

PYRROLES AND RELATED COMPOUNDS—VIII¹

MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL PROBLEMS—LXXVI² THE MASS SPECTRA OF PORPHYRINS

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(Received 4 May 1965)

Abstract—The molecular ion nearly always produces the strongest peak in mass spectra of porphyrins. The macrocyclic nucleus is remarkably stable and fragmentation gives mainly "benzylic" ions. In derivatives of porphin this involves cleavage at the bond once removed from the macrocycle, but in chlorins the entire substituent is lost from the reduced "pyrrole" ring. Methyl esters of chlorins derived from chlorophyll lose directly 147 and 159 mass units in complex processes marked by strong metastable peaks. All the spectra contain a prominent series of peaks from doubly charged ions; a novel feature is loss of ketene from propionate side-chains.

THE value of mass spectrometry in structural studies of natural products is now well established,³ and in this paper we describe some of our recent studies of the mass spectra of porphyrins, perhaps the most important and ubiquitous class of natural pigments. Previous spectral studies in the porphyrin field (especially electronic absorption and PMR spectra) have been of great theoretical, structural and biochemical interest, and there is no doubt that mass spectrometry will prove to be of equal and complementary value. Electronic absorption spectra⁴ can be determined with minute quantities of material, but they only give gross structural information (e.g. whether the macrocycle is a true porphyrin, or is partially reduced as in the chlorophylls and bacteriochlorophyll, and whether certain types of substituents are present), while PMR spectra enable the nature of the side chains to be deduced fairly completely. Indeed in some cases even "type"-isomers may be distinguished,⁵ but nevertheless at present the use of PMR is limited by solubility difficulties, and by the relatively large amounts of material needed. Apart from the blood and plant pigments, the quantities of material which can be isolated in a pure state are often minute and mass spectral studies should be particularly useful in structural work for establishing molecular weights and empirical formulae as well as deriving information on the nature of substituents, because so little material is required.

¹ Part VII: W. G. Terry, A. H. Jackson, G. W. Kenner and G. Kornis, *J. Chem. Soc.* (1965).

² Part LXXV: P. Brown, C. Djerassi, G. Schroll, H. J. Jakobsen and S.-O. Lawesson, *J. Amer. Chem. Soc.* **87**, (1965).

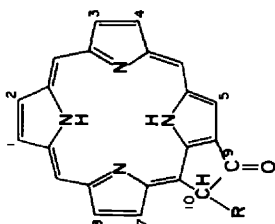
³ H. Budzikiewicz, C. Djerassi and D. H. Williams, *Structure Elucidation of Natural Products by Mass Spectrometry* Vols. I and II. Holden-Day, San Francisco (1964).

⁴ J. E. Falk, *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam (1964).

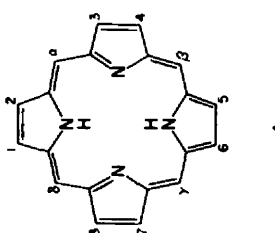
⁵ R. J. Abraham, A. H. Jackson and G. W. Kenner, *J. Chem. Soc.* 3468 (1961); R. J. Abraham, P. A. Burbidge, A. H. Jackson and G. W. Kenner, *Proc. Chem. Soc.* 134 (1963).

TABLE 1. PORPHYRIN STRUCTURAL FORMULAE

		Substituents									
		1	2	3	4	5	6	7	8		
Porphyrins	I (A)	Me	Me	Me	Me	Me	Me	Me	Me	R = CO ₂ Me	
	II (A)	Me	Et	Me	Et	Me	Et	Me	Et	R = CO ₂ Me	
	III (A)	Me	V	V	Me	Me	Et	Me	Me	R = CO ₂ Me	
	IV (A)	Me	Et	Me	Et	Me	P(Me)	P(Me)	Me	R = H	
	V (A)	Me	Et	Me	P(Me)	Me	P(Me)	P(Me)	Me	R = A(Me)	
	VI (A)	Me	P(Me)	Me	P(Me)	Me	P(Me)	P(Me)	Me	R = A(Me)	
	VII (A)	A(Me)	P(Me)	Me	A(Me)	Me	P(Me)	P(Me)	Me	R = CO ₂ Me	
	VIII (A)	Me	Et	Me	Et	Me	CO ₂ Me	P(Me)	Me	R = CO ₂ Me	
	IX (A)	Me	V	Me	V	Me	P(Me)	P(Me)	Me	R = A(Me)	
	X (A)	Me	V	Me	V	Me	P(Me)	P(Me)	Me	R = CO ₂ Me	
	XI (B)	Me	Et	Me	Et	Me	—	—	Me	R = CO ₂ Me	
	XII (A)	Me	CH(OH)Me	Me	CH(OH)Me	Me	P(Me)	P(Me)	Me	R = CO ₂ Me	
	XIII (A)	Me	H	Me	H	Me	P(H)	P(H)	Me	R = CO ₂ Me	
Chlorins (7,8-dihydroporphyrins)											
XIV	7,8-H (A)	Me	Et	Me	Et	Me	Et	Me	Et	R = CO ₂ Me	
XV	7,8-H (B)	Me	V	Me	Et	Me	Et	Me	Et	R = CO ₂ Me	
XVI	7,8-H (B)	Me	Et	Me	Et	Me	Et	Me	Et	R = CO ₂ Me	
XVII	7,8-H (B)	Me	V	Me	Et	Me	Et	Me	Et	R = H	
XVIII	7,8-H (A)	Me	V	Me	Et	Me	Et	Me	Et	R = A(Me)	
XIX	7,8-H (A)	Me	V	Me	Et	Me	Et	Me	Et	R = A(Me)	
XX	7,8-H (B)	Me	Et	Me	Et	Me	Et	Me	Et	R = CO ₂ Me	
XXI	7,8-H (B)	Me	Et	Me	Et	Me	Et	Me	Et	R = CO ₂ Me	
XXII	7,8-H (A)	Me	Et	Me	Et	Me	Et	Me	Et	R = A(Me)	
XXIII	7,8-H (A)	Me	Et	Me	Et	Me	Et	Me	Et	R = CO ₂ Me	
XXIV	7,8-H (B)	Me	V	Me	Et	Me	Et	Me	Et	R = CO ₂ Me	
XXV	7,8-H (B)	Me	V	Me	Et	Me	Et	Me	Et	R = A(Me)	
XXVI	7,8-H (B)	Me	V	Me	Et	Me	Et	Me	Et	R = CO ₂ Me	
XXVII	7,8-H (B)	Me	V	Me	Et	Me	Et	Me	Et	R = CO ₂ Me	
Abbreviations: V = CH=CH ₂ , Pr = CH ₂ CH ₂ CH ₂ , A(Me) = CH ₂ CO ₂ Me, P(H) = CH ₂ CH ₂ CO ₂ H, P(Me) = CH ₂ CH ₂ CO ₂ Me, P(Phy) = CH ₂ CH ₂ CO ₂ Phy											



A



B

Abbreviations: V = CH=CH₂, Pr = CH₂CH₂CH₂, A(Me) = CH₂CO₂Me, P(H) = CH₂CH₂CO₂H, P(Me) = CH₂CH₂CO₂Me, P(Phy) = CH₂CH₂CO₂Phy

Only two porphyrin mass spectra have so far been recorded,^{6,7} although recently a number of the structurally related phthalocyanine dyestuffs have also been studied.⁸ Our own work has been carried out with a large number of porphyrins obtained by degradation of haemin and chlorophyll,⁹ and by synthesis.¹⁰ It was found essential to use "direct" inlet systems,^{11,12} operating at temperatures up to 300°, on account of the relatively low volatility of porphyrins; in addition, most of the porphyrins with side chain carboxylic acid groups were converted to their more volatile methyl esters. (Haemin, and porphyrins containing more than two carboxyl groups, as well as many of the chlorophyll degradation products were in fact too involatile to obtain spectra from the free acids.)

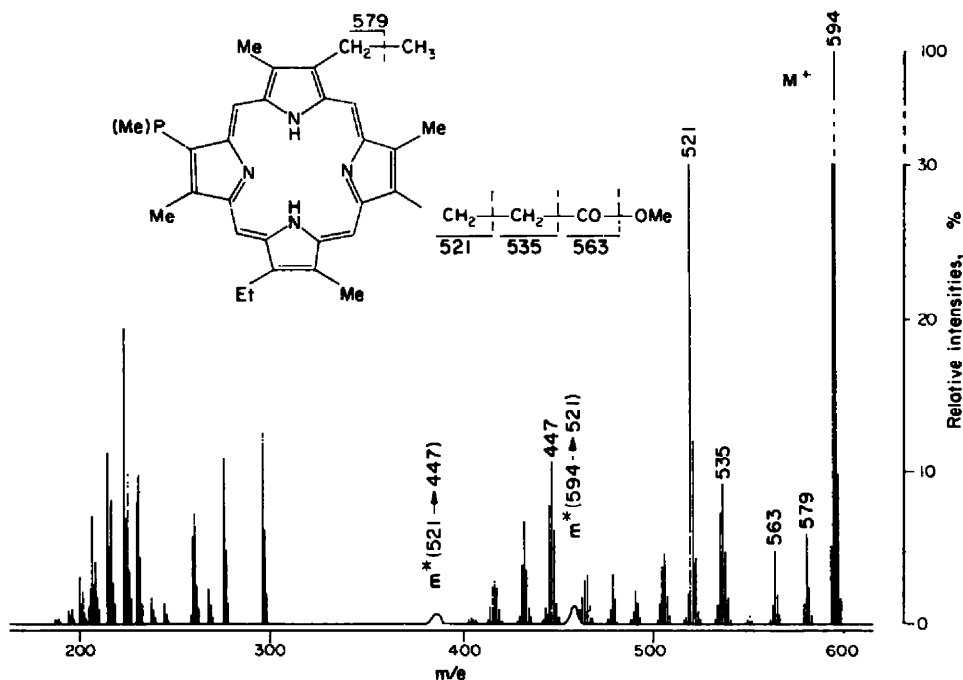


FIG. 1. Low resolution mass spectrum (MS9) of mesoporphyrin II dimethyl ester.

Tables 2 and 3 illustrate the main types of fragmentations occurring in porphins and chlorins (dihydroporphins) respectively, and include a representative selection of the various types of compounds which we have run and which may be obtained by degradation of the natural pigments.⁹ As can be readily seen from the typical spectrum shown in Fig. 1, the fragment ions fall into two distinct groups; the high mass group

⁶ A. Hood, E. G. Carlson and M. J. O'Neal in *The Encyclopaedia of Spectroscopy* (Edited by G. L. Clark) p. 616. Reinhold, New York (1960).

⁷ W. L. Mead and A. J. Wilde, *Chem. & Ind.* 1315 (1961).

⁸ H. C. Hill and R. I. Reed, *Tetrahedron* **20**, 1359 (1964).

⁹ H. Fischer and H. Orth, *Die Chemie des Pyrrols* Vol. II, Part 1. Akademische Verlag, Leipzig (1937); H. Fischer and A. Stern, Vol. II, Part 2 (1940).

¹⁰ A. H. Jackson, G. W. Kenner, G. McGillivray and G. S. Sach, *J. Amer. Chem. Soc.* **87**, 676 (1965).

¹¹ J. F. Lynch, J. M. Wilson, H. Budzikiewicz and C. Djerassi, *Experientia* **19**, 211 (1963).

¹² We are indebted to our colleague Dr. D. F. Shaw (Liverpool) for the design of a novel direct inlet system for use with the A.E.I. MS9 spectrometer.

TABLE 2. PORPHYRIN MASS SPECTRA

Porphyrin	Mol. wt.	Relative intensities of primary fragmentation products and molecular ions										
		M ⁺	-H	-CH ₃	-C ₂ H ₅	-2 CH ₃ or C ₂ H ₅ H	-OCH ₃	-HOCH ₃	-CO ₂ CH ₃	-CO ₂ CH ₂	-CH ₂ CO ₂ CH ₃	M ⁺⁺
I Octamethyl	422	100	11	5*	—	—	—	—	—	—	—	16
II Aetio I	478	100	4	21*	2	4	—	—	—	—	—	14
III Proto-aetio II†	474	100	4	20*	3	5	—	—	—	—	—	13
IV Tetramethyl- tetrapropyl‡	534	100	3	1	25*	—	—	—	—	—	—	16
V Meso IX dimethyl ester	594	100	4	5	—	—	5	—	—	4	21*	3
VI Copro III tetramethyl ester	710	100	3	—	—	—	6	—	—	11	43*	4
VII Uro II octamethyl ester	942	100	4	5	—	—	10	—	—	60	—	3
VIII Rhodo XV dimethyl ester	566	100	5	14	—	—	4	—	5§	3	31*	7
X Haemin dimethyl ester	644	100	8	—	—	—	4	—	—	3	20*	2
XI Phaeo-a ₈ dimethyl ester	606	100	4	2	—	—	—	19*	16§	61*	5	4

* An asterisk indicates that a metastable peak has been observed for the fragmentation.

† Synthesized by Mr G. L. Collier (Liverpool).

‡ A. H. Jackson, P. Johnston and G. W. Kenner, *J. Chem. Soc.* 2262 (1964).

§ Corrected for 'isotope peak' due to cleavage of CO₂CH₃

TABLE 3. CHLORIN MASS SPECTRA

Chlorin		Mol. wt.	Relative intensities of primary fragmentation products and molecular ions												
			M ⁺	H	CH ₃	C ₂ H ₅	OCH ₃	HOCH ₃	CO ₂ CH ₃	CH ₂ CO ₂ CH ₃	CH ₂ CH ₂ CO ₂ CH ₃	-147	-159	M ²⁺	
XIV	Aetichlorin†	480	100	6	12	25	—	—	—	—	—	—	—	—	42
XV	Phaeophorbide-a methyl ester	606	100	4	4	—	—	25	22*	2	9	30*	—	1	
XVI	Mesophaeophorbide-a methyl ester	608	100	4	3	—	—	20*	50*	2	5	19*	—	2	
XVII	Pyropheophorbide-a methyl ester	548	100	2	5	2	3	—	—	—	34*	—	—	6	
XVIII	Chlorin-c ₈ trimethyl ester	638	100	4	5	—	7*	—	13*	16*	10	9	20*	2	
XIX	Mesochlorin-c ₈ trimethyl ester	640	100	5	3	4	5*	—	12*	11*	9	6	20*	2	
XX	Phaeophorbide-b methyl ester	620	100	2	5	—	—	7	20	—	—	10	—	9	
XXI	Mesophaeophorbide-b methyl ester	622	100	2	13	—	—	5	13	2	2	9	—	4	
XXII	Rhodin-g ₇ trimethyl ester	652	100	5	—	—	—	—	24	22	15	12	30*	10	
XXIII	2-Vinylrhodochlorin methyl ester	566	100	5	8	—	2	—	—	2	35*	—	—	0	

* An asterisk indicates that a metastable peak has been observed for the fragmentation.

† $\gamma\delta$ -dideuterioaetichlorin (prepared by Mr. P. A. Burbidge, Liverpool, by exchange in deuteriotrifluoroacetic acid-) has a very similar spectrum, singly charged ions being shifted two mass units higher, and doubly charged ions, one unit higher.

consists of singly charged ions and is separated by a blank region of the spectrum from the lower mass group which consists of doubly charged ions (as is clearly indicated by the appearance of ions at half mass numbers, especially "isotope" peaks). The virtual absence of peaks below m/e 200 indicates that fragmentation of the nucleus itself is negligible. The other main features of porphyrin mass spectra are:

- (i) The molecular ion is nearly always by far the most intense peak in the spectrum,
- (ii) Side chain fragmentations are usually "benzylic" in character, fission occurring at the bond β to the nucleus,

i.e.
$$[\text{Porphyrin} - \text{CH}_2 - \text{R}]^+ \rightarrow \text{Porphyrin} - \text{CH}_2^+ + \text{R}^{\cdot}$$

(iii) The doubly charged ions are usually of comparable intensity to the singly charged ions (i.e. up to 30% of the molecular ion),* and the doubly charged molecular ion is not necessarily the most intense.

These features are all qualitatively consistent with the well known stability of the highly aromatic macrocyclic ring system in porphyrins which allows wide delocalisation of one or two positive charges in the species produced by electron impact in the mass spectrometer.

Comparison of the various spectra (cf. Tables 2 and 3) allows one to assess the relative stabilities of the various side-chains commonly found in porphyrins, i.e. vinyl > CHO > Me > Et > CH₂CH₂CO₂Me > n-Pr > CH₂CO₂Me etc. and this type of information should be very useful in structural determinations, especially where successive fragmentations may be observed. In most porphyrin spectra this successive fragmentation of the various side chains is readily observed and may be accompanied by additional hydrogen transfers and the singly charged ions taper off to very low intensity by about m/e 400 (Fig. 1); in the coproporphyrin (VI) spectra for example fragments and metastable peaks corresponding to successive benzylic type fissions of each of the propionate ester side chains may be seen. It should be noted that in successive cleavage of propionate residues each step causes loss of 73 mass units until the last, which involves loss of 74 (confirmed by the metastable peak).

Differences between the spectra of "type" isomers¹³ (e.g. dimethyl esters of mesoporphyrins II and IX) do not seem to be greater than the usual differences between mass spectra of a single compound run on different occasions. The spectra of mesomethylporphyrins (e.g. mesomethyl- and mesodimethyl-aetioporphyrins, and γ -phyllporphyrin XV) do not show any evidence of expulsion of the mesomethyl groups (which might have been anticipated on steric grounds¹⁴) for they are very closely similar to those of the parent compounds.

We have also examined the spectra of a number of porphyrin metal complexes e.g. haemin (X) (cf. Table 2) and magnesium, copper and nickel derivatives, and these are very similar to those of the parent porphyrins. Unless very special precautions are taken, porphyrins will abstract traces of metal ions from solvents etc. and the resulting traces of metal complexes are observed in most of our free porphyrin spectra as characteristic clusters of ions at masses 56-63 higher than the molecular ion (Fig. 2). These peaks are presumably due to transition metals (e.g. Cr, Fe, Ni, Cu etc.) and their intensities are of the order of 1% of the molecular ion. However there is usually insufficient

* Exceptionally the doubly charged molecular ion is 50% of the singly charged molecular ion (e.g. magnesium derivative of II).

¹³ H. Fischer and G. Stangler, *Liebigs Ann.* **459**, 62 (1927).

¹⁴ R. B. Woodward, *Angew. Chem.* **72**, 652 (1960).

metal to detect during elemental analysis for carbon and hydrogen, and this strongly suggests that the metal complexes are more volatile than the parent porphyrin. However we have so far been unable to obtain a spectrum of either chlorophyll-*a* or -*b* (XXVI or XXVII) although phaeophytin-*a* (XXIV) gave a poor spectrum which exhibited a weak molecular ion, weak ions corresponding to fission of the 10-CO₂Me group, and a somewhat stronger ion at *m/e* 278 (presumably a phytadiene arising from fission of the phytol ester).

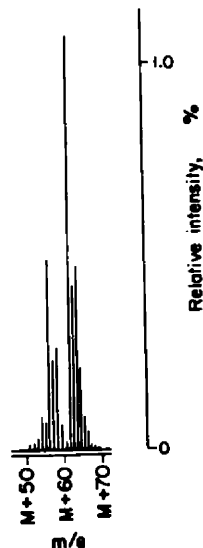
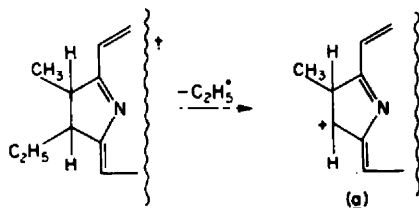


FIG. 2. Characteristic appearance of molecular ions due to traces of porphyrin metal complexes in porphyrin mass spectra.

Chlorin spectra, although generally rather similar to those of unreduced porphyrins, exhibit a number of additional interesting features which are mainly associated with fragmentations from the partially reduced ring (conventionally ring D in chlorophyll derivatives), and from the so-called isocyclic ring present in the chlorophylls and many of their derivatives. For example the major fragmentation in the spectrum of aetiochlorin (XIV) is loss of an ethyl radical whereas in aetioporphyrin (II) the main fragmentation is loss of a methyl radical (from the ethyl groups); in aetiochlorin, therefore, the predominant fission of ethyl must clearly be from the partially reduced ring as indicated in the partial formulae below, and the resulting ion (*a*) is "benzylic" in



character but somewhat different from the porphyrin fragmentation products. Similar fragmentations involving fission of the complete propionate ester side-chains at the 7-position in various chlorophyll derivatives are also observed and indeed these are the principal fragmentations in two of the spectra (Table 2—Compounds XVII and XXIII).

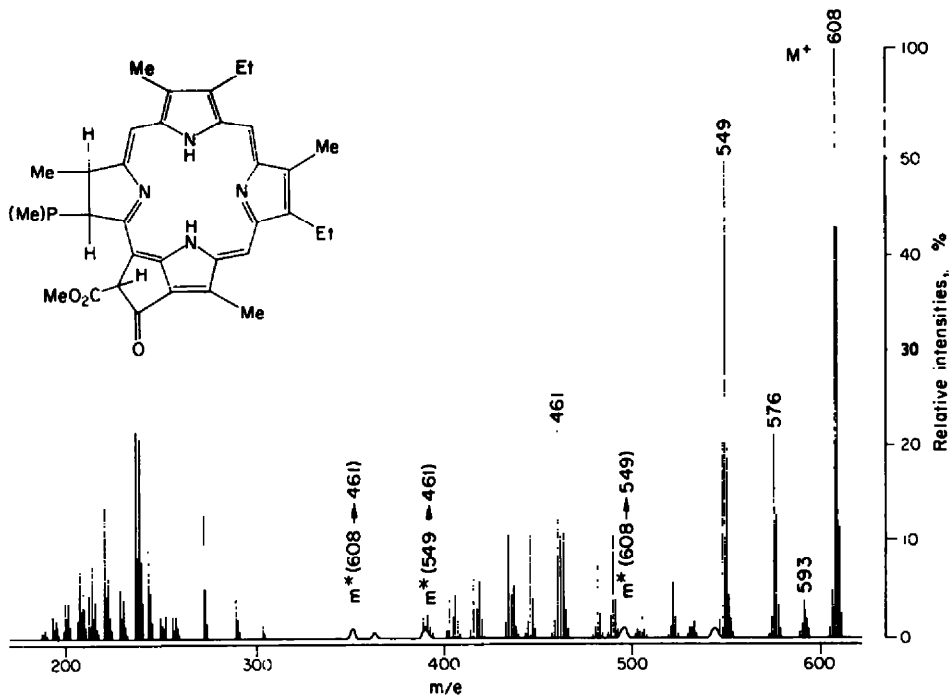
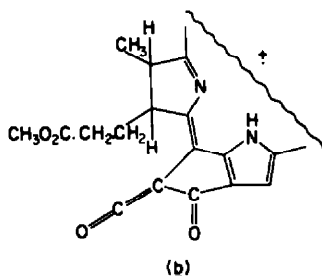


FIG. 3. Low resolution mass spectrum (MS9) of mesophaeophorbide—a methyl ester.

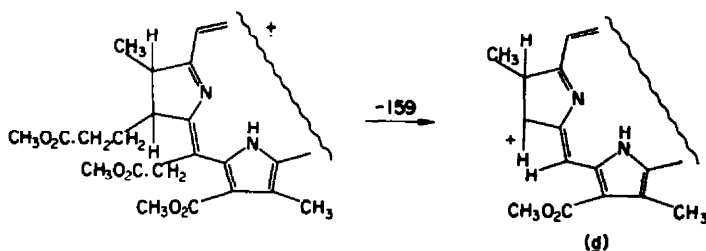
The lability of the 10-CO₂Me group in the isocyclic ring of chlorophyll derivatives is clearly shown by spectra of compounds XV, XVI (Fig. 3), XX and XXI and by phaeophytin-a (XXIV) (referred to above), and a similar fission of the corresponding group in the related ring-opened compounds (i.e. XVIII, XIX and XXII) is also observed. Loss of methanol also appears to be associated with the isocyclic—CO₂Me group (spectra XV, XVI, XX and XXI) and may be due to formation of a stable ion, represented by the partial formula (b); a similar cleavage is observed in the spectrum of methyl phaeoporphyrin-a₅ (XI).



The remarkable direct loss of 147 mass units from the molecular ion in spectra of compounds XV, XVI (Fig. 3), XX and XXI (attested in the first two spectra by large metastable peaks) is also associated with loss of this—CO₂Me group, together with the 7-CH₂CH₂CO₂Me group and one extra hydrogen atom, and the ion produced probably has structure (c) or (c').



Similar losses of 147 mass units from the molecular ion occur in the spectra of the isocyclic ring-opened compounds chlorin- e_8 (XVIII), mesochlorin- e_8 (XIX) and rhodin- g_7 (XXII) methyl esters as well as very pronounced cleavages of 159 mass units from the molecular ions. The latter fragmentations give rise to the strongest peaks in each spectrum (except for the molecular ion) and occur by direct fission of the molecular ion as shown by the appearance of intense metastable peaks; these cleavages presumably involve fragmentation of the 7- $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ and $\gamma\text{-CH}_2\text{CO}_2\text{Me}$ groups with transfer of one hydrogen atom from the departing groups giving perhaps species such as the ion (d). The postulated expulsion of the γ -mesosubstituent may



perhaps be facilitated by steric interactions between it and the 6-, and 7-substituent.¹⁴ The direct fragmentations of 147 and 159 mass units from the molecular ions of these chlorins are especially noteworthy in so far as they are confirmed by the appearance of metastable peaks. Hitherto it has been generally accepted that "If a metastable peak with a maximum at m^* is present in the spectrum which can be related by the equation $m^* = m_2^2/m_1$ to the masses of two other intense peaks m_1 and m_2 , it can be assumed with reasonable certainty that the fragment of mass m_2 arises in a *one-step decomposition* (our italics) from the species of mass m_1 ".¹⁵ This view can only be reconciled with the fission processes we have observed, if one assumes that a very complex series of concerted hydrogen migrations occur in each case, and accordingly a more reasonable explanation would seem to be that the fragmentations giving rise to the observed ions (M-147 and M-159) and associated metastable peaks result from two or three individual cleavages succeeding each other so rapidly as to be virtually simultaneous.

The origin of the doubly charged ions in the spectra of both porphyrins and chlorins has been investigated by high resolution mass spectrometry using the A.E.I. MS9 spectrometer (at Liverpool) and the results for mesoporphyrin II dimethyl ester (cf. Fig. 1) are presented in Table 4. A few of the doubly charged species correspond to the singly charged ions, and the doubly charged molecular ion is nearly always observed. Others, e.g. doubly charged ions at m/e 260, 230, 223, 216, 208 in the spectrum of mesoporphyrin II dimethyl ester (Fig. 1) correspond to the singly charged ions at m/e 521,

¹⁵ K. Biemann, *Mass Spectrometry Organic Chemical Applications* p. 154. McGraw-Hill, New York (1962).

461, 447, 433, 417, 403 respectively minus one hydrogen atom.¹⁶ A noteworthy feature of the spectra is the novel cleavage of CH_2CO and associated fragmentations from all porphyrins containing propionate ester side chains. This is well illustrated by ions m/e 276 and 239 in the spectrum of mesoporphyrin II dimethyl ester (cf. Fig. 1 and Table 4); the corresponding fragmentations are not observed in the singly charged ion region. The overall process may be represented as follows:

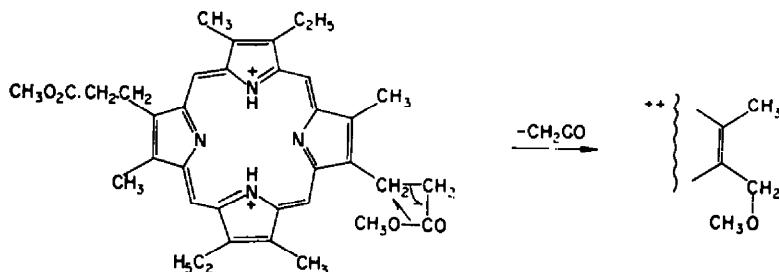


TABLE 4. HIGH RESOLUTION ANALYSIS OF THE ORIGIN OF THE PRINCIPAL PEAKS IN THE DOUBLY CHARGED ION REGION OF THE MASS SPECTRUM OF MESOPORPHYRIN II DIMETHYL ESTER (Cf. Fig. 1)

m/e	Accurate mass*	Neutral fragments ejected	Probable structures of neutral fragments
	Calculated	Observed	
297	297.16029	†	
276	276.15501	276.1551 ± 0.0005	$\text{C}_2\text{H}_5\text{O}$ CH_2CO
267	267.14973	267.1502 ± 0.0006	$\text{C}_2\text{H}_6\text{O}_2$ $(\text{CO}_2\text{CH}_3 + \text{H})$
260	260.14191	260.1420 ± 0.0005	$\text{C}_3\text{H}_6\text{O}_2$ $(\text{CH}_2\text{CO}_2\text{CH}_3 + \text{H})$
244	244.12880	244.1294 ± 0.0008	$\text{C}_4\text{H}_{10}\text{O}_2$ $(\text{CH}_2\text{CO}_2\text{CH}_3 + \text{CH}_2\text{OH} + \text{H})$
239	239.13662	239.1370 ± 0.0006	$\text{C}_3\text{H}_8\text{O}_2$ $(\text{CH}_2\text{CO}_2\text{CH}_3 + \text{CH}_2\text{CO} + \text{H})$
231	231.13917	231.1398 ± 0.0008	$\text{C}_4\text{H}_8\text{O}_4$ $(\text{CH}_2\text{CO}_2\text{CH}_3 + \text{CO}_2\text{CH}_3)$
230	230.13134	230.1312 ± 0.0004	$\text{C}_5\text{H}_{10}\text{O}_4$ $(\text{CH}_2\text{CO}_2\text{CH}_3 + \text{CO}_2\text{CH}_3 + 2\text{H})$
224	224.13134	224.1311 ± 0.0006	$\text{C}_6\text{H}_{10}\text{O}_4$ $(2\text{CH}_2\text{CO}_2\text{CH}_3)$
223	223.12352	223.1237 ± 0.0006	$\text{C}_6\text{H}_{12}\text{O}_4$ $(2\text{CH}_2\text{CO}_2\text{CH}_3 + 2\text{H})$
216	216.11569	216.1157 ± 0.0005	$\text{C}_7\text{H}_{14}\text{O}_4$ $(2\text{CH}_2\text{CO}_2\text{CH}_3 + \text{CH}_3 + \text{H})$
209	209.10787	209.1077 ± 0.0006	$\text{C}_8\text{H}_{16}\text{O}_4$ $(2\text{CH}_2\text{CO}_2\text{CH}_3 + 2\text{CH}_3)$
208	208.10004	208.1000 ± 0.0004	$\text{C}_8\text{H}_{18}\text{O}_4$ $(2\text{CH}_2\text{CO}_2\text{CH}_3 + 2\text{CH}_3 + 2\text{H})$
202	202.10004	202.0994 ± 0.0007	$\text{C}_8\text{H}_{18}\text{O}_4$ $(2\text{CH}_2\text{CO}_2\text{CH}_3 + \text{C}_2\text{H}_6 + \text{CH}_3)$
201	201.09222	201.0918 ± 0.0005	$\text{C}_9\text{H}_{20}\text{O}_4$ $(2\text{CH}_2\text{CO}_2\text{CH}_3 + \text{C}_2\text{H}_6 + \text{CH}_3 + 2\text{H})$

* Determined with the A.E.I. MS9 spectrometer; resolution 12,500 (10% valley).

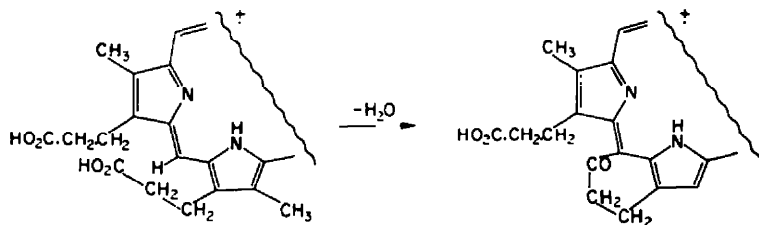
† The doubly charged molecular ion was used as the primary reference standard, and observed ratios of m/e for all of the other ions were obtained by successive comparisons of neighbouring peaks.

This new type of ester fragmentation, which to the best of our knowledge has not been previously observed, is thus probably due to some special feature of the doubly charged ion.

Some of the other spectra not recorded in the tables are also worthy of special comment. With haematoporphyrin dimethyl ester (XII), for example, the molecular ion readily loses two molecules of water from the hydroxyethyl side chains to give the base peak (m/e 590; 100%) i.e. the molecular ion of protoporphyrin dimethyl ester (IX) and thereafter the spectrum is very similar to both haemin and protoporphyrin esters.

¹⁶ cf. J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry* p. 311. Elsevier, Amsterdam (1960).

The spectrum of deuteroporphyrin IX free acid (XIII) (principal singly charged ions at m/e 510 (M^+ : 100%), 492 (100%), 466 (33%), 464 (33%), 451 (35%), 422 (80%), 405 (27%), and 391 (21%)) is quite different from any of the spectra recorded in the tables. The major fragmentation corresponds to loss of H_2O , and this may perhaps arise by cyclisation of one of the propionate side-chains onto the neighbouring *meso*-position.



(Similar Friedel-Crafts type cyclizations occur on treatment of porphyrins containing propionic acid side-chains with concentrated sulphuric acid.⁹) Other large peaks correspond to losses of CO_2 , $2CO_2$, HCO_2H as well as the expected benzylic type fragmentations of CH_2CO_2H , and $CO_2 + CH_2CO_2H$ (the origin of the peak at m/e 391 is not entirely clear). The losses of carbon dioxide may be of thermal origin rather than occurring from the ionized species.

We have also determined the mass spectra of nickel octamethyltetraazaporphin, and of a hexamethyldiethylcorrole¹⁷ and its nickel complex.¹⁷ As might be expected their spectra are very similar to the analogous porphyrins and likewise reflect the aromatic character and stability of the azaporphin and corrole ring systems.

EXPERIMENTAL

Three different instruments were used to obtain the mass spectra recorded in this paper, C.E.C. No. 21-103C and Atlas CH4 (at Stanford) and A.E.I. MS9 (at Liverpool). With some of the compounds spectra were run on all three machines and these showed only minor differences, e.g. in peak intensities, due presumably to differences in operating conditions and design. As discussed earlier all spectra were obtained by the use of "direct inlet" systems,^{11,13} and the operating conditions used for obtaining spectra were as follows: ionizing energy 70 eV., ionizing current 50 μ a, and source temp up to 280°.

In addition to the spectra described in the Tables and in the text, we have also determined the spectra of a large number of other porphyrins and will be glad to make these available on request for comparative purposes. The following are a representative selection: N-methylaetioporphyrin, *meso*-monomethyl- and *meso*-dimethylaetioporphyrins, nickel and magnesium aetioporphyrin, 2,6,7-triethyl-1,4,5,8-tetramethyl-3-methoxycarbonylethylporphin, mesoporphyrin III dimethyl ester, 2-ethyl-4,6,7-trimethoxycarbonylethyl-1,3,5,8-tetramethylporphin, coproporphyrin tetramethylesters I, II, III and IV, 2-ethyl-6,7-dimethoxycarbonylethyl-1,3,4,5,8-pentamethylporphin, 4-ethyl-6,7-di-methoxycarbonylethyl-1,2,3,5,8-pentamethylporphin, protoporphyrin IX dimethyl ester, tetramethoxycarbonylmethyl-tetramethylporphin, 2,3,7-triethyl-5-methoxycarbonyl-1,4,6,8-tetramethylporphin, 6-ethoxycarbonyl-2,4-diethyl-7-methoxycarbonylethyl-1,3,5,8-tetramethylporphin, pyrroporphyrin XV methyl ester and its copper derivative, γ -formylpyrroporphyrin XV methyl ester, γ -phyllporphyrin free acid and methyl ester, 2-acetyl- and 2-vinyl-2-desethyl- γ -phyllporphyrin XV methyl esters, deuteroporphyrin IX dimethyl ester.

Many of the above compounds, and those described in the Tables and in the text, were prepared

¹⁷ A. W. Johnson and I. T. Kay, *Proc. Chem. Soc.* 89 (1964).

in the course of our synthetic¹⁸ and NMR^{5,19} studies in the porphyrin field, and some of the spectra not discussed here will be recorded briefly in future publications. Samples of the coproporphyrin, uroporphyrin and phylloporphyrin methyl esters were obtained from Dr. S. F. MacDonald (Ottawa), and all four coproporphyrin esters were also synthesised by Mr. J. Wass (Liverpool), the III and IV type isomers being prepared by application of our recently described new porphyrin syntheses.¹⁰ The corrole samples were supplied by Professor A. W. Johnson and Dr. I. T. Kay¹⁷ (Nottingham).

Acknowledgements—We thank Dr. S. F. MacDonald, Professor A. W. Johnson and Dr. I. T. Kay for the samples mentioned in the Experimental and Mr. P. A. Burbidge for the preparation of most of the chlorins. We are grateful for financial support from the Nuffield Foundation and Parke, Davis and Co. (to Liverpool University) and the National Institutes of Health (Grants No. GM-11309 and AM-04257 to Stanford University). The purchase of the Atlas CH-4 mass spectrometer was made possible by NASA grant No. NSG81-60.

¹⁸ A. H. Jackson, G. W. Kenner and D. Warburton, *J. Chem. Soc.* 1328 (1965).

¹⁹ R. J. Abraham, A. H. Jackson, G. W. Kenner and D. Warburton, *J. Chem. Soc.* 853 (1963).