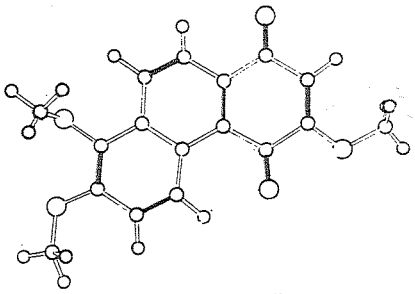
structures were solved by direct methods (MULTAN), all data collected on an Enraf-Nonius CAD-4 diffractometer, graphite monochromated CuKα radiation. Crystal data for (I): $P\bar{1}$, D_x= 1.450 Mg m^{-3}, M.W.=298.3, Z=2($C_{17}H_{14}O_5$), a= 4.128(1), b=13.163(1), c=13.918(1) Å, α=65.30 (1), β=84.54(1), γ=88.80(1)°, 940 refl.>3σ(I), final R=8.65%, unit weight.



(II): $P2_1/c$, D_x=1.405 Mg m^{-3}, Z=4($C_{17}H_{14}O_5$), a=8.442(1), b=25.129(1), c=6.717(1) Å, β = 98.18(1)°, 1881 refl. > 3σ(I).
(III): $P2_1/c$, D_x=1.425 Mg m^{-3}, Z=4($C_{16}H_{12}O_4$), a=8.278(1), b=23.328(1), c=6.511(1) Å, β = 95.91(1)°, 1241 refl. > 3σ(I), final R=6.01%.
(IV): $P\bar{1}$, D_x=1.472 Mg m^{-3}, Z=2($C_{16}H_{12}O_5$), a= 7.221(1), b=10.071(1), c=10.474(1)Å, α=64.46(1), β=68.97(1), γ=80.85(1)°, 1507 reflections with I > 3σ(I).

Structural details of cypripedin and the synthetic compounds and the results of their allergenicity tests will be presented.

03.1–9 CRYSTAL STRUCTURE OF THE HYDROGEN OXALATE OF FORMAMIDOXIME. By I. Kjøller Larsen, Royal Danish School of Pharmacy, Dept. of Chemistry BC, Universitetsparken 2, DK-2100 Copenhagen, Denmark.

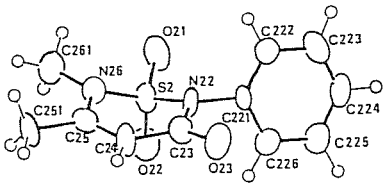
Formamidoxime, H_2N-CH=N-OH, inhibits DNA synthesis in cells and bacteria by the same mechanism as hydroxyurea, i.e. by inhibition of the enzyme ribonucleotide reductase. A subunit of this enzyme contains at the active site a tyrosine free radical, which is involved in the bioreduction process. This free radical group is destroyed (reduced) by hydroxyurea analogues, and the most important parameters for inhibitory effect of the compounds are the one-electron oxidizability together with the planarity of the molecules (Kjøller Larsen, I., Sjöberg, B.-M. and Thelander, L. Eur. J. Biochem. (1982) 125, 75).

Formamidoxime has been proposed to exist in equilibrium between the tautomers H_2N-CH=N-OH ⇌ HN=CH-NH-OH in solution, but crystallizes in the amidoxime form, and ab initio molecular-orbital studies (HF/STO-3G) indicate, that this form is much more stable than the hydroxyamidine form (Jeffrey, G.A., Ruble, J.R., McMullan, R.K., DeFrees, D.J. and Pople, J.A. Acta Cryst. (1981) B37, 1381).

The structure determination of the salt of formamidoxime was undertaken in order to establish the tautomer form of the protonated molecule ($H_3\overset{+}{N}$-CH=N-OH or $H_2\overset{+}{N}$=CH-NH-OH). Low temperature data of good quality were used, and the structure refined to an R-value of 0.028. The protonated molecules (two per asymmetric unit) are on the hydroxyamidine form, $H_2\overset{+}{N}$=CH-NH-OH, and the structure is intensively hydrogen bonded. The crystals are very unstable and undergo solid state transformations into other crystalline forms, all with a short needle axis of about 3.5 Å.

03.1–10 2-PHENYL-3-ONE-5,6-DIMETHYL-1,2,6-THIADIAZINE 1,1-DIOXIDE. By C. Rodellas, M. Martinez-Ripoll and S. Garcia-Blanco, Dept. Rayos X, Inst. Rocasolano, Serrano 119, Madrid-6, Spain.

The title compound belongs to a series of analogues of pyrazoles with potencial analgesic and antiinflamatory properties (J. Elguero et al., J. Org. Chem. 1982, 47, 536). A knowledge of the three-dimensional structures of these drug molecules, together with the associated changes in the molecular geometry may give a better understanding of the molecular mechanism of their action.
C11 O3 N2 S H12, orthorhombic, $Pna2_1$, Z=8, a= 22.824(3), b=5.626(2), c=17.6968(7) Å, V=2272(3) Å^3, Dc=1.47 g.cm-3, μ(CuKα)=24.9 cm-1. R=0.038, wR=0.068 for 869 observed reflexions.
There are two crystallographically independent molecules. The figure shows one of them. In both cases the thiadiazine ring is envelope conformated with the S atom at the flap, but deviated in opposite sense in one molecule respect to the other.



03.1–11 METAL ION COMPLEXES OF CYCLO-(L-PRO-GLY)$_3$. A SYNTHETIC CYCLIC HEXAPEPTIDE. G. Kartha and K.K. Bhandary, Biophysics Department, Roswell Park Memorial Institute, Buffalo, New York 14263, USA.

The conformational interconversion of cyclo-(L-prolyl-glycyl)$_3$ (cPG3) in different media and when complexed with alkali and alkaline earth metal ions have been studied by NMR[1]. From these studies and X-ray crystallographic studies on the crystals of cPG3 obtained from polar solvents it has been established[2] that the hexapeptide assumes an asymmetric structure with one of the peptide links cis. Our earlier studies[2-3] on the metal complexes of cPG3 have shown that in the crystalline state the hexapeptide adopts a symmetric structure with all peptide links trans. In all the complexes of cPG3 with metal ions studied so far the peptide has an approximate or exact three-fold symmetry. We have obtained a variety of metal ion complexes with varying stoichiometries[3].

We now have obtained a crystalline complex of cPG3 with sodium ion. The complex contains 3 sodium ions to two hexapeptides. One sodium ion is sandwiched between two peptides as in the case of the complexes of Ca^{2+} ion and Ca^{2+} & Na^+ ions with cPG3 where Ca^{2+} ion is sandwiched between the two peptide molecules. The sandwiched Na^+ ion is coordinated by six glycyl carbonyls at an average Na^+-O distance of 2.369(8)A. The prolyl carbonyls of the two hexapeptides on either side of the sandwich are coordinated to two sodium ions which lie on either side of the sandwich. An interesting feature of this complex is that the sodium ions on either side of the sandwich have the glycyl carbonyls also "coordinated" to them at an average distance of 2.7A. This distance is about 0.4Å shorter than that found for sodium ions in the complex of cPG3 with Ca^{2+} & Na^+. This shows a clear movement of the sodium ion towards

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.

Work supported by NIH GM 22490 grant and State of New York.

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03.1–12 CONFORMATION OF DIASTEREOISOMERIC OCTAPEPTIDES, CYCLO-(D-ALA-GLY-L-PRO-L-PHE)$_2$ AND CYCLO-(D-ALA-GLY-L-PRO-D-PHE)$_2$. K.K. Bhandary and G. Kartha, Biophysics Department, Roswell Park Memorial Institute, Buffalo, New York 14263, USA and K.D. Kopple Department of Chemistry, Illinois Institute of Technology, Chicago, Ilinois, USA 60616.

The diastereomeric cyclic octapeptides, cyclo-(Ala-Gly-L-Pro-Phe)$_2$, were synthesized by Kopple et al.[1] in order to produce cyclic octapeptide backbones of C_2 symmetry. We report here the conformations of two cyclic octapeptides, cyclo-(D-Ala-Gly-L-Pro-L-Phe)$_2$ and cyclo-(D-Ala-Gly-L-Pro-D-Phe)$_2$ as determined by x-ray crystallographic techniques.

The octapeptides 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)$_2$ there are two type I β-turns while in cyclo-(D-Ala-Gly-L-Pro-D-Phe)$_2$ there are two type II β-turns. The peptide links in both the structures are trans with the non-planarity parameter ω 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 octapeptide cyclo-(D-Ala-Gly-L-Pro-L-Phe)$_2$ shows 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 stretches 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-(D-Ala-Gly-L-Pro-D-Phe)$_2$, 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 c(D-Ala-Gly-L-Pro-L-Phe)$_2$. All the peptide links are trans with the non-planarity parameter ω between Gly and L-Pro varying by 13°.

Work supported by GM 22490 and State of New York.

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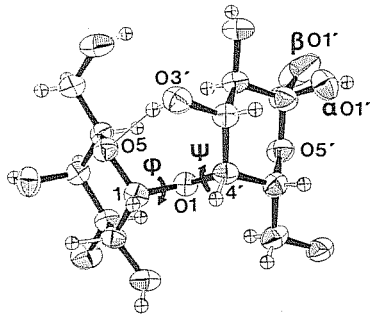
03.1–13 CRYSTAL STRUCTURE OF GALABIOSE: AN INTERNAL PART OF THE FORSSMAN ANTIGEN. By G. Svensson, J. Albertsson, C. Svensson, Inorganic Chemistry 2 and G. Magnusson, Organic Chemistry 2, Chemical Center, University of Lund, P.O.Box 740, S-220 07 Lund, Sweden

The disaccharide unit α-D-galactopyranosyl-(1→4)-β-D-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 Galα1 → 4Gal glycosidic linkage (figure below). The crystals (3) are orthorhombic, space group $P2_12_12_1$ 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 τ angle (C1-O1-C4') of 117.5°. The ϕ^H and ψ^H torsion angles are H1-C1-O1-C4' = -18.9° and H4'-C4'-O1-C1 = 34.9°; the corresponding ϕ^{O5} and $\psi^{C3'}$ angles are O5-C1-O1-C4' = 98.1(2)° and C3'-C4'-O1-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 O3'···O5 intramolecular hydrogen bond of 2.787(3) Å with the C3'-O3'···O5 and C5-O5···O3' angles 101.6(1) and 120.7(2)° respectively. The geometry of the Galα1 → 4Gal linkage, with an angle 116.5° between the least-squares planes through the six-rings, causes a characteristic folding of the Forssman antigen.



Galabiose

The structure is disordered, containing about equal amounts of α (57 %) and β-galabiose (43 %). Further, the C6-OH groups exist both in *gauche-trans* (≈70 %) and in *trans-gauche* (≈30 %) conformation. The crystal packing is governed by hydrogen bonds engaging all oxygen atoms except the intramolecular acceptor O5 and the glycosidic O1.

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