	135	23	163	7
74	4	107	33	136	6	164	3
75	2	108	8	137	15	165	4

Over.

Mass Spectrum of Methyl 3-acetylpolyporenate A (Cont'd).

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
169	6	202	2	467	2		
170	2	203	3	482	1		
171	6	205	3	509	39		
172	2	211	3	510	14		
173	8	213	5	511	3		
174	2	215	2	524	2		
175	8	217	4	527	1		
176	3	225	3	542	4 M		
177	6	227	3				
179	3	229	3				
183	3	231	2				
185	6	239	4				
187	7	241	3				
188	2	243	2				
189	6	253	2				
190	2	255	3				
191	4	257	2				
197	3	449	35				
199	6	450	11				
200	2	451	4				
201	6	454	2				

MASS SPECTRUM OF THE COMPOUND P.B.2

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
50	3	77	13	101	8	130	4	154	3
51	4	78	5	105	30	131	13	155	6
52	3	79	25	106	7	132	5	;56	5
53	13	80	5	107	45	133	21	157	15
54	5	81	62	108	8	134	7	158	5
55	76	82	9	109	54	135	29	159	20
56	10	83	23	110	8	136	6	160	5
57	21	84	7	111	8	137	10	161	15
58	2	85	17	112	2	138	2	162	4
59	30	86	2	113	8	139	2	163	5
60	8	87	5	115	6	141	7	165	4
64	4	88	5	116	2	142	5	167	4
65	5	91	25	117	8	143	12	168	3
66	3	92	5	118	3	144	5	169	10
67	44	93	34	119	33	145	20	170	4
68	10	94	7	120	6	146	5	171	12
69	68	95	44	121	55	147	16	172	5
70	8	96	7	122	9	148	5	173	15
71	12	97	10	123	15	149	11	174	4
72	2	98	3	124	3	150	2	175	9
73	8	99	4	125	3	151	4	176	3
74	10	100	5	129	8	153	3	177	5

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
178	2	207	4	245	2	299	2	435	3
179	6	209	4	246	3	307	2	449	81
180	2	211	5	247	2	311	3	450	28
181	4	212	2	251	2	312	2	451	10
182	2	213	8	253	5	313	10	452	2
183	7	214	2	254	2	314	3	464	3
184	3	215	5	255	5	321	4	465	10
185	11	217	4	256	2	323	2	466	5
186	4	219	2	257	4	325	2	467	100
187	11	221	2	259	3	326	2	468	34
188	5	223	4	261	2	327	3	469	8
189	7	224	2	262	2	328	2	470	2
190	2	225	6	263	2	329	4	482	14
191	3	226	4	265	3	330	2	483	5
193	2	227	6	267	3	331	2	484	2
195	3	228	3	269	3	339	4	498	2
196	2	229	5	271	3	341	2	500	10
197	6	230	2	273	2	353	2	501	4
198	3	231	3	279	6	361	2	509	9
199	10	237	3	280	3	394	2	510	4
200	3	239	7	281	4	395	2	567	34
201	10	240	3	293	4	407	2	568	13
202	3	241	6	295	4	409	2	569	3
203	4	242	3	296	2	412	2	582	4
204	2	243	3	297	2	433	2	585	2
205	3	244	2	298	2	434	2	600	4 M

MASS SPECTRUM OF THE COMPOUND D.Q.1

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
50	2	82	4	113	3	137	6	170	2
51	2	83	12	115	22	141	2	171	11
53	5	84	2	116	4	142	3	172	4
54	2	87	3	117	5	143	65	173	17
55	49	88	2	118	9	144	7	174	5
56	9	91	14	119	34	145	19	175	11
57	14	92	3	120	8	146	5	176	5
59	80	93	24	121	50	147	17	177	3
60	3	94	16	122	10	148	4	183	5
65	2	95	32	123	13	149	8	184	2
67	14	96	3	124	2	153	26	185	27
68	2	97	6	125	2	154	3	186	6
69	42	99	2	126	2	155	4	187	37
70	3	100	2	127	4	156	2	188	9
71	4	101	13	129	6	157	9	189	23
73	2	105	24	130	2	158	5	190	4
74	3	106	5	131	13	159	18	191	2
77	5	107	30	132	4	160	5	197	4
78	2	108	17	133	23	161	16	198	2
79	13	109	25	134	7	162	4	199	10
80	2	110	3	135	24	163	5	200	4
81	25	111	4	136	10	169	5	201	11

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
202	4	229	2	281	8	345	5	469	7
203	6	230	2	282	3	346	2	482	7
204	2	239	7	283	3	347	2	483	7
205	2	240	3	291	2	353	2	484	2
209	2	241	10	295	3	367	2	485	3
211	5	242	3	296	2	371	9	495	2
212	2	243	2	297	5	372	3	500	2
213	13	253	5	298	2	373	2	569	5
214	5	254	2	307	3	383	2	570	3
215	9	255	9	309	64	427	19	582	3
216	2	256	3	310	17	428	6	583	2
217	2	257	3	311	4	435	4	585	36
218	3	265	2	313	2	441	3	586	14
223	2	266	2	323	3	442	3	587	3
225	8	267	5	324	15	443	4	598	5
226	3	269	2	325	10	449	3	599	2
227	13	270	2	326	3	451	3	600	44 M
228	3	279	5	327	3	467	100	601	16
		280	2	331	3	468	35	602	4

MASS SPECTRUM OF THE COMPOUND D.Q.7

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
50	5	74	5	101	16	127	57	150	2
51	5	77	9	102	3	128	33	153	2
52	2	78	3	105	30	129	10	154	3
53	8	79	17	106	6	130	3	155	87
54	3	80	3	107	36	131	15	156	12
55	52	81	30	108	7	132	5	157	17
56	6	82	5	109	39	133	27	158	5
57	22	83	16	110	6	134	8	159	20
58	2	84	3	111	8	135	30	160	6
59	30	85	6	113	2	136	10	161	17
60	4	87	5	115	3	137	21	162	6
63	3	88	4	116	2	138	9	163	9
64	3	91	21	117	7	139	8	165	41
65	4	92	4	118	3	141	4	166	6
66	2	93	30	119	42	142	4	167	5
67	42	94	6	120	9	143	10	168	3
68	9	95	84	121	61	144	4	169	8
69	66	96	10	122	13	145	21	170	13
70	6	97	18	123	20	146	6	171	17
71	12	98	3	124	3	147	20	172	5
72	2	99	3	125	4	148	5	173	19
73	2	100	13	126	3	149	11	174	6

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
175	14	203	9	237	4	293	3	357	6
176	5	204	2	239	9	294	2	358	2
177	5	205	2	240	5	295	4	359	2
181	3	209	4	241	11	297	4	369	2
182	3	210	23	242	4	307	7	373	2
183	8	211	8	243	5	308	3	383	7
184	3	212	3	251	4	309	92	384	4
185	14	213	14	253	5	310	24	385	3
186	6	214	6	254	2	311	5	399	3
187	43	215	11	255	11	323	8	411	2
188	11	216	3	256	4	324	18	425	2
189	27	217	6	257	3	325	12	427	38
190	6	221	3	265	3	326	3	428	11
191	4	223	5	266	2	327	9	429	4
195	4	224	4	267	5	328	2	430	4
196	2	225	8	269	4	335	5	438	2
197	100	226	3	270	2	336	2	440	2
198	14	227	14	279	4	339	5	441	10
199	13	228	4	281	6	340	2	442	8
200	5	229	10	282	3	341	4	443	4
201	15	230	3	283	3	342	2	447	4
202	6	231	3	291	3	343	2	456	4

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.
457	15	480	26	498	3	554	4	595	3
458	4	481	7	508	4	567	2	597	56
461	3	482	2	509	2	579	2	598	22
462	2	492	2	510	2	580	2	599	5
463	2	493	3	512	7	581	5	610	9
476	2	494	8	513	2	582	4	611	7
477	15	495	9	526	2	583	4	612	57 M
478	6	496	3	539	2	584	2	613	23
479	75	497	10	553	7	594	4	614	6