LOCALISATION OF SUBSTITUENTS IN PORPHYRINS: THE MASS SPECTROMETRIC FRAGMENTATION BEHAVIOR OF MESO-SUBSTITUTED PORPHYRINOGENS

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The mass spectra of meso-substituted porphyrinogens are analysed with respect to a possible localisation of substituents in the porphyrin ring system.

In a preceding paper (1) the possibilities and limitations have been discussed for the localisation of substituents in porphyrinogens, i.e., hexahydro derivatives of porphyrins the pyrrole units of which are separated by CH₂-groups. It was shown that their mass spectra exhibited three triades comprising one, two, or three pyrrole units together with zero, one, or two of the flanking CH₂-groups (usually peak groups due to hydrogen rearrangement reactions). Careful analysis of the mass spectra thus allows to establish which pyrrole rings are linked together in the case of unsymmetrical substitution. In the following the influence of meso substituents on this general fragmentation behavior will be discussed.
\(\alpha,\gamma\text{-Dialkyl octaethyl porphyrinogens}^{1} (2-4)\)

The main process is the loss of one meso substituent (yielding conjugation between two pyrrole units) the relative importance of which increases with the bulkiness of the meso group. The second meso group is lost with rearrangement of one H in either direction (from \(M^{++}\), however, both meso groups are eliminated with high abundance, \(m/e 269\), in accordance with the even electron rule). Both these species allow a differentiation between peripheral and meso substituents which in the unreduced compound is possible only for certain sterically highly hindered compounds (4). Skeletal fragmentation follows essentially the rules established for octaethyl porphyrinogen (1) (1) including the rather extensive H rearrangements\(^2\) (the most abundant ions of the various peak groups differ frequently by one or two amu from the values given in Table 1). Ions comprising two or three

1From \(\alpha,\gamma\text{-dialkyl- or from }\alpha,\gamma\text{-dialkyl-}\alpha,\gamma\text{-dihydroporphyrins (2) with Pd/Al}_{2}O_{3}(5\%)/H_{2}\text{ in ethyl acetate (tenfold excess of catalyst (3))}.\)

2Deuterium labelling at 1 shows that the ethyl hydrogens do not participate to any major extent.
pyrrole units can be observed with or without preceding loss of one meso substituent (the latter ones prevailing with increasing size of the meso groups: m/e 310 in Fig.1 is one of the most abundant ions, m/e 338 in Fig.2 of medium, m/e 366 in Fig.3 of minor abundance; analogously in the group comprising 3 pyrrole units).

Chloroporphyrinogen e₆ trimethyl ester¹ (5)

Again, loss of the meso substituent (m/e 571) yields the most abundant ion. Since three different types of pyrrole units are present the mass spectrum is obviously more complex. From the monopyrrolic units rings A (and B) are clearly recognizable, ring D can just be discerned. Di- and tripyrrolic units are formed with and without the γ-substituent. The characteristic peak groups are labelled accordingly in Fig.4. It should be mentioned here that the mass spectrum of 5 is almost indistinguishable from that of tetrahydrochlorin e₆ trimethyl ester² (α,β,γ,N or more likely (NMR) α,β,γ,N) which suggested ready H-rearrangement.

Hexahydrochlorin e₆ trimethyl ester³

Since loss of the γ-substituent does not yield any more a conjugated system its elimination is of rather reduced abundance. The skeleton fragment ions found in Fig.4 can be recognized here as well though in part shifted by 1 or 2 amu.

Summary:

For meso substituted hexahydro porphyrins loss of meso substituents is always pronounced and allows their ready recognition.

¹From chloroporphyrin e₆ trimethyl ester with Pd/C (10%).
²From chlorin e₆ trimethyl ester with raney-Ni/H₂ (high excess of catalyst) in CH₂Cl₂.
³From chlorin e₆ trimethyl ester with Raney-Ni/H₂ (high excess of catalyst) in THF.
Table 1

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<td>CH₂ CH₂</td>
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<td>447</td>
<td>461</td>
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a This part of the spectrum contains also doubly charged ions which should not be confused with the skeletal fragments.

b These numbers correspond to those indicating the fragments in Figs. 1-3.
Fig. 1 Mass spectrum of \( \alpha, \gamma \)-dimethyl porphyrinogen (MAT 751, 100 eV, probe 130°C, source 250°C).

Fig. 2 Mass spectrum of \( \alpha, \gamma \)-diethyl porphyrinogen (MAT 751, 100 eV, probe 130°C, source 250°C).

Fig. 3 Mass spectrum of \( \alpha, \gamma \)-di-\( \gamma \)-propyl porphyrinogen (MAT 751, 100 eV, probe 120°C, source 250°C).
**Fig. 4** Mass spectrum of chlorophyllinogen e₆ trimethyl ester (MAT 731, 70 eV, probe 180°C, source 300°C)
As long as secondary fragmentation of the ions formed by the cleavage between the pyrrole units is not extensive (1) fragments comprising one, two, or three pyrrole units can be identified. However, ample hydrogen rearrangement processes, occasionally low abundance of characteristic ions and overlaps of the various triades may in cases make it necessary to obtain a complete high resolution spectrum to sort out the structure-relevant ions.

REFERENCES
3 The experimental details for the preparation of all compounds described here may be found in: W. Neuenhaus, "Diplomarbeit" Universität Köln, 1976.

Received, 11th July, 1977