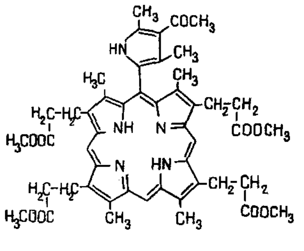
FEATURES OF THE MASS SPECTROMETRIC BEHAVIOR OF PORPHYRIN SYSTEMS WITH A VOLUMINOUS SUBSTITUENT IN THE meso POSITION

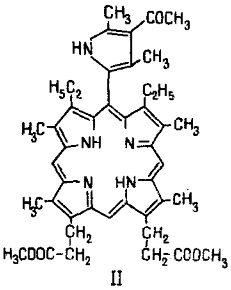
B. V. Rozynov, A. F. Mironov,
and R. P. Evstigneeva

UDC 547.979.733

The investigation of the mass-spectrometric behavior of porphyrin systems has shown that the introduction of small substituents into the meso position of the porphyrin ring, although it introduces some specific features into the mechanism of their decomposition on electron impact, does not substantially affect the overall nature of the mass spectrum distinctive of porphyrin systems, for which the maximum intensity of the peak of the molecular ion with very low intensities of the peaks of ions in the region of small mass numbers is characteristic [1-3]. In this connection, it appeared of interest to study the change in the nature of the mass spectrum of porphyrin with the introduction of a voluminous substituent having a conjugated ring system into the meso position. We have studied the mass-spectrometric behavior of the tetramethyl ester of β-meso-(3-acetyl-2, 4-dimethyl-5-pyrryl) coproporphyrin II (I) and the dimethyl ester of α-meso-(3-acetyl-2,4-dimethyl-5-pyrryl)mesoporphyrin III (II), which each contain a pyrrole radical in the meso position.



I



II

As can be seen from Fig. 1, the general nature of the mass spectra of the compounds studied differs radically from the mass spectra of porphyrins not containing a voluminous substituent in the meso position. The intensities of the peaks of the molecular ions [m/e 729 for (I) and 845 for (II)] in the mass spectra of these compounds are comparable with the intensities of the peaks of the ions formed as a result of the splitting out of the pyrrole substituent (m/e 594 and 710, respectively). The peaks of the ions arising in the elimination of other lateral substituents possess a considerably lower intensity. The intensities of the peaks in the region of high mass numbers are considerably less than the intensities of the peaks in the region of low mass numbers where the strongest peaks are those of the ions with m/e 137, 122, 108, and 94. The maximum intensity in the mass spectra of both porphyrins is possessed by the peak of the ion with m/e 122. The peak of the ion with m/e 137 is the peak of the molecular ion of 3-acetyl-2,4-dimethylpyrrole, the products of the further decomposition of which are represented by the peaks of ions with m/e 122, 108, and 94 [4]. The high intensity of the ions considered must be due to the partial formation of molecules of 3-acetyl-2,4-dimethylpyrrole by the thermal decomposition of the corresponding porphyrin derivative. A characteristic feature of the mass spectra of both porphyrins is the presence, with

---

M. M. Shemyakin Institute of the Chemistry of Natural Compounds, Academy of Sciences of the USSR. M. V. Lomonosov Moscow Institute of Fine Chemical Technology. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 197-199, March, 1971. Original article submitted December 24, 1970.

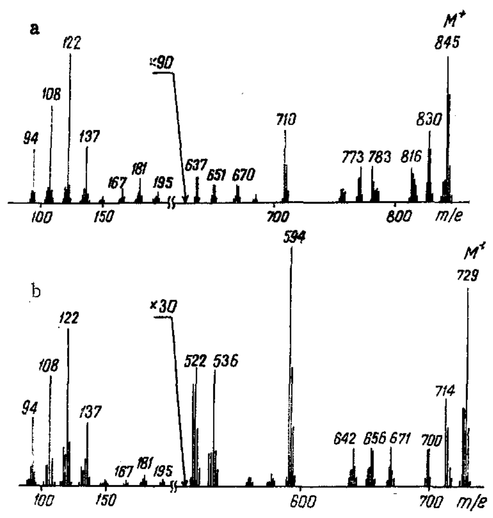


Fig. 1. Mass spectra of the tetramethyl ester of β-meso-(3-acetyl-2,4-dimethyl-5-pyrryl)coproporphyrin II (a) and the dimethyl ester of α-meso-(3-acetyl-2,4-dimethyl-5-pyrryl)mesoporphyrin III (b).

intensities comparable with those of the peaks of the molecular ions, of the peaks of ions with m/e 195, 181, and 167, the formation of which is due to the interaction of the eliminated residues of pyrrole and propionic acid. The intensities of the peaks of doubly-charged ions are the same as in the porphyrins considered earlier [1].

Thus, the presence of a voluminous substituent with a conjugated ring system in the meso position of a porphyrin leads to the predominant decomposition of the molecular ions at the bond between the voluminous substituent and the porphyrin ring with the predominant localization of the positive charge on the voluminous substituent split off. In our case, this process of decomposition leads to the appearance in the mass spectra of the compounds studied of a strong peak of the ion of 3-acetyl-2,4-dimethylpyrrole and a far weaker ion corresponding to the elimination of the pyrrole radical from the molecular ion. The features of the mass spectrometric behavior of the compounds (I) and (II) considered will be useful in establishing the structure of new meso-pyrryl-substituted porphyrins.

The mass spectra were obtained on a Hitachi RMV-6D instrument at a temperature of the ionizing chamber of 300°C and an energy of the ionizing electrons of 70 eV.

SUMMARY

Features of the mass-spectrometric behavior of the tetramethyl ester of β-meso-(3-acetyl-2,4-dimethyl-5-pyrryl)coproporphyrin II and the dimethyl ester of α-meso-(3-acetyl-2,4-dimethyl-5-pyrryl) mesoporphyrin III, each of which contains a voluminous pyrryl radical with a conjugated ring system in the meso position, have been investigated.

LITERATURE CITED

1. A. H. Jackson, G. W. Kenner, K. M. Smith, R. T. Aplin, H. Budzikiewicz, and C. Djerassi, Tetrahedron, 20, 2925 (1965).
2. H. Budzikiewicz, Advan. Mass Spectrom., 4, 313-315 (1968).
3. D. B. Boylan, Org. Mass Spectrom., 3, 339 (1970).
4. H. Budzikiewicz, C. Djerassi, and D. Williams, Interpretation of Mass Spectra of Organic Compounds, Holden-Day, San Francisco (1964) [Russian translation], Moscow (1966), p. 286.