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STRUCTURE DETERMINATION OF METHYLPHEOPHORBIDE A

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The investigated Methylpheophorbide a is a derivative of natural Chlorophyll a, containing the complete and unchanged ringsystem of Chlorophyll with inclusion of the isocyclic five membered ring fused to ring III. Methylpheophorbide a was prepared from Pheophytine (1), a partial reduction product of Chlorophyll. The preparation of single crystals for X-ray work occured from a 1:1 solution of Methanol-Acetone at 30° C.

Crystallographic data: Space group $P2_1$, Z = 2; a = 7,37 Å, b = 28,69 Å, c = 8,04 A, β = 110,92°. The asymmetric unit contains one molecule of Methylpheophorbide a, $C_{36}N_4O_5H_{38}$. 2282 independent reflections were measured with $CuK\alpha$ -radiation using a Siemens single crystal diffractometer ($\Theta \leqslant 60°$, $\Theta/2\Theta$ - scan, 5-point measuring procedure). The structure was solved using direct methods for phase determination. The computer programs used have been described earlier (2). Six starting reflections were given phases to begin the cyclic phase determination in a multisolution process. The correct structure was found in a Fourier synthesis phased with the 300 strongest reflections. The statistical criteria for phase determination did not indicate this correct solution as the best one. Anisotropic refinement of carbon, nitrogen and oxygen yielded an R-factor of 7. 7 %. Inclusion of 34 hydrogen atoms (out of 38) reduced the R-factor to 6, 2 %. The calculated bond distances are shown in fig. 1, the thermal motion is indicated in fig. 3. A Shoemaker-Trueblood analysis for rigid body motion revealed only the ringsystem as relative stable configuration. Ring IV is heavily distorted, a fact already observed earlier in phyllochlorine ester (3). The sterical conformation at carbon atoms 7 and 8 is also equivalent to this structure where the 7-8 axial-axial transconfiguration has been described for the first time. Fig. 2 shows hydrogen positions for ring III found in a difference Fourier synthesis.

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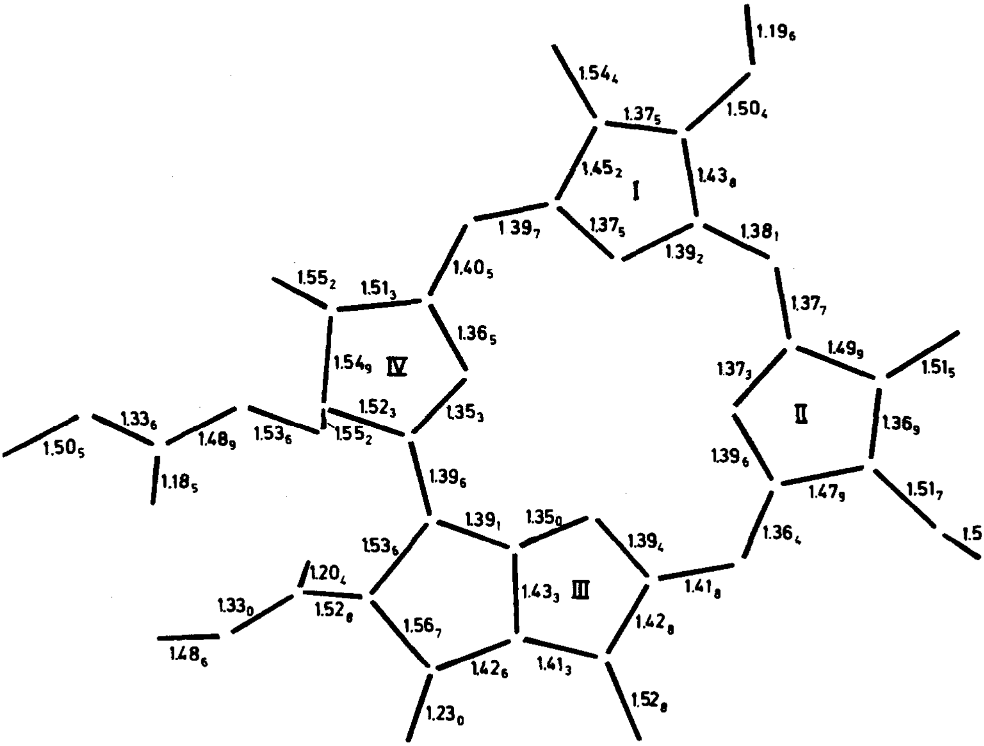

Fig. 1 Bond distances in Methylpheophorbide a at a refinement stage of R = 6,2 %

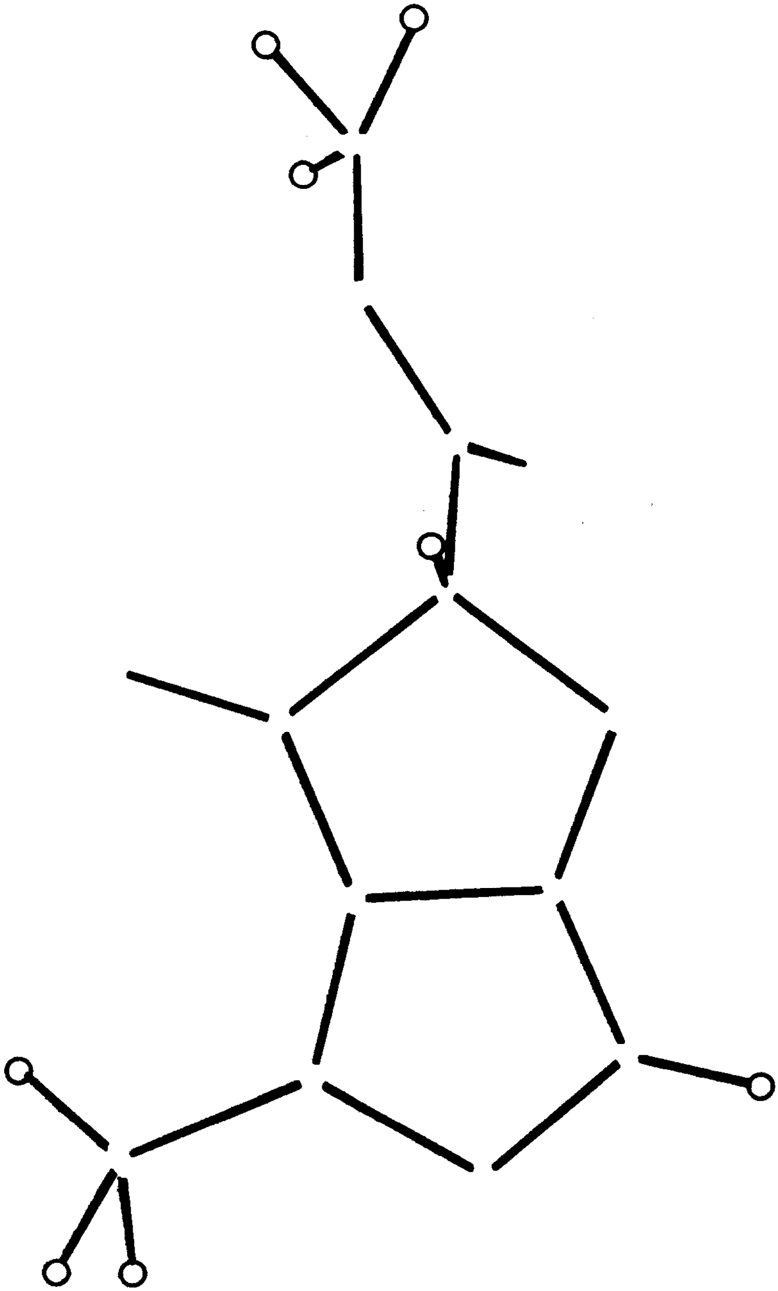

Fig. 2 Hydrogen positions at ring III after a difference Fourier synthesis (circles indicate hydrogens)

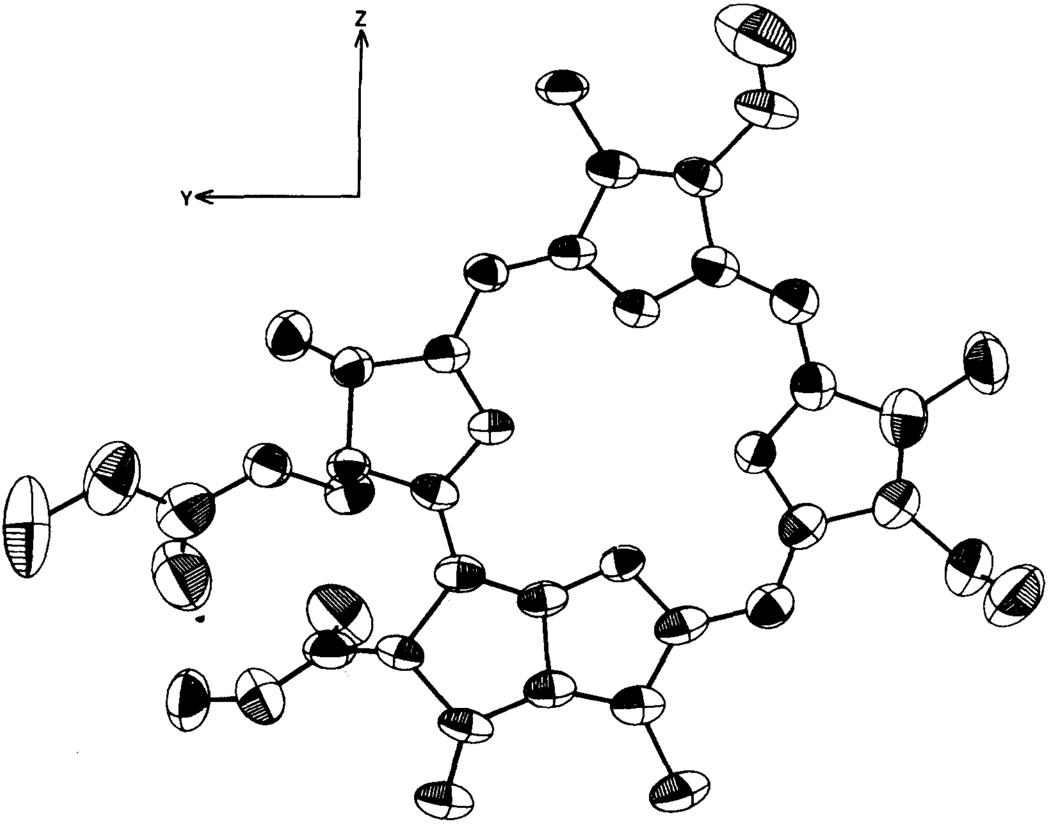

Fig. 3 y-z-projection of Methylpheophorbide a with thermal ellipsoids (50 % probability that the atom occurs within the ellipsoid)

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