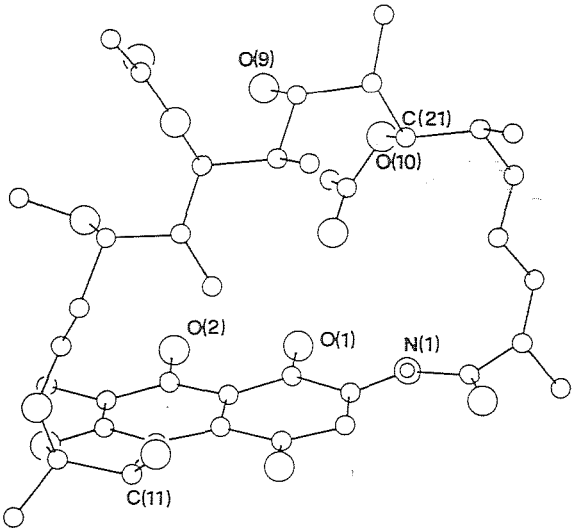
Crystal Data: S.G. P 2_1, a=11.860, b=9.139, c=20.423 Å, β=90.72° ,$C_{39}H_{49}NO_{13}.CH_3OH.H_2O$, F.W.=789.85, Dc=1.20 g.cm^{-3} for Z=2; Mo-K_α radiation.



In spite of the chemical substitution on position 21 of the ansa-chain and the reduction on position 11 of the chromophore rings, the conformation of the molecule is comparable with that of the other rifamycins. Further conformational and structural features will be discussed.

03.1–7 CAN THE CLATHRATES OF BINAPHTYL-DICARBOXYLIC ACID SERVE AS STRUCTURAL MODELS FOR THE RELATIONS IN THE ACTIVE SITE OF NATIVE SERINE PROTEASES?

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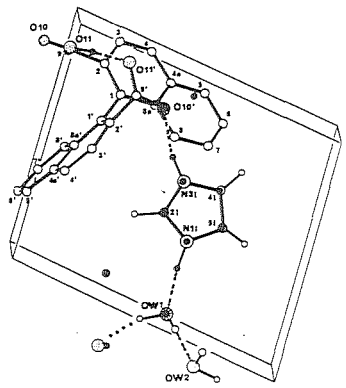
THE USE OF INCLUSION COMPOUNDS AS MODEL ENZYMES IS A RECOGNIZED APPROACH IN BIOORGANIC CHEMISTRY (Dugas,H., Penney,C. *Bioorganic Chemistry*, Springer, 1981). 1,1'-BINAPHTYL-2,2'-DICARBOXYLIC ACID (*BNDA*) HAS BEEN SHOWN TO ACT AS A VERSATILE COORDINATO-CLATHRATE HOST (Weber, *press*). THEREFORE WE ATTEMPTED TO GET COMPLEXES OF *BNDA* WITH *imidazole* BOTH IN AQUEOUS AND WATER-FREE MEDIA. THE STRUCTURE OF THE CRYSTALS OBTAINED FROM AN AQUEOUS SOLUTION (*Figure*) SHOWED SIMILARITY BOTH IN FORMAL STOICHIOMETRY (*BNDA:imidazole:2H$_2$O*) AND SPATIAL ARRANGEMENT (Δ-0.3 Å FOR SEVEN FITTED ATOMS) OF THE FUNCTIONS CORRESPONDING TO *Asp102, His57 and 2 internal water* FOUND IN THE NATIVE CRYSTALS OF *SGPA* (James,M.N.G., Sielecki,A., 1983, *Private communication*). A FURTHER POINT OF THIS STUDY IS ALSO ILLUSTRATED IN THE *Figure*, WHICH SHOWS THAT A PROTON IS TRANSFERRED FROM THE *-COOH* MIMICKING THE ROLE OF *Asp102* TO THE IMIDAZOLE RING IMITATING *His57* IN THE PROTEIN. THE WHOLE PROCESS SEEMS TO BE ATTENUATED BY THE PRESENCE OF THE WATER MOLECULES WHICH FORM CHAINS OF HYDROGEN BONDS TO DIFFERENTLY CHARGED MOIETIES THUS RENDERING FURTHER (ELECTROSTATIC) RESEMBLANCE TO THE SITUATION FOUND IN MANY SERINE PROTEASES (Kossiakoff,A.A., Spencer,S.A., 1981, *Biochemistry*, 20, 6462-6474.



Csöregh, Stensland, Czugler, *J.Amer.Chem.Soc., in the*

Crystal data: Form (I) $C_{22}H_{13}O_4^-.C_3H_5N_2^+.2H_2O$, triclinic $P\bar{1}$, Z = 2, R = 0.028 for 1975 obs. data

Form (II) $C_{22}H_{14}O_4.C_3H_4N_2$, monoclinic $P2_1/c$, Z = 4, R = 0.096 for 924 obs. data.

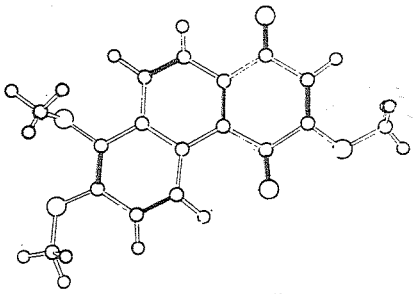
03.1–8 THE CRYSTAL STRUCTURES OF DI- AND TRIMETHOXYLATED 1,4-PHENANTHRENE QUINONES WITH DIFFERENT ALLERGENIC POTENCY.

By H.W. Schmalle and O.H. Jarchow, Mineralogisch-Petrographisches Institut der Universität, Grindelallee 48, 2000 Hamburg 13, FRG; B.M. Hausen, R. Werdin and K.H. Schulz, Abt. Allergologie der Universitäts-Hautklinik UKE, Martinistraße 52, 2000 Hamburg 20, FRG; and K. Krohn and U. Look, Institut für Organische Chemie der Technischen Universität, Schleinitzstraße, 3300 Braunschweig, FRG.

The first naturally occurring 1,4-phenanthrene quinone (PQ) with sensitizing potency, separated from the orchid Cypripedium calceolus L., has been identified by X-ray analysis and named cypripedin (2,8-Dimethoxy-7-hydroxy-1,4-PQ). Its two independent molecules showed slightly different conformations in the crystalline state (Schmalle & Hausen, Nat. Wiss. (1979) 66, 527). In order to study their sensitizing properties and cross-reactivities, a series of 12 cypripedin related PQs have been synthesized and used for sensitizing experiments in guinea pigs. As it was not possible to identify the position of one methoxy group in the quinonoid ring system by spectroscopic methods, X-ray structure determination has been performed for three PQs:

3,7,8-Trimethoxy-1,4-PQ (I)
3,5,8- " " (II)
3,8-Dimethoxy- " (III).
5,8- " -10-hydroxy-1,4-PQ (IV) was identified as a by-product of the quinone synthesis. All synthetic PQs are strong sensitizers if not being substituted in the C(2) and C(3) position of the quinonoid ring.The

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.

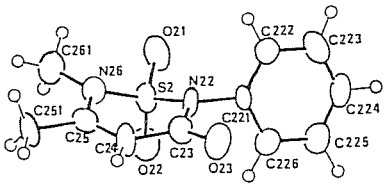
Formamidoxime, H_2N-CH=N-OH, inhibits DNA synthesis in cells and bacteria by the same mechanism as hydroxyurea, i.e. by inhibition of the enzyme ribonucleotide reductase. A subunit of this enzyme contains at the active site a tyrosine free radical, which is involved in the bioreduction process. This 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