Preliminary communication.

An X-ray study of tricyclic orthoesters of sugars

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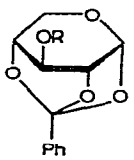
Tricyclic orthoesters of sugars are unique heterocyclic systems having a high degree of conformational rigidity, as shown for D-xylose derivatives[1,2]. Compounds of this type can be polymerised to give polysaccharides[3–6]. We now describe the preliminary data of an X-ray crystallographic study of α-D-xylopyranose 1,2,4-orthobenzoate (**1**) and 3-*O*-(*p*-bromobenzoyl)-α-D-xylopyranose 1,2,4-orthobenzoate (**2**).



1 R = H
2 R = *p*-BrC_6H_4CO

Orthoester **1**[7] (m.p. 144–145°, from ether–light petroleum) gave the following crystal data: mol. wt. 236.22; monoclinic, $a = 7.54 \pm 0.02$, $b = 11.98 \pm 0.03$, $c = 6.01 \pm 0.02$ Å, $\gamma = 91.5°$, $V = 542.9$ Å^3, $D_m = 1.45$ g.cm^{-3}, $Z = 2$, $D_{calc.} = 1.45$ g.cm^{-3}, space group $P2_1$. The unit-cell dimensions were found from oscillation and zero-layer Weissenberg photographs, about the needle-axis [001] and [010], taken with CuK_α-radiation.

A total of 930 independent, non-zero intensity reflections was collected by the equi-inclination Weissenberg multiple-film technique for the layers *hk*0–*hk*4 and *h*0*l*–*h*5*l*. The data were corrected for the Lorentz and polarization factors. The structure was solved by direct methods, using a new programme for non-centrosymmetric space groups[8]. The phases of 247 reflections were determined, and the resulting E-map[9] revealed the positions of all non-hydrogen substituents. By using these co-ordinates of atoms for computation of the phases, a first three-dimensional Fourier synthesis was calculated (Fig. 1). At this stage, the *R*-value was 0.24 for all the reflections observed. Refinement of the structure by the least-squares method is now in progress.

Orthoester **2** was synthesized in the usual way from compound **1**. It crystallised from chloroform–ether as perfect prisms. The crystal data are: m.p. 226–232°; mol. wt.

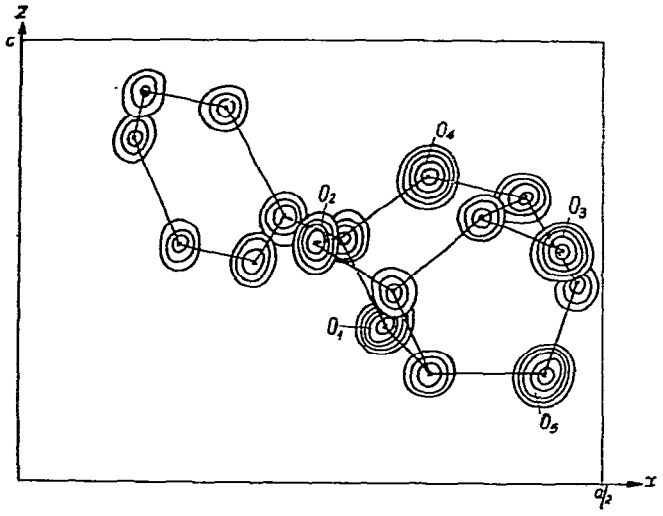


Fig. 1. Superimposed sections of the electron-density map parallel to (01C). Contours are at intervals $2e.Å^3$, beginning with $1e.Å^3$.

419.73; orthorhombic, $a = 24.18 \pm 0.04$, $b = 5.98 \pm 0.02$, $c = 11.61 \pm 0.02$ Å, $V = 1678.9$ Å^3, $D_m = 1.66$ g.cm^{-3}, $D_{calc.} = 1.67$ g.cm^{-3}, $Z = 4$, space group $P2_12_12_1$. The unit cell was found from rotation and Weissenberg photographs. Intensity data were recorded using Ni-filtered CuK_α-radiation. The intensities of 921 reflections were estimated visually from multiple-film Weissenberg photographs of the layers $hk0$–$hk4$ and $h0l$. Lorentz and polarization corrections were made, and all the reflections were placed on a common scale.

The structure was determined by the heavy-atom technique. The co-ordinates of the bromine atom were found from the Patterson map. All non-hydrogen atoms were located in the three-dimensional, electron-density map by using bromine phases. The initial R-value for all these atoms was 0.245. Co-ordinates of the atoms were refined by the least-squares method, giving an R-value of 0.11. Preliminary structural data obtained in this way are shown in Fig. 2. Conformational aspects of the structure will be discussed in detail elsewhere.

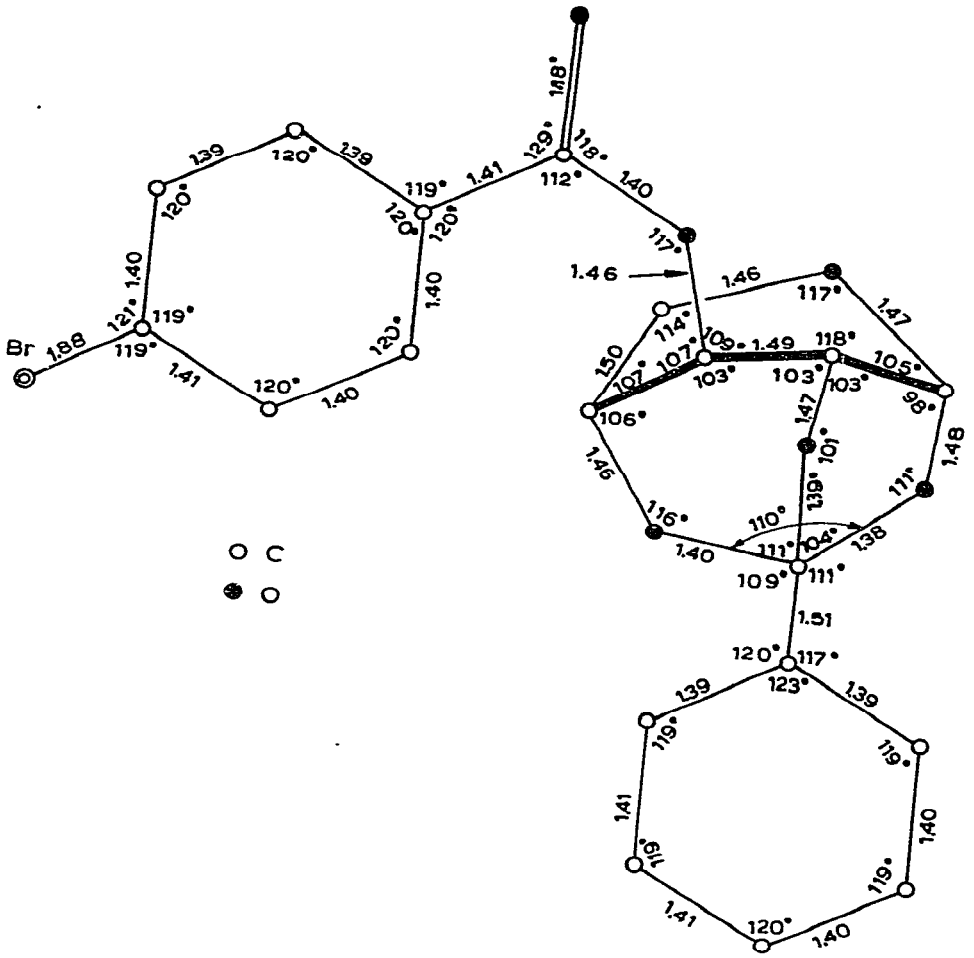


Fig. 2. Projection down the *a* axis of the unit cell (orthoester **2**).

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