## SHORT COMMUNICATIONS

# Reaction Mechanism of the Acetonation of L-Sorbose by Ketal Interchange

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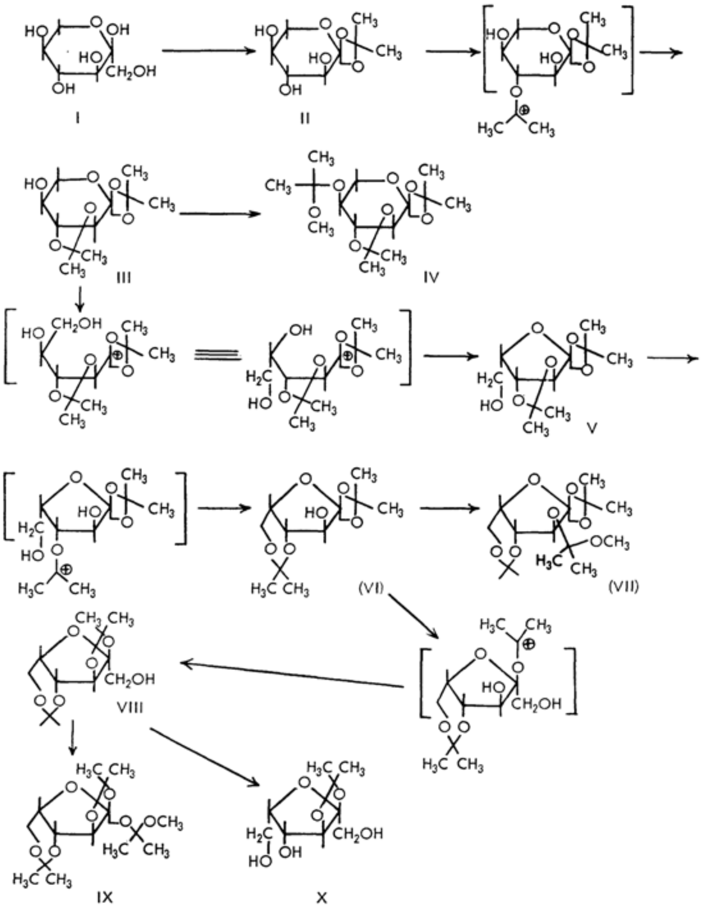
The acetonation of L-sorbose (I) is a very important reaction for the production of L-ascorbic acid. Previously we reported that, from the point of view of the reaction mechanism, the acetonation with acetone ketal[1] is different from the process of the acetonation with acetone,[2] and established the mechanism of the latter as I→1, 2-*O*-isopropylidene-α-L-sorbopyranose (II)[3] → the dimer of II → 2, 3 : 4, 6-di-*O*-isopropylidene-α-L-sorbofuranose



Scheme 1

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[1] K. Tokuyama and E. Honda, This Bulletin, 37, 591 (1964).

[2] K. Tokuyama, E. Honda and N. Hōki, *J. Org. Chem.*, 29, 133 (1964).

[3] H. Ohle, *Ber.*, 71, 762 (1938).

(VIII)[4]+I, in which the last element I takes this route further. In this paper, we present a reaction mechanism of the former acetonation.

The reaction of I with 2,2-dimethoxypropane (acetone dimethyl ketal) in the presence of *p*-toluenesulfonic acid gave a mixture syrup whose thin layer chromatogram exhibited multiple spots. The relative concentrations of the spots varied with the reaction conditions employed. Each component was separated in a pure state by thin-layer and fractional-gas chromatography, and their structures were determined to be 1,2-*O*- (II), 1,2:3,4-di-*O*- (III) and 5-*O*-1′-methoxyisopropyl-1,2:3,4-di-*O*-isopropylidene-α-L-sorbopyranose (IV), and 1,2:3,4-di-*O*- (V), 1,2:4,6-di-*O*- (VI),[1] 3-*O*-1′-methoxyisopropyl-1,2:4,6-di-*O*- (VII), 2,3:4,6-di-*O*- (VIII), 1-*O*-1′-methoxyisopropyl-2,3:4,6-di-*O*- (IX) and 2,3-*O*-isopropylidene-α-L-sorbofuranose (X),[5] respectively, by the infrared and NMR spectra and by the optical rotations. The analytical data are summarized below. III: colorless needles, m.p. 103—105°C (recrystallized from *n*-hexane), $[\alpha]_D^{27.5}$ $-91.2$ (*c* 1.051, acetone). Found: C, 55.75; H, 7.78. Calcd. for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75%. IV: colorless needles, m.p. 133—135°C (recrystallized from *n*-hexane), $[\alpha]_D^{24.0}$ $-82.2$ (*c* 1.017, chloroform). Found: C, 57.77; H, 8.37; $CH_3O$, 9.03. Calcd. for $C_{16}H_{28}O_7$: C, 57.81; H, 8.49; $CH_3O$, 9.38%. V: m.p. 80—83°C, $[\alpha]_D^{24.0}$ $-69.3$ (*c* 1.090, chloroform). Found: C, 55.85; H, 7.91. Calcd. for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75%. VII: syrup, $[\alpha]_D^{24.0}$ $+17.5$ (*c* 0.561, acetone). Found: C, 57.61; H, 8.26. Calcd. for $C_{16}H_{28}O_7$: C, 57.81; H, 8.49. IX: colorless syrup, $[\alpha]_D^{26.0}$ $-10.9$ (*c* 1.118, acetone). Found: C, 57.54; H, 8.55%. Calcd. for $C_{16}H_{28}O_7$: C, 57.81; H, 8.49%.

The above acetonated sugars (II→X) were also obtainable by the reaction of II with 2,2-dimethoxypropane; the mild acetonation of I gave II as a major product. On the other hand, the acetonation of X by ketal interchange gave only two products, VIII and IX. Therefore, the first intermediate of the acetonation process must be II.

On the basis of the above facts and the changes with time in the thin layer and gas chromatograms throughout the course of the acetonation by ketal interchange, the acetonation mechanism may be concluded to be as shown in Scheme 1.

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[4] T. Reichstein, *Helv. Chim. Acta*, **17**, 3111 (1934).

[5] T. I. Temnikova and V. V. Sklyarava, *Zh. Prikl. Khim.*, **21**, 1131 (1954).