X-Ray Crystal Structure and Properties of a New Trianhydrosucrose; 3,6-Anhydro-α-D-glucosyl-1,4:3,6-dianhydro-β-D-fructoside

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Summary The structure of 3,6-anhydro-α-D-glucosyl-1,4 : 3,6-dianhydro-β-D-fructoside has been determined by *X*-ray diffraction.

IN the study of the mechanism of alkaline degradation of sucrose, it became necessary to consider the possible involvement of sucrose anhydrides as intermediates in the degradation. Two different trianhydrides have previously been prepared from sucrose, *viz.* 1′,2 : 3,6 : 3′,6′-trianhydrosucrose (I) and 3,6-anhydro-α-D-galactosyl-1,4 : 3,6-dianhydro-β-D-fructoside (II). Compound (I) (m.p. 163·5—164·5°, $[\alpha]_D + 117°$ in water) was prepared by Lemieux and Barrette[1] by the action of sodium methoxide on a crude mixture containing 6,1′,6′-tri-*O*-toluene-*p*-sulphonylsucrose (III). Compound (II) (m.p. 191—192·5°, $[\alpha]_D + 137·5°$ in water) was similarly obtained from 2,3,6,3′,4′-penta-*O*-acetyl-4,1′,6′-tri-*O*-toluene-*p*-sulphonylsucrose (IV).

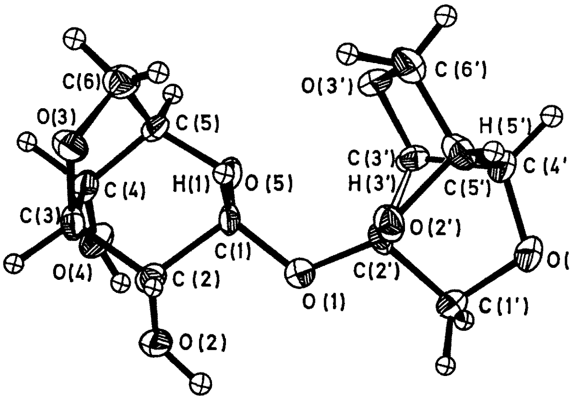

FIGURE. *Structure of* 3,6-*anhydro-α-D-glucosyl*-1,4: 3,6-*dianhydro-β-D-fructoside.*

The structures of (I) and (II) have been determined by chemical methods.[1,2] In attempting to repeat the preparation of (I), the 2,3,4,3′,4′- penta-*O*-acetate (V) of compound (III) was isolated in the pure state (m.p. 134—135°, $[\alpha]_D + 61·5°$). The trianhydride (VI)† which was obtained in high yield from purified (V) was different from (I) and (II), m.p. 196—197°, $[\alpha]_D^{32} + 94°$ (*c*, 2·2 in water). The structure of this compound was resolved by *X*-ray diffraction.

Colourless, prismatic crystals of the tri-anhydride were obtained from ethanol. *Crystal data*: $C_{12}H_{16}O_8$; *M*, 288·3, orthorhombic; $a = 6·437(1)$, $b = 11·298(1)$, $c = 16·754(1)$ Å; $U = 1218$ Å^3; $D_m = 1·57$ (by flotation); $Z = 4$; $D_c = 1·57$; $F(000) = 608$; $\mu = 11·66$ cm^{-1}; space group, $P2_12_12_1$; Cu-K_α radiation, Ni-filtered, Picker four-circle automatic diffractometer, using the ω-2θ scanning mode. 1161 reflections were collected up to 2θ equals 127°. The structure was solved by direct methods, using phases refined by the tangent formula.[3]

The molecule is shown in the Figure. C–C distances range from 1·50–1·56 and C–O distances from 1·41–1·49 with C(2′)–O(1) 1·37 and C(2′)–O(2′) 1·49, significantly different from the distances (1·43, 1·41Å respectively) found in sucrose.[4] All angles are close to tetrahedral except those about C(4),C(5),C(2′),C(3′),and C(4′); C(3)–C(4)–C(5),98·5(6); C(4)–C(5)–C(6),99·7(6); C(2′)–C(3′)–C(4′),90·5(6); C(3′)–C(4′)–C(5′), 92·6(6); C(3′)–C(2′)–O(1), 124·1(6)°. The estimated standard deviation for an interatomic distance is 0·01 Å, and for an angle 0·6°. A more detailed report of the crystallographic work is being prepared. The conventional and weighted *R*'s are 0·071 and 0·083 respectively.

Our trianhydride is therefore the title compound (VI). It is surprising that the alcoholysis of 6,1′,6′-tri-*O*-tosylsucrose (III) should result in formation of the 1′,2-anhydro-ring, whereas similar treatment of the related penta-*O*-acetate (V) should yield the preferential formation of the 1′,4′-anhydride. Two explanations appear possible. Lemieux and Barrette's alcoholysis of crude (III) yielded a complex mixture which might have contained both (I) and (VI), but from which only (I) crystallised (in 3·5% yield). Alternatively, it may be speculated that the acetylation of (III) results in a change of molecular configuration which, despite the fact that the acetyl groups are rapidly hydrolysed, makes less likely the formation of the 1′,2-linkage. The latter possibility is perhaps made more likely by the observation that in the other example of alcoholysis of an acetylated tri-*O*-tosyl-sucrose (IV) the formation of the 1′,4′-anhydro-ring is preferred to the 1′,2-ring.

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† Correct elemental analysis was obtained.

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