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HYDROGENOLYSIS OF CARBOHYDRATES

IX. FORMATION OF 2,6-ANHYDRO-β-D-FRUCTOFURANOSE AND ETHYL α- AND β-D-FRUCTOFURANOSIDE FROM SUCROSE[1]

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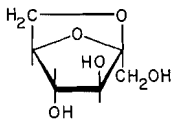
ABSTRACT

A compound formed during the hydrogenolysis of sucrose in ethanol or dioxane at 180° C, in the presence of copper chromium oxide catalyst, has been characterized as 2,6-anhydro-β-D-fructofuranose (2,5-anhydro-α-D-fructopyranose), a new type of anhydro-ketose. Ethyl α- and β-D-fructofuranosides are also produced when the hydrogenolysis reaction is carried out in ethanol, and various derivatives of these anomeric ketosides have been prepared.

Earlier papers of this series have described the hydrogenolysis of alkyl glycopyranosides in the presence of copper chromium oxide catalyst (1) at moderate temperature and pressure (2, 3, 4, 5, 6). A major effect observed in these reactions is the isomerization of carbinol groups but, particularly at temperatures above 180–200° C, glycosidic linkages also become unstable and extensive hydrogenolysis of hydroxyl groups occurs. Methyl β-L-arabopyranoside, for example, is isomerized to a mixture of methyl pentopyranosides at 180° C (4), whereas at 240° C it is converted in high yield to a mixture of 1,5-anhydro-2-deoxy-DL-pentitols (2, 5). In current studies the behavior of furanose glycosides towards these conditions of hydrogenolysis is being examined, and sucrose has been selected as a readily available substrate containing a furanosyl moiety.

In ethanol at 180° C,* sucrose readily afforded three derivatives of D-fructose, each in about 10% yield (based on the fructose unit of sucrose). Detected initially on paper chromatograms as compounds having high R_F values (relative to that of sucrose) and giving a typical ketohexose test with urea oxalate (7), these products have been isolated by column chromatography on charcoal (8) and cellulose (9) and characterized as 2,6-anhydro-β-D-fructofuranose (I) (2,5-anhydro-α-D-fructopyranose), and ethyl α- and β-D-fructofuranoside (III and II).



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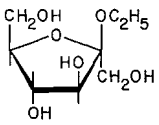

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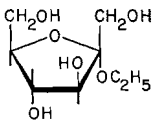

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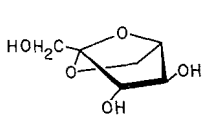

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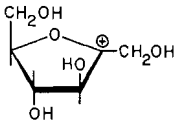

V

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**By analogy with the behavior of methyl α-D-glucopyranoside (3), the α-D-glucopyranosyl unit of sucrose was expected to be stable at 180° C.*

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The anhydride, m.p. 118–119° C, was found by the isothermal distillation method (10) to be monomeric. It did not reduce hot Fehling's solution nor react with sodium borohydride and, since it was recovered unchanged after prolonged treatment with methanolic ammonia, did not appear to contain an epoxy group. At room temperature, it was easily hydrolyzed by 0.1 *N* sulphuric acid affording D-fructose as the sole product. Tritylation of the anhydride in pyridine proceeded very slowly at room temperature, and two crystalline derivatives were isolated in low yield, one being a monotrityl and the other a ditrityl ether. The compound was resistant also to tosylation but, on prolonged treatment with tosyl chloride in pyridine, yielded a syrupy diester which, however, did not react with sodium iodide. These properties suggested that only the relatively unreactive C-1-carbinol group and/or secondary hydroxyl groups of the anhydride were being substituted, and hence that the normally reactive 6-position was involved in ring formation.

Attempts to methylate the anhydride fully with dimethyl sulphate – sodium hydroxide or with methyl iodide – silver oxide were unsuccessful, but several treatments with potassium in liquid ammonia (11) followed with methyl iodide under reflux, yielded a syrupy trimethyl derivative. On acid hydrolysis this ether afforded crystalline 1,3,4-tri-*O*-methyl-D-fructose (12), showing that both the 5- and 6-hydroxyl groups of the anhydride are involved in ring formation, and hence that the anhydride is 2,6-anhydro-D-fructofuranose (2,5-anhydro-D-fructopyranose).

Since the specific rotation of the anhydride, $[\alpha]_D$ −107°, is more strongly levorotatory than D-fructose itself, the 2,6-oxygen bridge of the compound appears to possess the β-configuration. The β-assignment is strongly supported by an examination of molecular models, which shows also that the 2,6-anhydro ring assumes a boat conformation (as in IV). The eclipsing of bonds and distortion of bond angles in such a molecule could account for the observed ease of acid hydrolysis of the anhydride, as had been anticipated by Mills (13), which contrasts with the relatively high acid stability of other anhydro sugars (epoxides excepted). That the 2,6-pyranoid ring of the compound is much less stable than the five-membered 2,5-ring (see 14, 15) was indicated by the rapid formation of ethyl α- and β-D-fructofuranoside when the anhydride was treated with ethanolic hydrogen chloride at room temperature. Moreover, the α-D-anomer predominated initially, which was to be expected from scission of a β-D-anhydro ring (16), and the observed rate of formation of the mixture of furanosides (rate of rotational change) closely paralleled that found with ethyl β-D-fructofuranoside.

The anhydride consumed no periodate, although it possesses a free glycol group (the *trans*-3,4-diol group), and with lead tetraacetate in acetic acid only a slow uptake of oxidant was found, caused most probably by gradual opening of the anhydro ring. This behavior is in accord with the recent report by Angyal and Young (17) that the camphane-2,3-*trans*-diols are virtually unoxidized by glycol-cleaving agents since the structure of the anhydride is closely analogous to that of the camphane diols. Dimler (18) has suggested that the 2,3-*trans*-diol group of 1,6-anhydro β-D-gluco- and α-galactofuranose, situated on a fused bicyclic system, resists glycol scission most probably because it is fixed rigidly in an arrangement highly unfavorable for complexing by the oxidants. The *trans*-glycol groups of the camphane-*trans*-diols and the anhydrofructose appear to possess a similar spatial arrangement, and their unreactivity can therefore be interpreted in the same way.*

Recently it has been found (H. R. Goldschmid and A. S. Perlin. Can. J. Chem. **38, 2178 (1960)) that these compounds are cleaved oxidatively by lead tetraacetate using pyridine as solvent (27).*

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It may be noted, however, that some *vic–trans*-diols which are not located on bicyclic ring compounds, i.e., the 2,3-*trans*-glycol groups on internal $(1 \rightarrow 4)$-linked units of oligosaccharides, are also resistant to attack by lead tetraacetate (19).

Several dimeric anhydrides of D-fructose are known to be formed by acid hydrolysis of D-fructans (20) and a 2,3-anhydro monomeric derivative of D-fructofuranose, as well as dimeric anhydrides, has been found recently among the products of direct nitration of D-fructose (21). The compound described here is yet another type of D-fructose anhydride. Also, it represents a class of rare anhydro-sugars, namely, that having the 1,4(2,5)-1,5(2,6)-bridged system. One other member of this class, 1,5-anhydro-β-D-ribofuranose, has been synthesized recently by Vis and Fletcher (22), and also has been converted to the 2,3-*O*-isopropylidene derivative, which proved to be indistinguishable from a compound described several years earlier but only tentatively identified (23). Derivatives of three related glycosans have been reported but incompletely characterized (see 14); these are 1,5-anhydro-2,3,6-tri-*O*-methyl-β-D-glucofuranose (24) and -α-L-idofuranose (25), and 2,3-di-*O*-acetyl-1,5-anhydro-β-L-rhamnofuranose (26).

Although 2,6-anhydro-β-D-fructofuranose cannot be regarded as a *hydrogenolysis* product derived from sucrose, it was not obtained when the reaction was carried out in the presence of argon rather than hydrogen. Considerable charring occurred under these latter conditions, however, and ethyl β-D-fructopyranoside was isolated from the reaction mixture, the furanosides being relatively minor products. Hence the hydrogenolysis conditions used may prevent decomposition of labile compounds, rather than serve directly in promoting formation of the furanose products. The occurrence together of the anhydride and of the anomeric furanosides suggests the possibility that all three products are formed from a carbonium-ion intermediate of the type encountered in the acid-catalyzed solvolysis of glycosides (see 15). A protonated form such as V, by reaction with the solvent, could yield the anomeric furanosides (II and III), and through intramolecular attack by the C-6-carbinol group give the 2,6-anhydride. Formation of an acyclic carbonium-ion intermediate (15) appears less likely in these reactions, since ethyl pyranosides would then be expected to predominate among the products at the high temperatures used. That the anhydride may be derived directly from sucrose rather than from the glycosides was shown by its formation also when the hydrogenolysis reaction was carried out in dioxane as solvent in place of ethanol. The anhydride itself undergoes ethanolysis readily by heat in the absence of added acid catalyst to yield the anomeric furanosides. Hence, the glycosides isolated from the hydrogenolysis mixture may be produced by solvolysis of the anhydride, as well as via a carbonium-ion intermediate such as V.

The α- and β-anomers of ethyl D-fructofuranoside were isolated as analytically pure syrups,* the β-anomer being readily cleaved by invertase. On tosylation, the β-glycoside furnished a crystalline diester which was converted by treatment with sodium iodide in acetone to a syrupy, monoiodo monotosyl derivative. In pyridine solution (27) the ditosylate consumed 1 mole of lead tetraacetate, in agreement with the expectation that the ester groups were located at positions-1 and -6; presumably, that at position-1 is not readily replaceable by iodide ion (28, 29). The β-anomer also furnished a crystalline 1,6-di-*O*-trityl derivative, the terminal location of the ether groups being shown by the fact that the compound, in pyridine, consumed a mole of lead tetraacetate; the ditrityl ether was characterized further as a crystalline diacetate. Tritylation of the α-glycoside

**The α-anomer of methyl D-fructofuranoside has been obtained in crystalline form (30).*

followed by acetylation afforded a crystalline di-*O*-acetyl dityrityl ether. After deacetylation the dityrityl ether was shown, also by oxidation with lead tetraacetate in pyridine, to be the 1,6-derivative.

No ethyl D-glucosides were detected among the reaction products, in accord with the expectation that the D-fructofuranosyl linkage should be cleaved preferentially. Further, as shown by the formation of D-sorbitol, the D-glucosyl unit appeared to be converted mainly to the free sugar and then reduced. The presence of D-mannitol in the mixture suggested that some D-fructose also was formed during the reaction. In addition to these products, glycerol and a small proportion of erythritol were isolated, but the origin of these fragments was not determined.

In contrast to the behavior of sucrose, the derived octaacetate was completely stable to the hydrogenolysis conditions, even at 240° C. The (2 → 6)-linked poly-D-fructan, inulin, although converted in small proportion in ethanol to the furanosides, appeared to yield none of the anhydride.

EXPERIMENTAL

Paper chromatography was carried out with butan-1-ol:ethanol:water (40:11:19) as solvent, and with urea oxalate (7) and ammoniacal silver nitrate (31) as spray reagents.

Column chromatography on cellulose was carried out using benzene:ethanol:water (500:50:1), (500:100:1) and ethanol.

Evaporations were carried out at 40–50° C, and optical rotations were measured at approximately 25° C. Melting points are corrected, and boiling points recorded are air-bath temperatures.

Hydrogenolysis of Sucrose in Ethanol and Separation of the Products

Sucrose (20 g) in absolute ethanol (75 ml) was heated at 180° C and a pressure of 1100 p.s.i. of hydrogen in the presence of copper chromium oxide catalyst (2 g) for 6 hours. The catalyst was filtered off and the filtrate concentrated, yielding a colorless syrup. Paper chromatographic examination of the syrup indicated the presence of the following components: hydroxymethylfurfural; glycerol; erythritol; ketohexose derivatives at R_F 0.60, 0.48, and 0.35; fructose; mannitol; sorbitol; sucrose; and slower-moving materials streaking to the origin.

The syrupy reaction product was chromatographed on a column of coconut charcoal (32). The glycerol (0.35 g) and erythritol (0.25 g) (m.p. 120° C, undepressed) were eluted with water.

By adding 5% ethanol to the column and then fractionating the mixture of eluted products on a cellulose column, the following were obtained: component R_F 0.60 (0.85 g), fructose (0.5 g), glucose (2.0 g), and admixed D-mannitol and D-sorbitol (1.5 g). D-Mannitol (m.p. 166° C, undepressed) was isolated by fractional crystallization, and D-sorbitol was characterized as the hexaacetate (m.p. 99° C, undepressed).

The charcoal column was washed finally with 10% ethanol yielding a mixture of products. This mixture was resolved on a cellulose column, giving component R_F 0.48 (0.9 g), component R_F 0.35 (0.85 g), and unchanged sucrose (9.5 g).

2,6-Anhydro-β-D-fructofuranose (I)

The chromatographically pure syrup (component R_F 0.35) solidified on prolonged storage, and was recrystallized from acetone, m.p. 118–119° C and $[\alpha]_D$ −107° (*c*, 1, H_2O) (no mutarotation). Calculated for $C_6H_{10}O_5$: C, 44.44%; H, 6.22%; mol. wt., 162. Found:

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C, 44.49%; H, 6.37%; mol. wt., 157 (by isothermal distillation (10) in methanol at 50° C).

The compound did not reduce Fehling's solution, was unaffected by treatment under reflux for 6 hours with 1% methanolic ammonia, and also by treatment for 3 days at room temperature with aqueous sodium borohydride. With sodium metaperiodate no uptake of oxidant was found in 24 hours reaction time, and with lead tetraacetate in acetic acid the consumption of oxidant was 0.1 mole in 8 hours reaction time.

In 0.05 *N* sulphuric acid at 25° C the observed rotation of the anhydride solution (1.0%) decreased slightly from α_D −1.00° (3 minutes) → α_D −0.97° (5 hours, constant, 1 dcm tube). Paper chromatographic examination showed that most of the anhydride was hydrolyzed in 2 hours, and that conversion to fructose was complete within 5 hours; accordingly, the calculated $[\alpha]_D$ of the hydrolyzate was −89° (D-fructose shows $[\alpha]_D$ −92°). The product was characterized further by conversion to D-glucose phenylosazone, m.p. 209° C (decomp.), and indistinguishable from an authentic sample by X-ray diffraction.

The observed rotation of the anhydride in ethanolic hydrogen chloride (0.5%) at room temperature rose rapidly to $[\alpha]_D$ +0.44° (7 minutes), then decreased slowly to −0.09° (18 hours) (*c*, 1.2, 1 dcm tube). Paper chromatographic examination of the reaction mixture indicated that ethyl α-D-fructofuranoside was formed as the major product during the first 10 minutes reaction time. Under similar conditions, rotational changes shown by ethyl β-D-fructofuranoside were a rapid rise to $[\alpha]_D$ +0.32° (9 minutes), then dropping slowly to 0.03° (19 hours); ethyl α-D-fructofuranoside showed $[\alpha]_D$ +0.22° (2 minutes)→ −0.07° (20 hours), D-fructose, $[\alpha]_D$ +0.18° (14 minutes)→ −0.24° (18 hours). These values are similar to the data reported by Purves and Hudson (30, 33) for the methyl D-fructofuranosides and D-fructose.

Acetylation of the anhydride with acetic anhydride – pyridine at room temperature afforded a triacetate, b.p. 110–120° C at 0.05 mm, $[\alpha]_D$ −108° (*c*, 1.3, $CHCl_3$). Calculated for $C_{12}H_{16}O_8$: C, 50.00%; H, 5.60%; acetyl, 44.8%. Found: C, 50.17%; H, 5.79%; acetyl (sapon.), 44.4%.

Treated with benzoyl chloride and pyridine in cold chloroform, the anhydride yielded an amorphous tribenzoate, $[\alpha]_D$ −163° (*c*, 1.1, $CHCl_3$). Calculated for $C_{27}H_{22}O_8$: C, 68.35%; H, 4.67%. Found: C, 67.90%; H, 4.73%.

*1,3,4-Tri-O-methyl-*D*-fructose*

The anhydride (0.20 g) was dissolved in liquid ammonia (20 ml) and potassium was added portionwise until a stable blue color developed in the solution. After evaporation of the ammonia, methyl iodide (3 ml) was added and the solution heated under reflux for 3 hours and then stored at room temperature for 18 hours. The methyl iodide was evaporated off, the methylation procedure repeated twice, and the final reaction mixture was extracted with chloroform. The chloroform extract afforded a syrup which was distilled, b.p. 60–70° C at 0.05 mm. Paper chromatographic examination of the distillate showed the presence of a major component and a minor, slower-moving component which corresponded to 1,3,4-tri-*O*-methyl-D-fructose (below), indicative of partial hydrolysis. Calculated for $C_9H_{16}O_5$: methoxyl, 45.6%. Found: (two preparations) methoxyl, 42.9%, 41.7%.

The distillate (105 mg) was hydrolyzed with *N* sulphuric acid, the solution was neutralized with barium carbonate and extracted with chloroform. On evaporation, the aqueous layer yielded a syrup (99 mg) which consisted of a single component (paper chromatogram). Purified by distillation (b.p. 115–120° C at 0.05 mm) the product solidi-

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fied, and was recrystallized from carbon tetrachloride, m.p. 72–73° C and $[\alpha]_D$ −49.6° (*c*, 1.3, H_2O) (lit. (12), m.p. 73° C and $[\alpha]_D$ −51.8° (H_2O)). Calculated for $C_9H_{18}O_6$: C, 48.36%; H, 8.3%; methoxyl, 41.89%. Found: C, 48.34%; H, 8.17%; methoxyl, 41.79%.

In acetic acid, the trimethyl D-fructose consumed no lead tetracetate in 4 hours reaction time, showing the absence of a free *vic*-diol at the 2,3-position (34) and also at the 1,2-position (35). After reduction with sodium borohydride, 1 mole of formaldehyde was produced (chromotropic acid method (36)) in 1 hour reaction time. This behavior showed the absence of methoxyl groups at positions-2, -5, and -6, and hence confirmed that the product was the 1,3,4-tri-*O*-methyl derivative.

Tritylation of 2,6-Anhydro-β-D-fructofuranose

In a preliminary experiment, using 2.2 moles of trityl chloride per mole of anhydride in pyridine at room temperature, some unchanged anhydride was present in the reaction mixture after 1 week (paper chromatogram). The anhydride (162 mg) in pyridine (4 ml) was treated at room temperature for 10 days with triphenylchloromethane (615 mg). Ice water was added, the reaction mixture was extracted with benzene, and the extract washed successively with water, sodium bicarbonate solution, and water, then dried over sodium sulphate, and the benzene was evaporated off. The oily product (720 mg) was fractionated on a column of reagent silicic acid using chloroform as the solvent. After elution of triphenylcarbinol, a ditrityl derivative (85 mg) was isolated and recrystallized from ethanol, m.p. 224–226° C and $[\alpha]_D$ −38.5° (*c*, 0.8, $CHCl_3$). Calculated for $C_{44}H_{38}O_5$: C, 81.75%; H, 5.92%; mol. wt., 643. Found: C, 81.88%; H, 6.00%; mol. wt., 621 (melting point depression in camphor).

Continued washing of the column with chloroform eluted a monotrityl derivative (145 mg) which, after recrystallization from dichloromethane – *n*-hexane, had a melting point of 150–153° C, $[\alpha]_D$ −43.7° (*c*, 1.0, $CHCl_3$). Calculated for $C_{25}H_{24}O_5$: C, 74.24%; H, 5.98%. Found: C, 74.24%; H, 5.98%.

Di-O-tosyl-2,6-anhydro-β-D-fructofuranose

The anhydride (200 mg) in pyridine (5 ml) was treated with *p*-toluenesulphonyl chloride (500 mg) at room temperature for 18 hours. A few drops of water were added, and after 30 minutes the reaction mixture was poured into ice water and extracted with benzene. After successive washings with water, sodium bicarbonate solution, and water, the benzene extract was dried and concentrated affording a glass (139 mg). The product, treated in acetone with sodium iodide in a sealed tube at 100° C, yielded only a trace of sodium *p*-toluenesulphonate in 24 hours reaction time, $[\alpha]_D$ −29.1° (*c*, 1.4, $CHCl_3$). Calculated for $C_{20}H_{22}O_9S_2$: C, 51.04%; H, 4.71%; S, 13.62%. Found: C, 51.60%; H, 4.91%; S, 14.17%.

Ethyl β-D-Fructofuranoside (II)

The syrupy, chromatographically pure glycoside had $[\alpha]_D$ −36° (*c*, 1, H_2O), was readily degraded to fructose by treatment with invertase, and was hydrolyzed to fructose at room temperature within 2 days by 0.1 *N* sulphuric acid. It consumed 1.0 mole of sodium periodate per mole.

On acetylation with acetic anhydride in pyridine at room temperature, the glycoside (200 mg) afforded a tetraacetate (310 mg), b.p. about 150° C at 0.06 mm, $[\alpha]_D$ −25° (*c*, 1.1, $CHCl_3$). Calculated for $C_{16}H_{24}O_{10}$: C, 51.06%; H, 6.43%; acetyl, 45.8%. Found: C, 51.07%; H, 6.52%; acetyl (sapon.), 46.1%.

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1,6-Di-O-trityl Ethyl β-D-Fructofuranoside

The glycoside II (200 mg) in pyridine (4 ml) was treated at room temperature with trityl chloride (600 mg) for 48 hours. Isolated after treatment with ice water and extraction into benzene, the product (490 mg) was crystallized from ethanol, m.p. 180–183° C and $[\alpha]_D$ −2.3° (*c*, 1.0, $CHCl_3$). Calculated for $C_{46}H_{44}O_6$: C, 79.74%; H, 6.40%. Found: C, 79.91%; H, 6.60%.

Treated with lead tetraacetate in pyridine (27) at 0° C the ditrityl derivative consumed 1 mole of oxidant per mole in 0.5 hour.

The ditrityl glycoside (100 mg) treated with acetic anhydride – pyridine afforded a diacetate (95 mg) which, after recrystallization from ethanol, had a melting point of 207–208° C, $[\alpha]_D$ +35.8° (*c*, 1.3, $CHCl_3$). Calculated for $C_{50}H_{48}O_8$: C, 77.30%; H, 6.23%. Found: C, 77.07%; H, 6.29%.

1,6-Di-O-tosyl Ethyl β-D-Fructofuranoside

To the glycoside II (400 mg) in pyridine (5 ml) at 0° C was added a solution of *p*-toluenesulphonyl chloride (750 mg) in chloroform (10 ml). After 2 hours at 0° C and 18 hours at 25° C the reaction mixture was diluted with chloroform (30 ml), treated with a few drops of water, and 30 minutes later was washed successively with ice water, copper sulphate, sodium bicarbonate, and water. The solution was dried over sodium sulphate and concentrated, yielding a crystalline product (230 mg) which was recrystallized from ethanol – *n*-hexane, m.p. 125–127° C (decomp.), $[\alpha]_D$ −12.8° (*c*, 1.0, $CHCl_3$). Calculated for $C_{22}H_{28}O_{10}S_2$: C, 51.15%; H, 5.46%; S, 12.41%. Found: C, 51.02%; H, 5.46%; S, 12.13%.

In pyridine, the ditosyl derivative consumed 1.0 mole of lead tetraacetate per mole in 1 hour reaction time.

The ditosylate (100 mg) was heated at 100° C with sodium iodide (75 mg) in acetone (6 ml) for 24 hours. Sodium *p*-toluenesulphonate (35 mg), which crystallized out on cooling, was filtered off. After evaporation of the acetone, the residue was taken up in chloroform, washed with water, and recovered as an oil (72 mg), $[\alpha]_D$ −22.5° (*c*, 1.0, $CHCl_3$). Calculated for $C_{15}H_{21}O_7SI$: S, 6.79%; I, 26.87%. Found: S, 6.68%; I, 25.94%.

Ethyl α-D-Fructofuranoside (III)

The syrupy, chromatographically pure material showed $[\alpha]_D$ +65° (*c*, 1, H_2O), was not attacked by invertase, and was hydrolyzed to D-fructose within 15 hours at room temperature by 0.1 *N* sulphuric acid. It consumed 1 mole of sodium periodate per mole. Calculated for $C_8H_{16}O_6$: C, 46.15%; H, 7.75%; ethoxyl, 21.6%. Found: C, 45.98%; H, 8.13%; ethoxyl, 21.1%.

Acetylated at 25° C with acetic anhydride – pyridine, the glycoside yielded a tetraacetate, b.p. about 135° C at 0.01 mm, $[\alpha]_D$ +76° (*c*, 1.4, $CHCl_3$). Calculated for $C_{16}H_{24}O_{10}$: C, 51.06%; H, 6.43%; acetyl, 45.8%. Found: C, 51.22%; H, 6.65%; acetyl (sapon.), 45.8%.

3,4-Di-O-acetyl-1,6-di-O-trityl Ethyl α-D-Fructofuranoside

The glycoside III (205 mg) was treated with trityl chloride (615 mg) in pyridine (4 ml) at room temperature for 7 days, and the reaction mixture was worked up as described previously. The syrupy product (722 mg) was fractionated on a silicic acid column using chloroform as solvent, affording a crystalline ditrityl ether (260 mg) and, by continued elution, an oily product which probably was a monotrityl derivative. Despite repeated recrystallization from ethanol the ditrityl ether had a broad melting point (about

140–150° C). On acetylation at 100° C with acetic anhydride – sodium acetate, a di-*O*-acetyl di-*O*-trityl derivative was obtained, m.p. 142–144° C and $[\alpha]_D$ +44.7° (*c*, 1.4, $CHCl_3$). Calculated for $C_{50}H_{48}O_8$: C, 77.30%; H, 6.23%. Found: C, 77.32%; H, 6.32%.

The product was deacetylated with sodium methoxide in chloroform–methanol, the solvent was evaporated, and the residue treated at 0° C with lead tetraacetate in pyridine. Found: 1.0 mole of oxidant consumed per mole in 0.5 hour.

Hydrogenolysis of Sucrose in Dioxane

Sucrose (5 g) and copper chromium oxide catalyst (0.5 g) in dioxane (75 ml) were heated for 6 hours at 180° C under hydrogen at 1100 p.s.i. An oil consisting mainly of unchanged sucrose separated out on cooling, and the dioxane solution was evaporated. The residue (2.9 g) showed heavy streaking on a paper chromatogram. By chromatography on a cellulose column, a fraction corresponding (paper chromatogram) to the anhydride (I) was isolated (167 mg). After recrystallization from acetone, the product had a melting point of 118–119° C, undepressed. The X-ray diffraction powder diagram of the product was indistinguishable from that of the anhydride (I).

Ethanolysis of Sucrose

Sucrose (10 g) in dry ethanol (75 ml) was heated for 6 hours at 180° C in an atmosphere of argon (10 p.s.i.). The resulting dark-brown solution was concentrated to a syrup which, from paper chromatographic examination, appeared to contain hydroxymethylfurfural, ethyl D-fructofuranosides (II and III), a trace of anhydride (I), fructose, and sucrose. By column chromatography on cellulose the glycoside mixture was found to contain ethyl β-D-fructopyranoside (105 mg), m.p. 150–151° C and $[\alpha]_D$ −160° (*c*, 1.0, H_2O). Calculated for $C_8H_{16}O_6$: C, 46.15%; H, 7.75%. Found: C, 46.21%; H, 7.86%. The derived tetraacetate had a melting point of 83–84° C and $[\alpha]_D$ −127° (*c*, 1.2 $CHCl_3$). Calculated for $C_{16}H_{24}O_{10}$: C, 51.06%; H, 6.43%. Found: C, 51.33%; H, 6.57%.

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