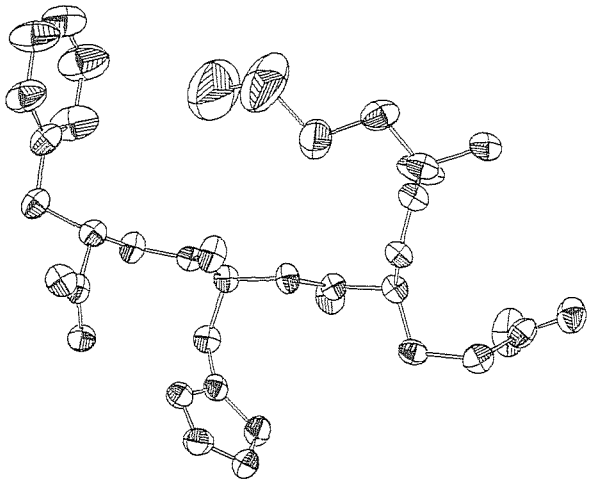
03.2-15 THE CRYSTAL STRUCTURES OF ACTH 4-10 AND ACTH 4-7. By G. Admiraal, A.B. Verweij and Aafje Vos, Laboratorium voor Chemische Fysica, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands.

The backbone structure of ACTH 4-10 could be determined by visual inspection of the Patterson synthesis and extension of the fragment found by the program DIRDIF (P.T. Beurskens et al, Nijmegen, The Netherlands) This structure has been presented at earlier conferences (Admiraal, Verweij and Vos, Abstracts Sixth European Crystallographic Meeting, Barcelona, Spain, 5A52).

The linear polypeptide ACTH 4-7 (Met-Glu-His-Phe), molecular formula $C_{25}H_{34}N_6O_7S$. H_2O crystallizes in the monoclinic space group C2 with a= 23.333(6), b= 5.4741(11) $_{23}$c= 24.783(5)Å, β= 115.03(2)°, Z= 4, d(calc) = 1.31 g.cm^{-3}. The structure determination proved to be difficult. Both MULTAN and symbolic addition by the program SIMPEL (H. Schenk et al., Amsterdam, The Netherlands) failed to give a solution. Reliable peaks corresponding with S---S distances were not found in (sharpened) Patterson syntheses. Patterson search for a dipeptide fragment (C_α-C(=O)-N-C_α-C(=O)-N-C_α) for various values of the torsion angles ∅ = C-N-C_α-C and ψ = N-C_α-C-N gave by far the best fit for ∅ = -90 and ψ =-33°. With this fragment as starting point the structure was solved by DIRDIF. Anisotropic refinement gave R = 5.8%.

The structure of the molecule is shown in the figure. At C_α(His) the conformation of the peptide backbone is extended (∅ = -172, ψ = 171°) and at the other C_α atoms there are helix type bends. The Met and Phe groups show disorder. Difference Fouriers revealed peaks for all H atoms, indicating that the NH_2 and the His group are protonated. The CO_2 group of Glu is hydrogen bonded to NH_3^+ via a water molecule. No further solvent molecules were discovered in the difference maps.

Successive molecules in the crystal are linked by hydrogen bonds along b and c. At (0yz) successive layers of molecules interact via hydrogen bonds and at (½yz) by hydrophobic forces. The conformation of the molecule will be compared with that of other tetrapeptides and the hydrogen bonds in the crystal will be described in more detail.



03.2-16 THE CRYSTAL AND MOLECULAR STRUCTURE OF THE SIDEROPHORE FERRIC PSEUDOBACTIN. By M. B. Hossain, C. L. Barnes, D. van der Helm, M. Teintze and J. Leong. Chemistry Departments Oklahoma University, Norman, OK, 73019, USA and University of California, San Diego, La Jolla, CA, 92093, USA.

Previously it was shown[1,2] that pseudobactin, the siderophore of a specific plant growth-promoting Pseudomonas strain, is able to mimic the plant growth enhancement of its producer.

Ferric pseudobactin ($C_{42}H_{55}N_{12}O_{16}Fe$), crystallizes in space group I2, a = 29.006(23), b = 14.511(13), c = 28.791(21), β = 96.05(5), with 2 molecules and 26 water molecules in the asymmetric unit. All 12946 unique data (8989 with I > 2 σ(I)) with 2θ ≤ 53° using MoKᾱ, were taken at -135°C. Final R-factor is 0.08.

The structure consists of a linear hexapeptide, L-Lys-D-threo-β-OH-Asp-L-Ala-D-allo-Thr-L-Ala-D-N^δ(OH)-Orn, in which the ornithine is cyclized, and the N^ε-amino group of lysine is bonded by an amide group to a large quinoline derivative. The three groups forming the iron chelation are the cyclized ornithine, the β-OH-aspartic acid and the ortho di-hydroxy group on the quinoline moiety. The latter two have not been observed before in siderophores and establishes the compound as a member of a new family. This is, as well, the first molecular structure for a siderophore obtained from Pseudomonas species. In the crystal structure a dimer is formed, which constitutes the asymmetric unit. The molecules in the dimer are related by a pseudo 2-fold axis. The dimer may be important for the specificity of the compound.

1) J. W. Kloepper, J. Leong, M. Teintze and M. N. Schroth, Nature 286, 885-886 (1980).
2) J. W. Kloepper, J. Leong, M. Teintze and M. N. Schroth, Current Microbiol. 4, 317-320 (1980).

03.2-17 THE X-RAY STRUCTURE OF AN UNDECAPEPTIDE HELIX-MODEL OF ALAMETHICIN: α- OR 3_{10}-HELIX? By T.Butters, P.Hütter, G.Jung, N.Pauls, H.Schmitt and W.Winter, Institut für Organische Chemie der Universität, 74 Tübingen; G.M.Sheldrick, Institut für Anorganische Chemie der Universität, 34 Göttingen; FRG.

The membrane exciting peptide antibiotics alamethicin, suzukacillin and trichotoxin include N-terminal helices, according to their 13-C-NMR and CD-spectra. All data have been interpreted in terms of α-helices, but some authors have argued, that these peptides, containing the unusual amino acid 2-methylalanine (=Aib), may show 3_{10}-helical N-termini, because short peptides with Aib-residues crystallize with incipient 3_{10}-helix conformations.

We have synthesized and crystallized the following model of the alamethicin N-terminus:

Boc-L-Ala-Aib-L-Ala-Aib-L-Ala-L-Glu(OBzl)-L-Ala-Aib-L-Ala-Aib-L-Ala-OMe **1**

1 crystallizes in $P2_1$, Z=2 and 6 dichloromethane solvent molecules. The solution of the phase problem by direct methods proved to be very difficult (90 nonhydrogen atoms), but was recently achieved by a novel random-phases + E-Fourier recycling procedure. The current R-value in isotropic refinement is 0.128 for 4327 observations with $F \geq 3\sigma(F)$.
Nine of the eleven amino acids are part of a α-helix, only the last two C-terminal amino acids form a β-turn.