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Preparation and catalytic hydrogenolysis of some ω-halogenoalkyl β-D-fructopyranosides; a convenient route to simple alkyl β-D-fructopyranosides

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Abstract. The acid-catalysed reactions of D-fructose, sucrose and inulin with ω-halogenoalkyl alcohols yield the corresponding β-D-fructopyranosides. Catalytic hydrogenolysis of these glycosides provides a simple route to some crystalline alkyl β-D-fructopyranosides of potential biological interest.

Introduction

Some simple alkyl β-D-fructopyranosides have been claimed to have interesting medicinal or biological properties[1–3], including[3] the suppression of IgE antibody formation. The specific synthesis of glycosides of D-fructose (**1**) is not readily achieved. The acid-catalysed glycosidation of **1** is capricious and normally leads to anomeric mixtures of furanosides and pyranosides, requiring chromatographic separation. The early stages of the reaction are under kinetic control which favours furanosides when performed at room temperature for short periods[4]. Unlike the aldosides, fructofuranosides and fructopyranosides are hydrolysed at similar rates[5], so that the overall control of eventual ring size during the reaction is difficult. The only glycosides of **1** which are available without the use of chromatography are the benzyl derivative **2**[5] and the 2-chloroethyl compound **3**[6]. In connection with studies on new carbohydrate-based non-ionic surfactants and mesogens, we required compound **3** and some homologues thereof. This paper deals with the preparation of these compounds from certain commercially available ω-halogenoalkyl alcohols and D-fructose or the D-fructose-containing substrates, *e.g.*, sucrose and inulin. During these studies, it seemed appropriate to investigate the catalytic hydrogenolysis of the products as a convenient source of simple alkyl β-D-fructopyranosides. Some aspects of these reactions are described.

Results and discussion

Treatment of D-fructose (**1**) with 2-chloroethanol containing *ca.* 1% hydrogen chloride gave the known[6] glycoside **3** (89%). Compound **3** is currently the most easily obtainable crystalline derivative of **1**. It is now available commercially, but is too expensive, in view of the simplicity and efficiency of this procedure.

It is of interest to note that some aspects[6] of the formation of **3** are unusual, *viz.*, the reaction mixture never becomes homogeneous, and the product is not the expected furanoside but the β-D-pyranoside. Fischer glycosidation of **1**, when conducted for a short reaction period (2 h), would be expected to lead to kinetically favoured furanosides. Treatment of sucrose under the same conditions also gave **3** (70%), but the required reaction period was much longer, *viz.*, 15 h. No experimental details of this reaction were reported[6]. It was tentatively suggested that reactions leading to compound **3** may have occurred in the solid phase rather than in solution.

The fructose unit in sucrose is present in the furanose form, and the molecule must, therefore, undergo initial hydrolysis, followed by rearrangement to the pyranose form to account for the formation of **3**. The mutarotation of **1** in various solvents, but not alcohols, has been studied[7] comprehensively by ^{1}H-NMR spectroscopy. At lower temperatures, the equilibrium is in favour of the β-pyrano anomer, which is also present in the crystalline form of **1**. In view of these observations, we decided to elaborate on various aspects of the formation of compound **3**.

Treatment of 1,2;4,5-di-*O*-isopropylidene-β-D-fructopyranose (**4**)[8], or the 2,3;4,5 isomer (**5**)[8] with 2-chloroethanol + hydrogen chloride yielded **3** in 75 and 84% yields, respectively. In each case, a clear homogeneous solution was obtained at the outset, and a fine precipitate was produced as the reaction proceeded. Recrystallisation of this material yielded pure **3**. The results indicate that deacetalation with concomitant glycosidation occurs, though not necessarily in the solid phase.

When sucrose was treated with 2-chloroethanol in the described manner, followed by acetylation (acetic anhydride + pyridine) of the resultant crude solid material, analysis (GLC) showed it to be composed of the known[6] tetraacetate **6**, and α-D-glucopyranose pentaacetate (**7**) in the ratio 57:43. This result demonstrates that the D-glucose released during the reaction by hydrolysis of sucrose does not undergo glycosidation and can, therefore, easily be removed from the crude product by recrystallisation from water under buffered conditions.

When inulin was treated with 2-chloroethanol and hydrogen chloride for 72 h, the fructoside **3** was isolated in 77%

yield. The reaction of inulin with 2-chloroethanol had not been reported earlier[6]. There is much interest in its application as an alternative source of useful carbohydrate derivatives. It was not unexpected that it would lead to **3** in good yields, in view of its high D-fructose content. The melting-point behaviour of compound **3** merits some comment. In the original publication[6], it was described as melting at 146–147°C. The material obtained from all of our above reactions melted in the range 137–142°C with decomposition, and with sintering from 134°C onwards. An authentic[6] sample of **3** was shown to melt at 139–143°C, also with decomposition, and a mixed melting point with a sample of our material showed no depression. More recently, the melting point of **3** has been cited[9] as 139–141°C. Anomalous melting-point behaviour with fructopyranosides is not unprecedented[5]. Elemental analysis and subsequent reactions confirmed the purity of our material.

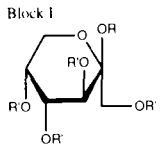
Application of the above reaction conditions to the reaction of **1**, sucrose, and inulin with 2-bromoethanol, 3-chloro-1-propanol, and 4-chloro-1-butanol yielded the expected β-D-fructopyranosides **8–10** in good to modest yields (89–14%). The yield of compound **10** was disappointingly low and was due to the greater solubility of this product in the reaction mixture. When a higher concentration of **1** was used, analysis of the product mixture showed it to contain unreacted **1** and the desired **10**, which on recrystallisation provided pure compound **10** in 21% yield. Treatment of **1** with 6-chloro-1-hexanol in a similar manner failed to yield the expected glycoside **11**. After a period of 8 days at room temperature, only unreacted **1** was recovered from the mixture.

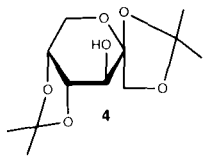
The pyranosidic nature of compounds **8–10** was established by comparison of the ^{1}H-NMR spectra of the corresponding tetraacetates **12–14**, obtained in the conventional manner (acetic anhydride + pyridine) with the values recorded[6] for the known peracetate **6** of compound **3**.

The scope of the simple glycosidation procedure was then investigated further. Treatment of **1** with 2-butoxyethanol, 2-methoxyethanol, 2-(2-ethoxyethoxy)ethanol, 3-hydroxypropionitrile, 1-octanol, and 2,2,2-trichloroethanol failed to yield the corresponding crystalline glycosides. Analysis (TLC) of the respective product mixtures indicated that **1** was either too insoluble in these alcohols or that a complex mixture of soluble equilibrated products was obtained, the nature of which was not investigated.

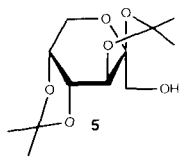
Commercial 4-chloro-1-butanol contains varying amounts (2–4%) of hydrogen chloride as an impurity, probably resulting from its spontaneous cyclisation to tetrahydrofuran. This fact is noted in the majority of manufacturer's catalogues. Qualitative investigation of the other ω-halogenoalkyl alcohols used in this study showed that they also contained significant amounts of the hydrogen halides (HCl or HBr) probably resulting from autohydrolysis. We showed that the amounts of hydrogen halide were in fact sufficient to catalyse the described glycosidation reactions, without the need to add additional hydrogen chloride as the catalyst. Compound **3**, **8**, **9** and **10** were obtained in this manner in yields approximating to those recorded for the normal acid-catalysed reactions.

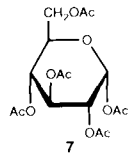
Exhaustive reductive hydrogenolysis of compound **8–10** over palladium on charcoal in the presence of sodium hydrogen carbonate at 45–50°C for 10 h yielded the corresponding alkyl β-D-fructopyranosides **15–17**. The hydrogenolysis of compound **3** in the same manner was, however, incomplete and resulted in only 52–58% conversion to **15**. A longer reaction period (32 h) with intermediate refreshment of the catalyst resulted in essentially complete reduction. The facility with which carbon–halogen bonds undergo hydrogenolysis depends on the





1 R = R' = H
2 R = $CH_2C_6H_5$, R' = H
3 R = CH_2CH_2Cl, R' = H
6 R = CH_2CH_2Cl, R' = Ac
8 R = CH_2CH_2Br, R' = H
9 R = $CH_2CH_2CH_2Cl$, R' = H
10 R = $CH_2CH_2CH_2CH_2Cl$, R' = H
11 R = $(CH_2)_6Cl$, R' = H
12 R = CH_2CH_2Br, R' = Ac
13 R = $CH_2CH_2CH_2Cl$, R' = Ac
14 R = $CH_2CH_2CH_2CH_2Cl$, R' = Ac
15 R = CH_2CH_3, R' = H
16 R = $CH_2CH_2CH_3$, R' = H
17 R = $CH_2CH_2CH_2CH_3$, R' = H
18 R = CH_3, R' = H





nature of the halogen atom and its environment[10]. The relative reactivity of chloro atoms in carbohydrate derivatives is not always predictable[11], and reductive dechlorination may be resisted even under very forcing conditions[12]. It has earlier[6] been demonstrated that treatment of **3** with methanolic hydrogen chloride gave methyl-β-D-fructopyranoside **18** in 50% yield. This is in agreement with the remarkable selectivity also shown[5] when the benzyl derivative **2** was treated under similar conditions to give **18** in 80% yield.

Adoption of this approach as an alternative for the synthesis of compounds **15–17** was unsuccessful. Compounds **3**, **8–10** did not dissolve when they were treated with the appropriate alcohols containing 1% hydrogen chloride and were recovered unchanged even after extended reaction periods of up to 4 days. When the mixtures were warmed gently to obtain solution, analysis (TLC) indicated the presence of complex mixtures of unreacted starting compounds and acid-catalysed products.

The transformations described here represent a useful non-chromatography route to glycosides of D-fructose (**1**). The chemistry of **1** has not developed at a rate comparable to the other common monosaccharides, although it is the second most abundant monosaccharide in nature. This is due mainly to a lack of readily available protected derivatives, especially glycosides.

Experimental

General methods

Optical rotations were determined with a Perkin–Elmer automatic polarimeter, model 241 MC on 1% solutions at 20°C. Thin-layer chromatography (TLC) on precoated plates of silica gel (Merck) was performed with dichloromethane/methanol (4/1, v/v). Detection was by spraying with 3% H_2SO_4 in ethanol and heating at 140°C. GLC was conducted with a Hewlett–Packard HP 5890 gas chromatograph, using a capillary column (25 m) of HP-1, a temperature program from 100° to 250° at 15°/min, followed by 10 min at 250° (isothermal), and nitrogen at 2 ml/min (0.5 atm) as the carrier gas. Compounds were identified by co-injection with authentic samples. ^{1}H and ^{13}C NMR were performed on a Bruker AM 400 spectrometer operating at 400 and 100.6 MHz, respectively, on solutions in $CDCl_3$ (internal Me_4Si) or D_2O (external dioxane at 67.8 ppm for ^{13}C). Chemical-ionisation mass spectra, induced with methane gas at 200°C and emission current 0.5 mAmp, were determined on a VG 7070E spectrometer (% of basepeak given in parenthesis). Inulin (ex dahlia tubers) purchased from Sigma Chemicals, and sucrose were powdered finely and dried *in vacuo* (80°C/15 mmHg) prior to use.

2'-Chloroethyl β-D-fructopyranoside (**3**)[6]

(a) From D-fructose (**1**). Powdered D-fructose (50.6 g, 0.28 mol) was added to 2-chloroethanol (400 ml) containing acetyl chloride (10 ml). The mixture was stirred at room temperature for 2 h and processed as described[6]. The crude product (65 g, 89%) was recrystallised from 5% aqueous sodium acetate to give pure **3** (49.4 g, 68%), m.p. 135–138°C (dec), $[\alpha]_D$ −147.5° (water); lit.[6] m.p. 146–147°C, $[\alpha]_D$ −148° (water).
The original filtrate from the above reaction mixture, kept apart from the washings, could be treated with additional amounts of **1** (50–55 g) for a total of 4 times to give further amounts of **3** (80–90%)[6].
In another reaction, **1** (2.5 g, 1.4 mmol) was added to 2-chloroethanol (20 ml) alone and the mixture stirred at room temperature for 4 h to give **3** (3.0 g, 90%), m.p. 136–138°C (dec), $[\alpha]_D$ −148° (water).

(b) From sucrose. Finely powdered sucrose (5 g, 14.6 mmol) was treated with a 1% solution of hydrogen chloride in 2-chloroethanol (16 ml) for 48 h at room temperature and processed as described in (a) to give **3** (2.37 g, 67%), m.p. 137–140°C (dec), $[\alpha]_D$ −146° (water).
In another experiment, the crude reaction product obtained from sucrose (2 g) in the same manner was acetylated in the usual way (acetic anhydride + pyridine) to give a mixture (TLC) of two compounds (4.63 g). GLC enabled identification of these as the tetraacetate **6**[6] and α-D-glucopyranose pentaacetate **7** by comparison with authentic samples.

(c) From inulin. Inulin (2.0 g) was treated with 2-chloroethanol containing 1% hydrogen chloride for 72 h at room temperature and then processed as described in (a) to give **3** (1.56 g, 58%), m.p. 136–138°C, $[\alpha]_D$ −148° (water).

2'-Bromoethyl β-D-fructopyranoside (**8**)

(a) From D-fructose (**1**). D-fructose (2.0 g, 11 mmol) was added to a stirred mixture of 2-bromoethanol (16 ml) and acetyl chloride (0.3 ml) and then set aside at room temperature for 2 h. The mixture was filtered and the crude product (3.0 g, 94%) recrystallised from 5% aqueous sodium acetate to give pure **8** (2.55 g, 80%), m.p. 127–129°C (dec), $[\alpha]_D$ −131.5° (water). Anal. $C_8H_{15}BrO_6$ (287.108) calcd.: C 33.47, H 5.27; found: C 33.79, H 5.33%. *M/z* 257 (4.33; $M^+ - CH_2OH$), 255 (4.38; $M^+ - CH_2OH$), 163 (2.99; $M^+ - CH_2CH_2Br$).
Treatment of **1** (30.0 g, 0.17 mol) with 2-bromoethanol (100 ml) alone at room temperature for 5 h followed by processing in the above manner; yielded **7** (24.5 g, 51%), m.p. 126–129°C (dec.), $[\alpha]_D$ −133.6° (water).
Treatment of a sample (175 mg, 0.6 mmol) of pure **8** with acetic anhydride (0.41 ml) and pyridine (1.6 ml) in the usual manner yielded 2-bromoethyl 1,3,4,5-tetra-*O*-acetyl-β-D-fructopyranoside (**12**) as a syrup (0.29 g, 72%), $[\alpha]_D$ −104° (chloroform). ^{1}H NMR ($CDCl_3$): δ 1.99, 2.07, 2.11, 2.17 (4s, each 3H, acetyl CH_3), 3.50–3.56 (m, 2H, H-2'a[a], H-2'b), 3.80–3.87 (m, 3H, H-6eq, H-1'a, H-1'b), 4.09 (d, 1H, $J_{1a,1b}$ −11.9 Hz, H-1a), 4.12 (dd, 1H, $J_{5,6ax}$ 1.3 Hz, $J_{6ax,6eq}$ −13.1 Hz, H-6ax), 4.30 (d, 1H, $J_{1a,1b}$ −11.9 Hz, H-1b), 5.39 (m, 2H, H-4 and H-5), 5.53 (d, 1H, $J_{3,4}$ 10.4 Hz, H-3) ppm. ^{13}C NMR ($CDCl_3$): δ 170.3, 170.1, 169.9 (acetyl, C=O), 99.0 (C-2), 68.8, 68.2 67.5 (C-3, C-4, C-5), 62.9, 62.2, 61.9 (C-1, C-6 and C-1'), 29.9 (C-2'), 20.9, 20.7 (acetyl CH_3) ppm. *M/z* 499 and 497 (0.1; $M + C_3H_7^+$), 439 and 437 (0.01; $M + C_3H_7^+ - AcOH$), 383 and 381 (10.1; $M^+ - CH_2OAc$), 331 (21.5; $M^+ - OCH_2CH_2Br$).

(b) From sucrose. Treatment of sucrose (5 g, 14.6 mmol) with 1% hydrogen chloride in 2-bromoethanol (20 ml) for 48 h at room temperature, followed by processing as in (a) gave **8** (2.80 g, 67%), m.p. 126–129°C (dec), $[\alpha]_D$ −130° (water).

(c) From inulin. Treatment of inulin (2 g) in the manner described above, but for 72 h, yielded **8** (1.31 g, 41%), m.p. 128–131°C (dec.), $[\alpha]_D$ −133° (water).

3'-Chloropropyl β-D-fructopyranoside (**9**)

(a) From D-fructose (**1**). D-fructose (9.8 g, 54 mmol) was added to a stirred mixture of 3-chloro-1-propanol (70 ml) and acetyl chloride (1.75 ml) and then set aside at room temperature for 3 h. The solid material (5.29 g, 37%) was collected by filtration and the filtrate treated with a further amount of **1** (9.46 g, 53 mmol) in the same manner. This process was repeated a further three times and the combined crude material (44.57 g, 66%) recrystallised from 5% aqueous sodium acetate to give pure **9** (33.1 g, 47%), 136–138°C (dec.), $[\alpha]_D$ −145°C (water). Anal. $C_9H_{17}O_6Cl$ (256.684) calcd.: C 42.11, H 6.88; found: C 42.15, H 6.65%. *M/z* 225 (50.41; $M^+ - CH_2OH$), 163 (16.1; $M^+ - OCH_2CH_2CH_2Cl$).
Acetylation of **9** (125 mg) in the usual manner with acetic anhydride (0.4 ml) and pyridine (1.6 ml) gave the tetraacetate **13** as a syrup (140 mg, 65%): $[\alpha]_D$ −118° ($CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.09–2.05 (m, 2H, H-2'a[b], H-2'b), 1.98, 2.07, 2.10, 2.16 (4s, each 3H, acetyl CH_3), 3.63-3.74 (m, 4H, H-1'a, H-1'b, H-3'a and H-3'b), 3.83 (dd, 1H, $J_{6eq,6ax}$ −13.1, $J_{5,6ax}$ 1.8 Hz, H-6ax), 3.90 (dd, 1H, $J_{5,6eq}$ 1.4 Hz, H-6eq), 4.12 (d, 1H, $J_{1a,1b}$ −11.9 Hz, H-1a), 4.31 (d, 1H, H-1b), 5.30 (dd, 1H, $J_{4,5}$ 3.5 Hz, H-4), 5.36 (m, 1H, H-5), 5.52 (d, 1H, $J_{3,4}$ 10.6 Hz, H-3) ppm. ^{13}C NMR ($CDCl_3$): δ 170.3, 170.1, 169.8 (acetyl C=O), 98.8 (C-2), 68.8, 68.3, 67.6 (C-3, C-4, C-5), 62.8, 61.9 (C-6, C-1), 57.8 (C-1'), 41.3 (C-3'), 32.3 (C-2'), 20.9, 20.8, 20.7 (acetyl CH_3) ppm. *M/z* 449 (5.29; $M + {}^+C_3H_7$), 425 (0.01; $M + H^+$), 365 (0.01; $M^+ + H^+ - AcOH$) 351 (20.64; $M^+ - CH_2OAc$), 331 (36.01; $M^+ - OCH_2CH_2CH_2Cl$), 271 (3.54; $M^+ - OCH_2CH_2CH_2CH_2Cl - AcOH$), 211. (29.42; $M^+ - OCH_2CH_2CH_2Cl - 2AcOH$).

(b) From sucrose. Sucrose (5.0 g, 14.6 mmol) was treated with 1% hydrogen chloride in 3-chloro-1-propanol (20 ml) at room temperature for 9 days and then processed as above in (a) to give **9** (2.70 g, 70%), m.p. 136–139°C (dec), $[\alpha]_D$ −143° (water).

(c) From inulin. Treatment of inulin (2.0 g) in the same above manner but for a period of 11 days yielded **9** (1.25 g, 43%), m.p. 137–142°C (dec.) $[\alpha]_D$ −143° (water).

4'-Chlorobutyl β-D-fructopyranoside (**10**)

Finely powdered D-fructose (**1**, 2.0 g, 11 mmol) was added to a stirred mixture of 4-chloro-1-butanol (10 ml) and acetyl chloride (0.2 ml), set aside at room temperature for 4 h, and then stored at 5°C for 16 h. The resultant solid material (0.71 g, 24%) was recrystallised from 5% aqueous sodium acetate to give compound **10** (0.4 g, 14%), m.p. 111–113°C (dec.) $[\alpha]_D$ −126° (water). Anal. $C_{10}H_{19}ClO_6$ (270.711) calcd.: C 44.37; H 7.07; found: C 44.38, H 7.02%. *M/z* 271 (0.67; $M + H^+$), 253 (4.82; $M^+ + H^+ - 2H_2O$), 239 (16.55; $M^+ - CH_2OH$), 163 (43.31; $M^+ + H^+ - HO(CH_2)_4Cl$), 145 (27.86; $M^+ + H^+ - HO\text{-}(CH_2)_4\text{-}Cl - H_2O$), 127 (12.53; $M^+ + H^+ - HO\text{-}(CH_2)_4\text{-}Cl - 2H_2O$).
In another experiment, **1** (8,0 g, 44 mmol) was added in portions with stirring to 4-chloro-1-butanol (35 ml) and the mixture set aside at room temperature for 8 h. The resultant solid material was washed with ice-cold 2-propanol and recrystallised as above to give **10** (2.48 g, 21%), m.p. 114–116°C, $[\alpha]_D$ −126° (water).
A portion of compound **10** (0.2 g, 0.7 mmol) was acetylated as described to give the tetraacetate **14** as a syrup (0.276 g, 85%), $[\alpha]_D$ −94.4° ($CHCl_3$). ^{1}H NMR ($CDCl_3$) δ, 1.77 (m, 2H, H-3'a[c], H-3'b) 1.87 (m, 2H, H-2'a, H-2'b), 1.98, 2.06, 2.10, 2.16 (4s, 3H each, acetyl CH_3), 3.47–3.65 (m, 4H, H-1' and H-4'), 3.81 (dd, 1H, $J_{6ax,6eq}$ 13.0 Hz, $J_{5,6ax}$ 1.6 Hz, H-6ax), 3.86 (dd, 1H, $J_{5,6eq}$ 1.1 Hz, H-6eq), 4.08 (d, 1H, $J_{1a,1b}$ −11.9 Hz, H-1b), 4.29 (d, 1H, Hz, H1a). 5.30 (dd, 1H, $J_{4,5}$ 3.5 Hz, H-4), 5.36 (m, 1H, H-5), 5.51. (d, 1H, $J_{3,4}$ 10.5 Hz, H-3) ppm. ^{13}C NMR ($CDCl_3$) 170.3, 170.1, 169.8 (acetyl C=O), 98.8 (C-2), 68.8, 68.3, 67.6 (C-3, C-4, C-5), 62.7, 61.8, 60.9 (C-6, C-1, C-1'), 44.5 (C-4'), 29.5, 27.0 (C-2', C-3'), 20.9, 20.6 (acetyl CH_3) ppm. *M/z* 481 (0.96; $M + C_3H_7^+$).421 (0.21; $M + C_3H_7^+ - AcOH$).439 (0.02; $M + H^+$), 379 (3.3; $M + H^+ - AcOH$), 331 (90.0; $M + H^+ - HO(CH_2)_4Cl$), 271 (14.4; $M + H^+ - HO(CH_2)_4Cl - AcOH$), 211 (79.3; $M + H^+ - HO(CH_2)_4Cl - AcOH$)

Ethyl β-D-fructopyranoside (**15**)

(a) From compound **3**. A suspension of **3** (2.0 g, 8.2 mmol) in water (100 ml) was treated with sodium hydrogen carbonate (1.0 g) and palladium on charcoal (5%, 200 mg) and the mixture hydrogenated at 45–50°C for 16 h. A further portion of Pd/C (200 mg) was then added and hydrogenation was continued for a further 16 h at 45–50°C. The insoluble material was removed by filtration, washed with water, and the combined filtrate and washings evaporated *in vacuo*. A solution of the residue in water (20 ml) was de-ionised by

[a] Ethyl atoms are primed.

[b] Propyl atoms are primed.

[c] Butyl atoms are primed.

successive percolation through columns (21×3 cm) of IRA-400 (HCO_3^- form) and IRA-120 H^+ form) ion-exchange resins. The combined eluates and washings were concentrated *in vacuo* and the residue (1.62 g, 94%) recrystallised from ethanol to give compound **15** (1.28 g, 75%), m.p. 153–155°C, $[\alpha]_D$ −155° (methanol) [lit.[1] m.p. 157–157.9°C, $[\alpha]_D$ −134° (methanol); lit.[3] m.p. 150–151°C, $[\alpha]_D$ −136° (methanol)]. ^{13}C NMR (D_2O): δ 101.8 (C-2), 70.9, 70.4 (C-3, C-4), 69.4 (C-5), 65.0, 62.5 (C-1, C-6), 57.9 (C-1′), 15.9 (C-2′) ppm. *M/z* 177 (100; $M^+ - CH_2OH$), 163 (72.26; $M^+ - OC_2H_5$), 145 (30.82; $M^+ - OC_2H_5 - H_2O$), 127 (18.76; $M^+ - OC_2H_5 - 2H_2O$).

(b) From compound **8**. Hydrogenolysis of **8** (5.0 g, 17.5 mmol) in the presence of sodium hydrogen carbonate (3.0 g) and Pd/C (5%, 500 mg) for 16 h at 45–50°C followed by treatment as described above in (*a*) yielded **15** (2.95 g, 81%), m.p. 152–154°C (from ethanol), $[\alpha]_D$ −155° (methanol).

n-Propyl β-D-fructopyranoside (**16**)

Hydrogenolysis of compound **9** (1.35 g, 16 mmol) in the above described manner gave **16** (0.878 g, 51%), m.p. 161–163°C (from ethanol), $[\alpha]_D$ −151° (methanol); lit.[3] m.p. 157–158°C, $[\alpha]_D$ −142° (methanol). ^{13}C NMR (D_2O): δ 101.7 (C-2), 70.9, 70.4 (C-3, C-4), 69.5 (C-5), 65.0, 63.4 (C-1, C-6), 62.6 (C-1′), 23.8 (C-2′), 11.2 (C-3′) ppm. M/z 191 (100; $M^+ - CH_2OH$), 163 (75.93; $M^+ - OC_3H_7$), 145 (54.30; $M^+ - OC_3H_7 - H_2O$), 127 (27.01; $M^+ - OC_3H_7 - 2H_2O$).

n-Butyl β-D-fructopyranoside (**17**)

Hydrogenolysis of compound **10** (1.0 g, 3.7 mmol) as described above in (*b*) gave **17** (0.35 g, 41%), m.p. 156–158°C (ethanol), $[\alpha]_D$ −145° (methanol). ^{13}C NMR (D_2O): δ 101.7 (C-2), 70.9, 70.4 (C-3, C-4), 69.5 (C-5), 65.1, 62.5 (C-1, C-6), 62.1 (C-1′), 32.6 (C-2′), 20.1 (C-3′), 14.4 (C-4′) ppm. *M/z* 205 (73.34; $M^+ - CH_2OH$), 177 (3.67; $M^+ - CH_2OH - H_2O$), 163 (100; $M^+ - OC_4H_9$), 145 (35.45; $M^+ - OC_4H_9 - H_2O$), 127 (15.73; $M^+ - OC_4H_9 - 2H_2O$).

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