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Structures were solved by direct methods (MULTAN), all data collected on an Enraf-Nonius CAD-4 diffractometer, graphite monochromated CuKα radiation. Crystal data for (I): P(r), a = 1.450 Mg m⁻³. M.W. = 298.3, Z = 2(C₇H₁₂O₅), a = 4.128(1), b = 13.163(1), c = 65.30(1), β = 96.54(1), R = 0.36 refl. > 3σ(I), final R = 0.65%, unit weight.

\[(\text{I}): \text{P}_2\text{O}_7, \text{D}_4 = 1.405 \text{ Mg m}^{-3}, \text{Z} = 4(\text{C}_6\text{H}_4\text{O}_5), a = 8.442(1), b = 25.129(1), c = 6.717(1), \beta = 98.18(1), 188 \text{ refl.} > 3\sigma(I), \text{R} = 0.36\%\]

\[(\text{II}): \text{P}_2\text{O}_4, \text{D}_x = 1.405 \text{ Mg m}^{-3}, \text{Z} = 4(\text{C}_6\text{H}_4\text{O}_5), a = 8.442(1), b = 25.129(1), c = 6.717(1), \beta = 98.18(1), 188 \text{ refl.} > 3\sigma(I), \text{R} = 0.36\%\]

\[(\text{III}): \text{P}_2\text{O}_6, \text{D}_z = 1.425 \text{ Mg m}^{-3}, \text{Z} = 4(\text{C}_6\text{H}_4\text{O}_5), a = 8.278(1), b = 25.328(1), c = 5.517(1), \beta = 95.91(1), 124 \text{ refl.} > 3\sigma(I), \text{R} = 0.60\%\]

03.1.9 CRYSTAL STRUCTURE OF THE HYDROGEN OXALATE OF FORMAMIDOXIME. By I. Jørgensen, Royal Danish School of Pharmacy, Dept. of Chemistry 5C, Universts setsparken 2, DK-2100 Copenhagen, Denmark.

Formamidoxime, H₂N-CH=N-OH, inhibits DNA synthesis in cells and bacteria by the same mechanism as hydroxamates. A subunit of this enzyme contains the active site a tyrosine free radical, which is involved in the bioreduction process. This free radical group is destroyed (reduced) by hydroxyurea analogues, and the most important parameters for inhibitory effect of the compounds are the total-electronization process of the coenzyme. The compound is one-electron oxidizable together with the myeloperoxidase. From these studies and X-ray crys tallyllographic studies on the crystals of formamidoxime, H₂N-CH=N-OH, we have obtained a crystalline complex of formamidoxime with metal ions. The complex contains 3 sodium ions to two hexapeptides. One sodium ion is sandwiched between two peptides, and the other sodium ion is coordinated by six glycyl carbonyl groups. The hexapeptide adopts an asymmetric structure with one of the peptide links trans, and the other peptide links cis. The crystal structure of this complex is presented in detail in the paper. We have obtained a variety of metal ion complexes with varying stoichiometries.
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the center of the peptide molecule. This structure might represent one of the steps involved in the shuttle mechanism of ion transport where the ion is captured at one end of a channel and transported to the other end by the conformational change that allows the ion to be released and recaptured.

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The diastereomeric cyclic octaepetides, cyclo-(Ala-Gly-L-Pro-L-Phe)2 were synthesized by Kopple et al. in order to produce cyclic octaepetide backbones of C2 symmetry. We report here the conformations of two cyclic octaepetides, cyclo-(D-ALA-Gly-L-Pro-L-Phe) and cyclo-(O-ALA-Gly-L-Pro-D-Phe) as determined by x-ray crystallographic techniques.

The octaepetides contain two β-turns, encompassing L-Pro-Phe residues, connected by straight stretches of D-Ala-Gly residues. As expected in the cyclo-(D-ALA-Gly-L-Pro-L-Phe) there are two type I β-turns while in cyclo-(O-ALA-Gly-L-Pro-D-Phe) there are two type II β-turns. The peptide links in both the structures are trans with the non-planarity parameter w deviating as much as 9°. In the crystalline state both the peptides show an approximate two fold symmetry.

When crystallized from a solution containing sodium thiocyanate the octaepetide cyclo-(O-ALA-Gly-L-Pro-L-Phe) showed a change in the backbone conformation. The approximate 2-fold symmetry observed in the absence of sodium thiocyanate is destroyed in the straight stretches of D-Ala-Gly. The major differences in the two structures occur in the ψ of D-Ala (changes from 179° to 30°) and φ of Gly (changes from 124° to 70°). When compared with the structure of cyclo-(O-ALA-Gly-L-Pro-D-Phe), the backbone torsion angles of one straight stretch from the link with D-Phe-D-Ala to the link Gly-L-Pro compares well while the other stretch compares well with the 2-fold symmetric structure of cyclo-(Ala-Gly-L-Pro-L-Phe). All the peptide links are trans with the non-planarity parameter w between Gly and L-Pro varying by 13°.

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The disaccharide unit α-D-galactopyranosyl-(1→4)-β-galactopyranose (β-galabiose) is an integral part of several naturally occurring glycolipids present at mammalian cell surfaces. It constitutes for example the terminal portion of blood group P antigens and an internal part of the Forssman antigen. Uropathogenic E. coli bacteria use this disaccharide unit as a specific receptor in adhesion to epithelial cells of the human urinary tract (1,2). The present X-ray structure determination of galabiose reveals the conformation about the Galα = 4Gal glycosidic linkage (figure below). The crystals (2) are orthorhombic, space group P212121 with a = 5.826(1), b = 13.904(3) and c = 17.772(4) Å; conventional R = 0.063 for 2758 observed reflections.

Both C–O bonds of the glycosidic linkage are axial with a ψ angle (Cl-Cl-C1'-C1) of 117.5°. The φ and ψ torsion angles are H1-C1-Cl-C1' = -18.2° and H4'-Cl'-C1'-C1 = 34.3°, the corresponding φ5 and φ1' angles are 05-C5-C1-C1' = 98.1(2)° and C3'-C4'-C1'-C1 = -81.9(3)°. The virtual torsion angle between the anomeric and aglyconic hydrogen atoms (H1 and H4') is 18.7°. The conformation is stabilized by an O5'-O5 intramolecular hydrogen bond of 2.787(3) Å with the C3'-trans-gauche-C4' angles of 101.6(1) and 120.7(2)° respectively. The geometry of the Galα = 4Gal linkage, with an angle 116.5° between the least-squares planes through the six-rings, causes a characteristic folding of the Forssman antigen.

References