1,2-*O*-Isopropylidene-β-D-fructofuranose. A New Acetal of D-Fructose

By GORDON J. F. CHITTENDEN

(*Department of Exobiology, The University, Toernooiveld 6525 ED Nijmegen, The Netherlands*)

Summary Reaction of D-fructose with 2,2-dimethoxypropane in 1,2-dimethoxyethane containing tin(II) chloride yields the hitherto unknown 1,2-*O*-isopropylidene-β-D-fructofuranose, characterised as a crystalline triacetate.

O-ISOPROPYLIDENE derivatives of sugars are important synthetic intermediates in carbohydrate chemistry.[1] Acetal exchange is frequently used[1,2] for introducing these groups. These reactions are considered to be under kinetic control and have led to products not always available from direct methods. The most commonly used reagent is 2,2-dimethoxypropane in *NN*-dimethylformamide with toluene-*p*-sulphonic acid as catalyst.[2] The use of 2-alkoxypropenes under similar conditions has also been described.[3] As part of acetalation studies and the use of tin(II) chloride as a catalyst in carbohydrate chemistry,[4] D-fructose was treated with 2,2-dimethoxypropane in 1,2-dimethoxyethane with this catalyst yielding a new isopropylidene acetal of D-fructofuranose of potential synthetic interest.† Only one isopropylidene derivative of D-fructofuranose is currently known.[5,6]

D-Fructose was treated at reflux temperature with 2,2-dimethoxypropane (4 mol. equiv.) and 1,2-dimethoxyethane containing tin(II) chloride (10^{-4} mol. equiv.) until dissolution was complete (*ca.* 30 min). The reaction was terminated by the addition of the theoretical quantity of pyridine required to complex the catalyst. The water-soluble portion of the product was lyophilised and the resultant syrup acetylated (Ac_2O–pyridine) to afford 24—28% of 3,4,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-β-D-fructofuranose (**1**), m.p. 81—83 °C, $[\alpha]_D^{22}$ −48.5° (1,2-dimethoxyethane), ^{1}H-n.m.r. (220 MHz, C_6D_6) *inter alia*, δ 5.44 (d, $J_{3,4}$ 6.5 Hz, 3-H) and 5.53 (dd, $J_{4,5}$ 5.0 Hz, 4-H). The coupling constants of these two prominent resonances, the

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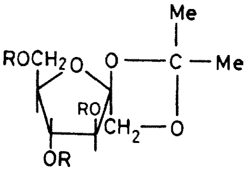
† Satisfactory analyses were obtained for compounds reported herein.

only ones occurring to low field, are near to those determined[7] for some β-D-fructofuranosides. This observation, in addition to the value of the optical rotation, substantiated the β-D-configuration of the product and ^{13}C-n.m.r. spectroscopy further supported this assignment. The mass spectrum of (**1**), in addition to M^+ yielded fragments *m/e* 117 and 72 consistent with the presence of a 1,2-*O*-isopropylidene attached to a keto-hexose.[8]



(**1**) R = Ac

(**2**) R = H

Deacetylation (NaOMe) of (**1**) yielded 1,2-*O*-isopropylidene-β-D-fructofuranose (**2**) as a syrup, $[\alpha]^{22}$ −40° (methanol).

The ethyl acetate-soluble portion of the reaction product was shown to consist almost entirely of the known 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose (g.l.c.) which is considered to be the kinetic control product from the reaction of D-fructose with acetone in the presence of an acid catalyst.[9]

In the absence of tin(II) chloride complete reaction was attained in 28 h (t.l.c.). The product did not contain (**2**) but was shown (g.l.c.) to be a mixture of the known[9] 1,2:4,5- and 2,3:4,5-di-*O*-isopropylidene-D-fructopyranoses in the ratio 4:1. Treatment of D-fructose under the usual conditions of acetal exchange[2] also did not yield (**2**).

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