

Preliminary communication

An X-ray crystallographic study of an aldotriouronic acid trihydrate: *O*-(4-*O*-methyl- α -D-glucopyranosyluronic acid)-(1 \rightarrow 2)-*O*- β -D-xylopyranosyl-(1 \rightarrow 4)-D-xylopyranose trihydrate

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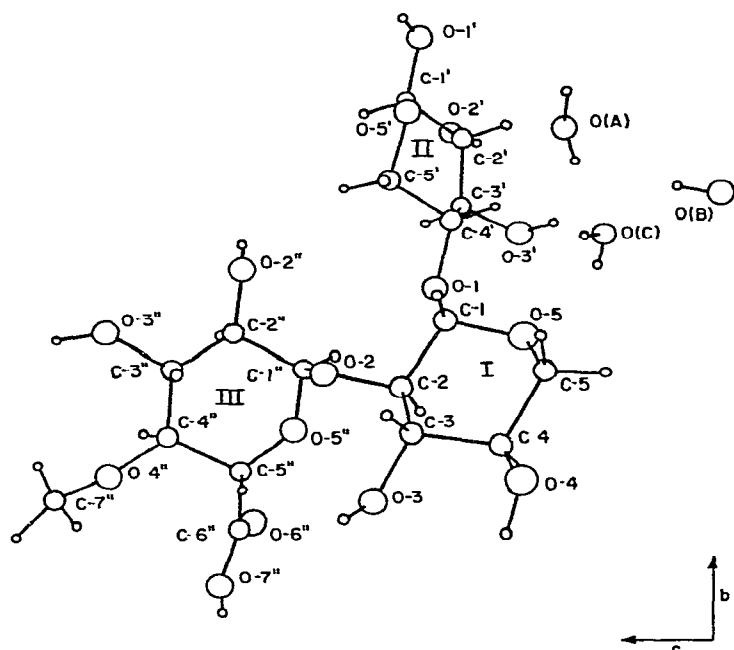
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(Received October 3rd, 1972; accepted October 17th, 1972)

The title aldotriouronic acid trisaccharide is a fundamental segment of the naturally occurring 4-*O*-methylglucuronoxylans found in hardwood hemicelluloses. The crystal structure of this compound has been determined from three-dimensional X-ray data obtained by the multiple-film, equi-inclination Weissenberg technique with nickel-filtered $\text{CuK}\alpha$ radiation, from crystals maintained at a temperature near the boiling point of liquid nitrogen. The structure was solved by using a combination of direct phasing methods and Patterson search methods, and the block-diagonal anisotropic refinement was terminated at a final *R* index of 0.066 for 2232 observations. One trisaccharide molecule and three water molecules of crystallization ($\text{C}_{17}\text{H}_{28}\text{O}_{15} \cdot 3\text{H}_2\text{O}$) comprise the asymmetric unit in a monoclinic unit-cell having the low-temperature (-193°) cell parameters of $a = 10.136$ (3), $b = 10.925$ (8), $c = 10.120$ (3), $\beta = 91.66$ (3), and space group P2_1 .

All three pyranose rings (Chart) adopt the C1(D) chair conformation, with all substituents, except that at $\text{C-1''}-\text{O-2}$, in equatorial orientation. Bond distances and bond angles (standard deviations $0.006\text{--}0.007$ Å, 0.4°) are in agreement with the values reported for other carbohydrate crystal structures¹. The bridge-oxygen angles corresponding to the glycosidic bonds, $\text{C-1}-\text{O-1}-\text{C-4'}$, $\text{C-1''}-\text{O-2}-\text{C-2}$, and $\text{C-4''}-\text{O-4''}-\text{C-7''}$ are 113.8 , 116.0 , and 113.6° . Conformational angles of -98.1 , 159.8 , 161.5 , and -100.4° were found for ϕ_1 , ϕ_1' , ϕ_2 , and ϕ_2' , respectively (as defined by Sundaralingam²) in the xylobiose residue. The conformation of the xylobiose residue is $(\phi, \psi) = (30^\circ, 35^\circ)$, when the conformational angles about the $\text{C-1}-\text{O-1}$ and $\text{O-1}-\text{C-4'}$ bonds are expressed in the convention followed by Sundararajan and Rao³.

The trisaccharide molecule is free of intramolecular hydrogen-bonds. The intramolecular hydrogen-bond between O-3' and O-5 found in other β -D-(1 \rightarrow 4)-linked disaccharide structures, cellobiose⁴, methyl β -cellobioside⁵, and α -lactose⁶, is not observed in this structure. The nonbonded distance between O-3' and O-5 is 3.964 Å, and the distance between O-5'' and O-3 is 3.648 Å.



The orientation of the trisaccharide molecule and the hydrogen-bonding pattern is such that there appears to be a planar aldobiouronic acid "polymer" along the *c* axis and a helical xylan "polymer" along the *b* axis; with the three water molecules of crystallization being clustered between the perpendicular chains and filling in an otherwise open structure. The packing arrangement allows fifteen hydrogen bonds to form, only five of which are between adjacent trisaccharide molecules. The remaining ten involve the three water molecules that play a major part in stabilizing the structure. O(B) and O(C) donate both of their hydrogen atoms and accept two, whereas O(A) donates both of its hydrogen atoms and accepts only one. One of the hydrogen atoms from O(B) appears to be involved in a bifurcated hydrogen-bond with O-5'' and O-6''.

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