PORPHYRINS.

17.* OXIDATION OF PORPHYRINS WITH A CYCLOPENTANE RING ON THE SURFACE OF SILICA GEL.

CHEMICAL PROPERTIES OF HYDROXYCYCLOPENTANOPORPHYRINS†

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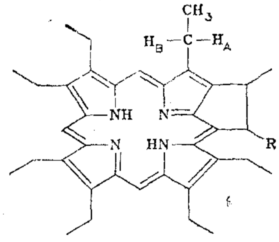
It was established that porphyrins with a cyclopentane ring are oxidized on the surface of silica gel by air oxygen to give 5^1-hydroxy-3^1,5^1-cycloporphyrins in 30-35% yields. Heating 5^1-hydroxy-3^1-methyl-3^1,5^1-cycloheptaethylporphyrin in CF_3COOH leads to splitting out of water and prototropic rearrangement of the intermediate unstable cyclopentenoporphyrin to the previously unknown exo-methylenecyclopentanoporphyrin.

In a previous communication [1] we described the thermal conversion of Schiff bases of meso-formyloctaalkylporphyrins to porphyrins with a cyclopentane ring, which made it possible to obtain these previously difficult-to-obtain compounds in high yields (up to 50-55%). Porphyrins with both unsubstituted and alkyl-substituted cyclopentane rings were obtained by this method.

In the chromatographic purification of porphyrin I on plates with a fixed layer of silica gel we observed that a new polar porphyrin, the establishment of the structure of which was the goal of the present research, developed during rechromatography of this plate.



I,II,VII–X

I R=H; II R=OH; VII R=$OSiMe_3$; VIII R=OAc; IX R=OEt; X R=$OCOCF_3$

According to data from the high-resolution mass spectrum, the isolated polar porphyrin had the composition $C_{37}H_{46}N_4O$, i.e., it differed from starting porphyrin I with respect to the presence of oxygen. The relative intensities of the peaks of the molecular ion and the principal fragments changed appreciably as a function of the conditions under which the spectra were recorded, but, in general, the mass spectrum had the following form of the high-m/z region: 562 (M^+, 100), 546 (48), 544 (78), 533 (13), and 531 (8). The principal fragment ion with m/z 544 corresponds to the $M^+ - H_2O$ process. The intense ion peak with m/z 546 is due to the porphyrin I impurity, which is formed as a result of thermolysis of the polar porphyrin in the ionization chamber of the mass spectrometer; this was confirmed by an analysis of the metastable ions by the DADI method. Consequently, oxidation of the adsorbed porphyrin by air oxygen and the formation of a hydroxyporphyrin occur during drying of the silica gel plate. The presence of a hydroxy group in the porphyrin is confirmed by the presence of a broad band at 3500 cm^{-1} in the IR spectrum. The electronic spectra of porphyrin I and the hydroxyporphyrin are virtually identical, and the cyclopentane ring is conse-

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*See [1] for communication 16.
†See [2] for our preliminary communication.

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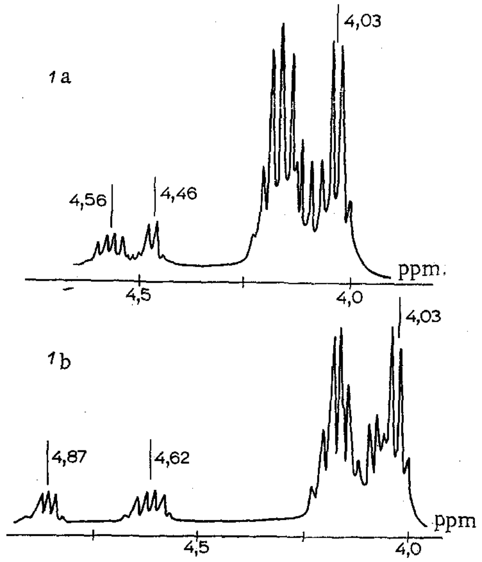
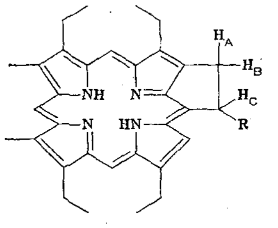


Fig. 1. PMR spectra of the trans and cis isomers of porphyrins in the region of the signals of the ring 3^1-H, H_A, and CH_2CH_3 protons: a) isomer IIa; b) isomer IIb (the spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard).

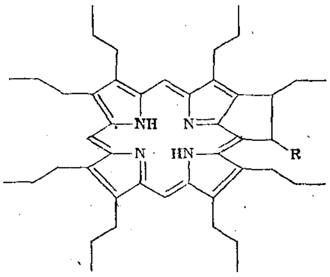
quently retained during oxidation. The PMR spectrum showed that the methylene group attached to the carbon atom in the 5^1 position of the cyclopentane ring underwent oxidation, and the 3^1,5^1-cyclo-3^1-methyl-5^1-hydroxy-2,7,8,12,13,17,18-heptaethyl-21H,23H-porphin structure (II) can consequently be assigned to the hydroxyporphyrin.

Two zones, one of which (the less mobile zone) contained $\sim$90% of the substance and was the trans isomer (IIa), since the SSCC of the protons of the exo ring did not exceed 1 Hz, were isolated by chromatography of porphyrin with a column packed with aluminum oxide in the CCl_4—chloroform—ether system (20:40:15). The more mobile zone contained the cis isomer (IIb), for which the SSCC of the protons in the 3^1 and 5^1 positions was 7.2 Hz. A characteristic feature of the PMR spectra of isomers IIa and IIb is the presence of nonequivalent protons in the methylene group of the ethyl substituent in the 2 position (Fig. 1).

The oxidation of porphyrins with a cyclopentane ring is a general reaction, and the methylene group in the 5^1 position always undergoes oxidation. For example, porphyrins V and VI, respectively, were obtained under similar conditions in the oxidation of porphyrins III and IV.*



III R=H; V R=OH



IV R=H; VI R=OH

With respect to their chemical properties, hydroxyporphyrins resemble known meso-hydroxymethylporphyrins very much. This porphyrin II is silylated quantitatively to give trimethylsilyl derivative VII, in the mass spectrum of which the molecular-ion peak is the

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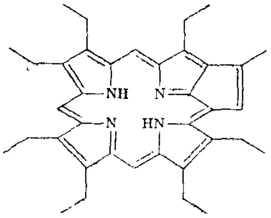
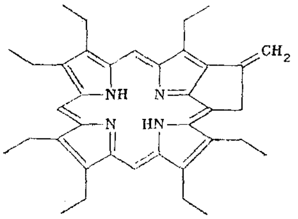
*The synthesis of octapropylporphyrin and its derivatives will be published in a future communication.

most intense peak. Porphyrin II is readily acetylated by acetic anhydride in pyridine to give ester VIII. The latter is converted quantitatively to ether IX on treatment with chloroform containing traces of alcohol and acid.

When porphyrin II is heated in CF$_3$COOH at 60°C for 2-3 h, the initial product is trifluoroacetoxy derivative X, which is then converted to a new porphyrin in 85-90% yield. Its composition C$_{37}$H$_{44}$N$_4$ (according to data from the high-resolution mass spectrum) corresponds to splitting out of trifluoroacetic acid from porphyrin X. We therefore initially assumed that the structure of a porphyrin with a cyclopentene ring (XI), i.e., similar to the porphyrin that is most likely formed in the fragmentation of the molecular ions of Schiff bases of meso-formylporphyrins [3] but virtually is not formed in their thermolysis [1], corresponds to the new porphyrin.



XI



XII

The following arguments seemed to us quite convincing for the assignment of structure XI to the new porphyrin. Porphyrin I is formed in quantitative yield when it is hydrogenated over Pd black. A band of medium intensity at 1629 cm^{-1}, which can be assigned to the C=C bond in the cyclopentene ring [4], is present in the IR spectrum. In addition, the electronic spectrum of the new porphyrin has an appreciable bathochromic shift as compared with the spectrum of saturated analog I, and in the spectra of the dication and its metal complexes we observed considerable splitting of both the α and β bands (10-15 nm), which could be explained by the alternative existence of the porphyrin in the form of both 18-π-electron and 20-π-electron conjugated macrorings. An analog containing a cyclopentene ring was previously synthesized with chlorin as the model [5]. All of these data would seem to confirm the presence of a cyclopentene ring.

The single and chief argument against porphyrin structure XI was the PMR spectrum, in which there were only three singlet signals corresponding to protons of the exo ring at 6.34 (1H), 5.94 (2H), and 5.95 ppm (1H). A triplet at 116.8 ppm with SSCC 161 Hz, which is typical for olefinic compounds, and a triplet at 45.4 ppm with SSCC 134 Hz, which corresponds to a quaternary carbon atom in the 5^1 position, were observed in the ^{13}C NMR spectrum in CDCl$_3$ + CF$_3$COOH without decoupling of the protons. These data indicate unambiguously that the new porphyrin has the XII structure rather than the XI structure.

In contrast to all of the known alkylporphyrins, porphyrin XII is readily deuterated by CF$_3$COOD. The protons of the exo ring, of course, undergo deuterium exchange, and the protons in the 3^2 position are exchanged first; deuterium exchange in the 5^1 position takes place considerably more slowly, which is readily observed in the PMR spectrum from the rapid disappearance of the signals of protons at 6.63 and 6.27 ppm (in a few hours) and slow disappearance of the signal at 6.11 ppm (after several days). This sort of deuterium exchange graphically demonstrates the existence of prototropic rearrangement in the exo ring.

Thus in both the thermolysis of Schiff bases of meso-formylporphyrins and in the splitting out of CF$_3$COOH from the corresponding trifluoroacetoxyporphyrins the intermediate cyclopentenoporphyrins must probably be stabilized through a prototropic rearrangement in which the 3^1-alkyl substituent participates. When this substituent is absent, as, for example, in porphyrin V, heating in CF$_3$COOH leads to destruction of the porphyrin ring.

In conclusion, it should be noted that the observed phenomenon of oxidation of porphyrins with cyclopentane rings on the surface of silica gel is of fundamental significance in the chromatographic isolation and establishment of the structures of petroleum and other "geological" porphyrins.

EXPERIMENTAL

The electronic spectra were recorded with an SF-18 spectrophotometer (LOMO). The IR spectra were recorded with a Perkin-Elmer 180 spectrometer. The PMR spectra were obtained

TABLE 1. Electronic Spectra of Porphyrins

Compound	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)
II^a	402 (289), 502 (14,6), 537 (6,0), 565 (6,1), 618 (8,15)
II^b	409 (400), 553 (17,0), 596 (7,1)
II^c	399 (220), 499 (15,7), 535 (5,4), 566 (7,1), 620 (10,1)
V^a	401 (225), 502 (14,7), 537 (6,0), 565 (7,15), 617 (7,2)
VIII^a	403 (266), 502 (14,7), 538 (5,8), 565 (6,95), 618 (8,4)
IX^a	403 (237), 503 (14,6), 537 (5,7), 566 (6,9), 618 (8,5)
XII^a	411 (271), 511 (13,4), 550 (12,4), 572 (9,1), 625 (2,7)
XII^b	419 (330), 552 sh (11,3), 563 (16,5), 600 (4,6), 612 (4,9)
XII^c	407 (302), 509 (14,7), 547 (13,0), 573 (9,1), 627 (3,6)
XIII^a	406 (224), 514 sh (9,5), 525 (12,6), 555 (13,2), 569 (23,7)
XIII^c	403 (221), 512 sh (9,35), 524 (12,8), 553 (13,9), 568 (25,8)
XIV^a	413 (306), 525 sh. (9,5), 537 (13,2), 566 sh (8,85), 581 (16,9)
XV^a	418 (151), 533 sh. (6,1), 545 (8,1), 571 (4,5), 589 (5,95)

[a] In chloroform. [b] In chloroform + 1% CF_3COOH. [c] In chloroform—ether (1:3).

with a Brucker WM-360 spectrometer. The mass spectra were obtained with a Varian MAT-311 spectrometer.

General Method for the Oxidation of Porphyrins with a Cyclopentane Ring. A 200-mg sample of the porphyrin with a cyclopentane ring was dissolved in 300 ml of destabilized chloroform (commercial-grade chloroform that had been passed through a column packed with activity I aluminum oxide). Silica gel (8-9 g) for TLC without a support (5 × 40L, Czechoslovakia) was added to a 30-ml portion of the solution, and the mixture was stirred until it was homogeneous and then poured out in a maximally thin layer on the surface of a polyethylene film or glass. After complete drying (20-30 min), the color of the adsorbent changed from bright red to brown. It was then collected and placed on a glass filter, and the substance was washed with chloroform—carbon tetrachloride (1:1) to separate the unchanged starting porphyrin. The adsorbent was then eluted with chloroform—ether (20:1), the principal fraction was evaporated, and the hydroxyporphyrin was crystallized from chloroform—methanol. The yields ranged from 30 to 35%.

3^1,5^1-Cyclo-3^1-methyl-5^1-hydroxy-2,7,8,12,13,17,18-heptaethyl-21H,23H-porphin (II). An 800-mg sample of porphyrin I yielded 300 mg of porphyrin II, from which 265 mg of trans-isomer IIa and 25 mg of cis-isomer IIb were obtained after additional separation with a column packed with aluminum oxide in a carbon tetrachloride—chloroform—ether system (2:4:1.5). PMR spectrum of isomer IIa (in $CDCl_3$): 10.13, 10.10, 10.02 (3H, all s, meso-H); 7.20 (1H, broad s, 5^1-H); 4.56 (1H, sextet, H_A in 2-CH_2CH_3); 4.46 (1H, q, J = 7.3 Hz, 3^1-H); 4.03-4.17 (13H, overlapped q, six CH_2CH_3, H_B); 2.03 (3H, d, J = 7.2 Hz, 3^1-CH_3); 1.98, 1.96, 1.94, 1.92, 1.90, 1.85 (21H, all t, CH_2CH_3); −2.94 and −3.83 ppm (2H, NH). PMR spectrum of isomer IIa in $CDCl_3$ + 1% CF_3COOH: 10.63, 10.56, 10.51 (3H, all s, meso-H); 7.53 (1H, d, J_{trans} = 1.8 Hz, 5^1-H); 4.52 (1H, sextet, J_{AB} = 14, J_{AX} = 7.5 Hz, H_A in 2-CH_2CH_3); 4.33 (1H, dq, 3^1-H); 4.08-4.15 (13H, overlapped q, six CH_2CH_3, H_B); 2.38 (3H, d, J = 7.2 Hz, 3^1-CH_3); 1.83, 1.81, 1.73, 1.68 (21H, overlapped t, CH_2CH_3); −3.10 and −4.35 ppm (4H, NH). PMR spectrum of isomer IIb (in $CDCl_3$); 10.15, 10.11, 10.03 (3H, all s, meso-H); 7.61 (1H, broad t, J_{cis} = 7.2, J_{H-OH} = 8.2 Hz, 5^1-H); 4.87 (1H, quintet, J_{H-CH_3} = 7.3 Hz, 3^1-H); 4.62 (1H, sextet, J_{AX_3} = 7.5 Hz, H_A in 2-CH_2CH_3); 4.03-4.20 (13H, six CH_2CH_3, H_B in 2-CH_2CH_3); 2.34 (1H, 5^1-OH, J = 8.2 Hz); 2.11 (3H, d, J = 7.3 Hz, 3^1-CH_3); 1.96, 1.94, 1.93, 1.90, 1.88, 1.86 (21H, all t, CH_2CH_3); −2.97 and −3.87 ppm (2H, NH). PMR spectrum of IIb (in $CDCl_3$ + 1% CF_3COOH): 10.62, 10.54, 10.50 (3H, all s, meso-H); 8.01 (1H, d, J_{cis} = 5.8 Hz, 5^1-H); 5.18 (1H, m, J_{H-CH_3} = 7.3 Hz, 3^1-H); 4.58 (1H, sextet, H_A in CH_2CH_3); 4.04-4.20 (13H, six CH_2CH_3, H_B in CH_2CH_3); 1.88, 1.84, 1.73, 1.71, 1.68, 1.66 (21H, all t, CH_2CH_3); 1.67 (3H, d, 3^1-CH_3); −3.15 and −4.27 ppm (4H, NH).

3^1,5^1-Cyclo-5^1-hydroxy-7,13,17-trimethyl-2,8,12,18-tetraethyl-21H,23H-porphin (V). PMR spectrum ($CDCl_3$): 10.08, 10.03, 10.00 (3H, all s, meso-H); 7.48 (1H, d, J_{CA} = 6.4 Hz, H_C); 4.57 (1H, dd, J_{AC} = 6.4, J_{AB} = 18.5 Hz, H_A); 3.80 (1H, d, J_{AB} = 18.5 Hz, H_B); 3.65, 3.61, 3.50 (9H, all s, ring CH_3); 4.3 and 3.99 (overlapped q, CH_2CH_3); 1.90, 1.88, 1.85, 1.84 (all t, CH_2CH_3); −3.0 ppm (NH). Mass spectrum, m/z (%): 504 (M^+, 60), 490 (80), and 488 (100).

3^1,5^1-Cyclo-5^1-hydroxy-3^1-ethyl-2,7,8,12,13,17,18-heptapropyl-21H,23H-porphin (VI). PMR spectrum (in $CDCl_3$): 10.14, 10.10, 10.03 (3H, all s, meso-H); 7.31 (1H, s, 5^1-H); 4.37 ppm (1H, dd, 3^1-H).

3^1,5^1-Cyclo-3^1-methyl-5^1-acetoxy-2,7,8,12,13,17,18-heptaethyl-21H,23H-porphin (VIII) and 3^1,5^1-Cyclo-3^1-methyl-5^1-ethoxy-2,7,8,12,13,17,18-heptaethyl-21H,23H-porphin (IX). A solution of 20 mg of porphyrin II in a mixture of 5 ml of pyridine and 0.5 ml of Ac_2O was allowed to stand for 24 h, after which it was poured into 50 ml of water, and the flocculent precipitate was removed by filtration with a paper filter washed with hot water, and dried to give porphyrin VIII, which was dissolved in chloroform–alcohol (98:2) and filtered through a layer of silica gel (2 × 20 cm). The principal fraction was evaporated to give 11 mg (52%) of porphyrin IX. Found from the high-resolution mass spectrum: M^+ 590.3993. $C_{39}H_{50}N_4O$. Calculated: M^+ 590.3980. PMR spectrum (in $CDCl_3$): 10.13, 10.09, 10.02 (3H, all s, meso-H); 7.05 (1H, s, 5^1-H); 4.58 (1H, q, 3^1-H); 3.63 (q); 1.29 (t, OC_2H_5); 2.05 (3H, d, J = 7.3 Hz, 3^1-CH_3); −2.96 and −3.79 ppm (2H, NH). PMR spectrum of porphyrin VIII (in $CDCl_3$): 10.15, 10.12, 10.04 (3H, all s, meso-H); 8.11 (1H, s, 5^1-H); 4.45 (1H, q, 3^1-H); 2.24 (3H, s, $COCH_3$); 2.10 (3H, d, 3^1-CH_3); −2.94 and −3.80 ppm (2H, NH).

3^1,5^1-Cyclo-5^1-methylene-2,7,8,12,13,17,18-heptaethyl-21H,23H-porphin (XII). A solution of 260 mg (0.463 mmole) of porphyrin II in 20 ml of CF_3COOH was heated at a bath temperature of 70°C for 1.5 h, after which it was poured into 250 ml of water, and the aqueous mixture was neutralized with ammonium hydroxide. The substance was extracted with chloroform and chromatographed with activity IV aluminum oxide, the principal fraction was evaporated, and the residue was crystallized from chloroform–methanol to give 241 mg (89%) of porphyrin XII in the form of well-formed prisms. PMR spectrum (in $CDCl_3$): 10.00, 9.96, 9.94 (3H, all s, meso-H); 6.30 and 5.89 (2H, two s, 3^1-CH_2); 5.95 (2H, s, 5^1-CH_2); −2.78 and −3.58 ppm (2H, NH). PMR spectrum (in $CDCl_3$ + 1% CF_3COOH): 10.51, 10.50, 10.43 (3H, all s, meso-H); 6.63 and 6.27 (2H, two s, 3^1-$=CH_2$); 6.11 (2H, s, 5^1-CH_2); −3.23 and −4.55 ppm (NH).

Nickel Complex (XIII) of Porphyrin XII. This complex was obtained in quantitative yield by heating porphyrin XII and nickel acetate in chloroform–methanol by the standard method. The product decomposed on silica gel during drying of the solvent. PMR spectrum (in $CDCl_3$): 9.84 (1H, s, meso-H); 9.73 (2H, s, meso-H); 6.22 and 5.82 (2H, two s, 3^1-$=CH_2$); 5.74 (2H, s, 5^1-CH_2).

Copper (XIV) and Zinc (XV) Complexes of Porphyrin XII. These complexes were similarly obtained and were unstable in air during chromatography on silica gel by TLC. They were stable in the crystalline state.

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