While ethanesulphonate salts of antifolate drugs crystallise well and have been extensively studied, carbohydrate salts have not. Trimethyloxacetic (TA; R.C. Wachtman Jr., MSc Thesis, University of Virginia, 1971) is presented for comparison. Introduction of a polar group into the 5-substituent will perturb the consistency in distance should serve as a useful anchor point for model-building.

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03.3-21 STRUCTURE OF DIGITOXIGENIN BISDIGITOXOSIDE

Digitoxigenin digitoxoside recrystallised from ethyl acetate and hexane is orthorhombic, \( P2_12_12_1 \), \( a=3.31\) Å, \( b=14.310(2) \) Å, \( c=23.959(3) \) Å, \( V=3915\) Å\(^3\), \( Z=4\).

The structure was solved by multiple refinement methods and refined by block diagonal least-squares to an \( R \) index of 10.4%. An ORTEP sketch of the molecule is shown below. The 5’-ring has a 13a,14b-half-chair conformation.

The torsion angle \( \theta \) is -116°, \( C(21) \ldots O(14) \) distance is 2.943 Å. Unlike digoxin and digitoxigenin, digitoxoside is not planar and the ring oxygen of the adjacent sugar: this distance is 3.982 Å (longer than 2.265 Å in digitoxin). There is a disordered solvent, presumably a molecule of ethyl acetate; this solvent molecule along with the OH of the cardiac steroid and those of the sugars form H-bonds in stabilising the structure.

The crystal and molecular structure of Cinchoninium tetrachlorocuprate 1.5-hydrate, \( (C_{19}H_{24}N_2O)_{2}^+[CuCl_4]_{2}^{-} \cdot 1.5H_2O \). By J. Oleksyn and S. A. Hodorowicz, Faculty of Chemistry, Jagiellonian University, Krakow, Poland.

Cinchona alkaloids - metal ions interactions are important as factors which could modify processes undergoing in living organisms. In reaction of \( MCl_2 \), where \( M=\text{Zn}, \text{Cd}, \text{Hg} \) and \( \text{Cu} \), with cinchoninium chloride, \( \text{CuCl}_2 \), tetrachloro-salts of general formula: \( (\text{Cin})\text{Cl}^+\text{[MCl}_4\]^{-} \cdot nH_2O \) were obtained (Dyrek, Polish J. Chem. 1976 50, 2027). Preliminary crystallographic investigation showed that only the Cu\(^{2+} \) compound is not isomorphous with the others (Chojnacki, Oleksyn, Hodorowicz, Polish J. Chem. 1975 49, 429; Oleksyn, Stadnicka, Hodorowicz, ibid. 1976 50, 1645). To explain this we have undertaken the crystal structure determination, which was carried out for 4426 independent reflections (3335 with \( |F_o| \geq 3\sigma(F_o) \) measured on a CAD-4 diffractometer. The positions of Cu\(^{2+} \) ions were found with Patterson method, while those of other atoms were obtained from Fourier and difference Fourier synthesis. The current R value after anisotropic refinement of non-hydrogen atoms (513 parameters) with H atoms in fixed positions, is 0.077.

The main difference between this structure and the group of isomorphous structures of \( (\text{Cin})\text{Cl}^+\text{[MCl}_4\]^{-} \cdot nH_2O \), where \( \text{M} = \text{Cu}, \text{Zn} \) and \( n=2 \), are the packing conditions resulting from the fact that the asymmetric unit consists of 2 salt and 3 water molecules. The N and O atoms of \( \text{Cin}^+ \), Cl\(^- \) ions, and \( \text{H}_2\text{O} \) molecules form a complicated net of hydrogen bonds (10 bond kinds of length 2.72 - 3.31 Å). The geometry of \( [\text{CuCl}_4]^{-} \) tetrahedrons and \( \text{Cin}^+ \) cations is comparable to that described for Cd salt (Oleksyn, Stadnicka, Hodorowicz, Acta Cryst. 1979 B34, 811).

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