SELECTIVE OXIDATION OF PORPHYRINS WITH A CYCLOPENTANE RING ON THE SURFACE OF SILICA GEL

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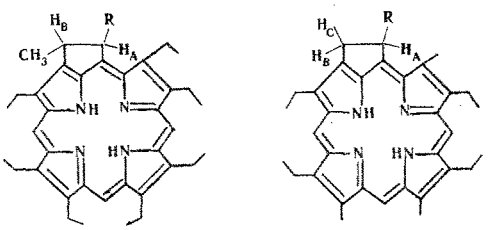
It has recently [1] been noted that it is desirable to use Al_2O_3 for the chromatographic purification of deoxophylloerythroetioporphyrin, since a certain amount of decomposition of the porphyrins with a cyclopentane ring that are adsorbed on the surface of silica gel are oxidized by air oxygen to porphyrins that contain a hydroxy group in the exocyclic ring only when the silica gel is dried to remove the solvent. Thus a new polar porphyrin with the composition $C_{37}H_{46}N_4O$, to which we assigned the $3^1,5^1$-cyclo-3^1-methyl-5^1-hydroxy-2,7,8,12,13,17,18-heptaethyl-21H,23H-porphyrin structure (II) on the basis of an analysis of the data from the IR, PMR, and mass spectra, is formed in 30-35% yield after repeated chromatography of porphyrin I after drying of the silica gel to remove the solvent. Mass spectrum, m/z (relative intensity, %): 562 (M^+, 100), 546 (48), and 544 ($M - H_2O$, 78). UV spectrum (in chloroform), λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 402 (289), 502 (14.6), 537 (6.0), 565 (7.1), and 618 (8.15). IR spectrum: ν_{OH} 3570 cm^{-1} ($CHCl_3$). It follows from the PMR spectral data (250 MHz, $CDCl_3$) that porphyrin II is primarily a mixture of conformers of the trans isomer, since the signal from H_A at 7.18 ppm shows up in the form of a singlet with $J_{AB} < 1$ Hz.

After preparative treatment of porphyrin II by air oxidation of 200 mg of porphyrin I adsorbed on 200 g of silica gel (5 × 40, Czechoslovakian SSR) and chromatography with a column filled with Al_2O_3 (activity II) in a CCl_4-CHCl_3–ether system (20:40:15), we also isolated a somewhat more labile mixture of conformers of the cis isomer of II (~5-7% of the total amount of hydroxyporphyrin), in the PMR spectrum of which in solution in $CDCl_3+CD_3OD$ we observed a doublet from H_A at 7.60 ppm with $J_{AB}=5.7$ Hz.



I, II III, IV

I, III R=H; II, IV R=OH

Porphyrins with an unsubstituted cyclopentane ring are also oxidized under similar conditions. For example, a deoxophylloerythroetioporphyrin isomer (III) is oxidized to porphyrin IV in 45-50% yield. Mass spectrum, m/z (relative intensity, %): 506 (M^+, 80), 490 (90), and 488 (100). UV spectrum (in chloroform), λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 401 (225), 502 (14.7), 537 (6.0), 565 (7.15), and 617 (7.25). IR spectrum (KBr pellet): ν_{OH} 3370 cm^{-1}. PMR spectrum ($CDCl_3$): δ 10.03, 10.08, and 9.99 (all s, meso-H); 7.48 (d, $J_{AB}=6.4$ Hz, H_A); 4.57 (dd, $J_{BC}=17.1$ Hz, H_B); 3.80 (d, H_C); 3.65, 3.61, and 3.50 ppm (all s, ring CH_3); −3.0 ppm (2H, NH).

The observed phenomenon of oxidation of porphyrins in the cyclopentane ring is consequently general in character and must be taken into account in the isolation and investigation of the structure of "geological porphyrins."

LITERATURE CITED

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