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Acetalation studies. Part IX[Φ]. Reaction of sucrose and some related sugars with acetone in the presence of iodine; a novel cleavage–isopropylidenation method[Ψ]

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Abstract. An efficient cleavage–isopropylidenation reaction of sucrose, catalyzed by iodine, is described. Related D-fructofuranosyl-containing oligosaccharides, some common disaccharides and their individual monosaccharide units were treated in a similar manner to yield isopropylidenated monosaccharide derivatives. The reaction conditions are particularly mild and selective. Some mechanistic aspects of the procedure are also discussed.

Introduction

The conventional acid catalyzed isopropylidenation of sucrose (saccharose, **1**) has been studied severally[1]. Interglycosidic-bond cleavage leading to the formation of acetals of D-glucose and D-fructose has invariably resulted. The monoacetal **2** and diacetal **3** were prepared eventually by acid-catalyzed exchange between **1** and 2,2-dimethoxypropane[2,3] or 2-methoxypropene[4]. Prolonged treatment at higher catalyst concentrations causes glycosidic bond fission, and several unusual acetals of D-glucose and methyl α-D-fructofuranoside have been isolated and characterized[5]. As part of recent studies[6] of the development of new mild catalysts for the acetalation of acid-sensitive substrates, sucrose (**1**) was treated with iodine in boiling acetone. Very efficient cleavage of the interglycosidic bond with concomitant isopropylidenation occurred to yield the diacetals **4**, **5**, and **6**. The related fructofuranosyl-containing oligosaccharides inulin (**7**), and raffinose (**8**), their constitutional monosaccharide units, D-fructose, D-galactose and D-glucose, and some common disaccharides were then treated under similar conditions. The results of this study and some related aspects are now described.

Results and discussion

When sucrose (**1**) was treated with a catalytic amount of iodine in boiling acetone for 4 h three products were yielded (TLC, solvent B). Further analysis (GLC) of the crude product mixture identified these as the di-*O*-isopropylidene compounds **4** (47%), **5** (37%) and **6** (11%). They were the only products produced and there appeared to be no unreacted compound **1** in the mixture (TLC, solvent A). Treatment of this mixture with 80% aqueous acetic acid, followed by selective ether extraction, yielded pure monoacetal **9**; compounds **5** and 1,2-*O*-isopropylidene-β-D-fructopyranose (**10**), resulting from the partial acid hydrolysis of **6**, were separated by fractional recrystallization. Compounds **5** and **9**, isolated directly, were sufficiently pure (GLC) for use as synthetic intermediates without further purification. These acetals have been obtained[7,8] previously from **1**, but the procedures described involve several tedious isolation and purification steps. The method described here represents an improved direct route which could be important for future large-scale use of sucrose (**1**).

In view of this observed facile cleavage–acetalation sequence, attention was directed towards the treatment of inulin (**7**) under similar conditions. There has been considerable interest expressed recently[9] in **7** as a potential raw material for the production of *inter alia* D-fructose, ethanol, 2,3-butanediol, D-mannitol, glycerol, 5-(hydroxymethyl)-2-furaldehyde and 4-oxopentanoic acid (laevulinic acid). Some of these proposals must be considered still speculative, but its use in medicine and food technology is established. The chemistry of **7** merits further study.

Thus, treatment of a stirred suspension of **7** in boiling acetone with a catalytic amount of iodine produced a clear solution after 16 h. Analysis (GLC) of the mixture revealed compound **5** (88%) and compound **6** (12%); pure compound **5** (58%) was isolated from the crude product (81%) by direct recrystallization. Diacetal **4** was not identified as a component of the product mixture. The D-glucose content of **7** varies between approximately 1.5 and 5% depending on the source and analytical procedure[10].

Conventional acid-catalyzed isopropylidenation of **7** was found[11] not to be a convenient source of the acetals **5** and **6**. Long reaction times (4–7 days) were required for the hydrolysis–isopropylidenation sequence during which considerable degradation and formation of coloured by-

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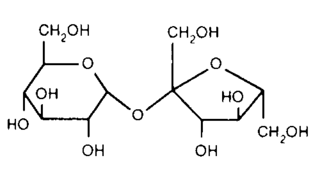
[Φ] Part VIII, see ref. 6.

[Ψ] Part of this work was presented at the 6th European Symposium on Carbohydrate Chemistry, Edinburgh Scotland, 8–13th September 1991.



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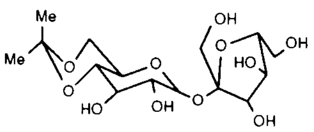

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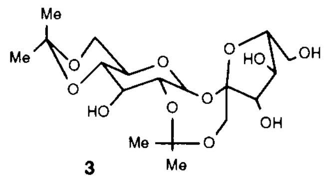

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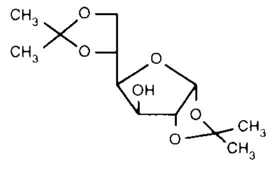

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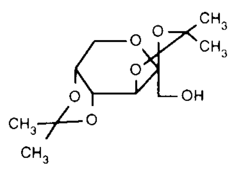

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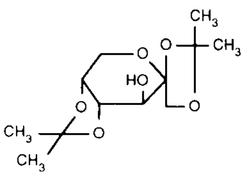

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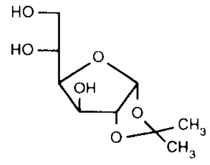

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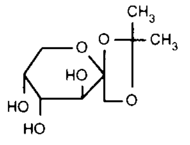

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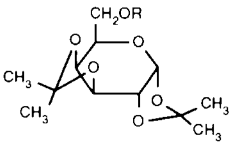


11 R = H

17 R = Ts

products was observed. The combined yields of **5** and **6** were not high (*ca.* 45%), and the product mixtures were difficult to purify. The known[12] acid-catalyzed formation of D-fructose anhydrides from **7**, and the complex series of reactions that D-fructose undergoes when treated with acid, probably attributed to the complexity of this system[11,12].

When raffinose (**8**), another common fructofuranosyl-containing tri-saccharide was treated under identical conditions for 72 h, compounds **4** (27%), **5** (37%), **6** (4%) and 1,2:3,4-di-*O*-isopropylidene-D-galactose (**11**, 28%) were identified (GLC) as the reaction products. No attempt was made to separate these compounds from the crude syrupy product, which was obtained in 84% yield.

Treatment of **8** in the same way, but for only 6 h, followed by acetylation of the insoluble portion of the crude reaction product yielded β-D-melibiose octaacetate (**12**, 46%). The parent disaccharide **13** is normally[13] prepared by fermentation of **8** with top yeast (baker's yeast). During fermentation the sucrose-type linkage is cleaved by the invertase present forming **13** and D-fructose. The method described here represents a simple alternative, albeit in lower yield.

The formation of **11** from **8** suggested that the cleavage reaction may not be restricted to only non-reducing fructofuranosyl linkages. We decided therefore to investigate the effects of the reagent combination on a number of common disaccharides containing only pyranosyl linkages. D-Melibiose (**13**), D-cellobiose (**14**), D-maltose (**15**) and D-lactose (**16**) were chosen as models. The results of these experiments are depicted in Table I.

The observed order of reactivity parallels that for the normal acid-catalysed hydrolysis of these saccharides[14], but with a much lower degree of cleavage. The relatively high reactivity of **13** was not unexpected in view of the result obtained with raffinose (**8**). D-Cellobiose is known[14] to be more resistant to hydrolysis than the other disaccharides. The results indicate that the majority of pyranosyl linkages would probably be unaffected by the mixture under the usual reaction conditions, *i.e.* low catalyst concentration and short reaction times. The reaction of other glycopyranosides is currently being investigated.

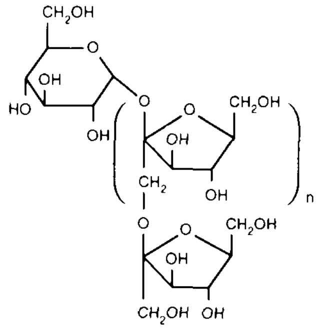
Table I Reactivity of disaccharides with acetone containing iodine.

Substrate	Substrate recovered (%)	Products		
		Compound	Composition[a]	Yield (%)
D-melibiose (**13**)	54	**4** + **10**	43:34	27
D-cellobiose (**14**)	94	–	–	–
D-maltose (**15**)	64	**4**	68	16
D-lactose (**16**)	66	**4** + **11**	39:24	16

[a] Determined by GLC.

Iodine is a recognized[15] catalyst or reagent in organic chemistry, but has not previously found wide application in carbohydrate chemistry. The cleavage of **1** by iodine in *N*,*N*-dimethylformamide at 100°C to yield 5-(hydroxymethyl)-2-furaldehyde has been reported[16]. The reaction was restricted to the released D-fructose unit. D-Glucose was recovered essentially unchanged, and no degradation occurred in the absence of iodine. A mechanism involving the generation of a carbocation on D-fructofuranose, followed by a series of dehydration steps, was proposed.

Iodine has recently[17] been proposed as a catalyst for the isopropylidenation of some simple monosaccharides and sugar alcohols with acetone. The amount of iodine employed (300 mg/g substrate) seems excessive in view of its earlier reported[18,19] uses as a dehydrating and condensing agent. Carbohydrate acetals and dithioacetals are cleaved[20] by dilute solutions of iodine in methanol. The product mixtures are composed mainly of furanoside mixtures approximating to the early stages of conventional acid catalysed methanolysis. Simple glycosides and disaccharides, including some sucrose derivatives, are unaffected under the conditions which may be considered more forcing than those employed in the current study.



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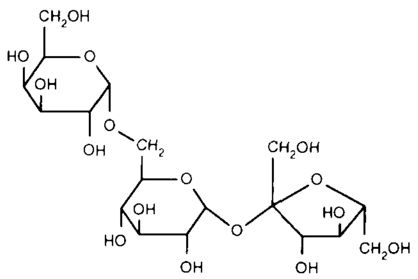

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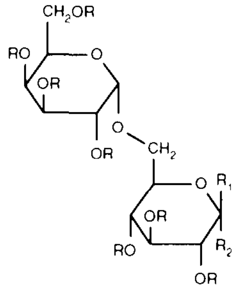
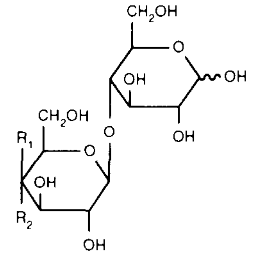
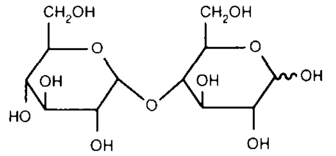






12 R = Ac, R_1 = OAc, R_2 = H

13 R = H, R_1 = H, R_2 = OH

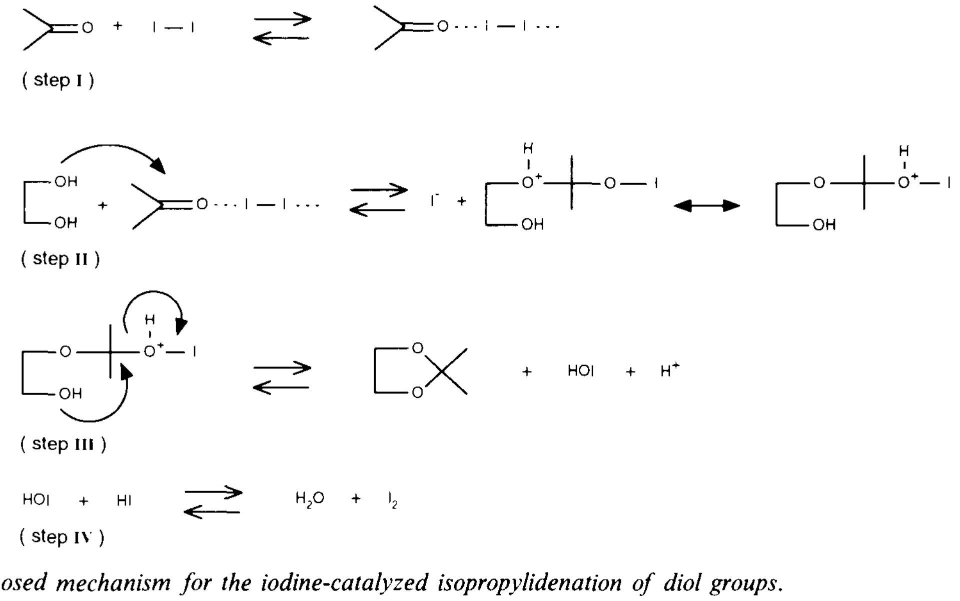
14 R_1 = H, R_2 = OH

16 R_1 = OH, R_2 = H

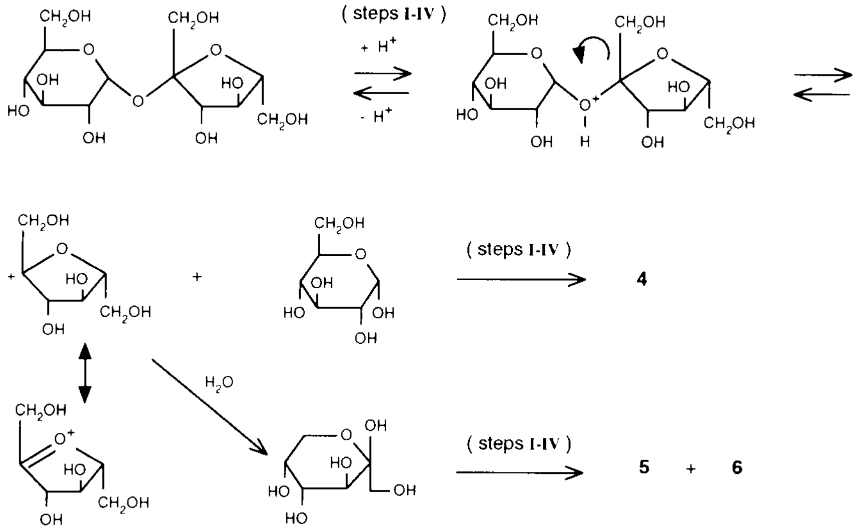
15

The mechanism of the reactions described herein probably occurs by two closely associated processes. The sequences are initiated by the formation of an acetone–iodine addition complex[21] followed by the partial or complete acetalation of suitable vicinal diol groups (1A). This leads to the subsequent generation of mildly acidic conditions which are sufficient to cause cleavage of acid sensitive glycosidic bonds. The facile and mild acid hydrolysis of sucrose (**1**), and related saccharides, occurs by the collapse of an oxonium ion to give D-glucose and a D-fructofuranosyl carbocation which reacts further with water to give D-fructose (1B). The released monosaccharides then undergo further isopropylidenation by a process which is analogous to the conventional acid-catalyzed reaction. The proposed sequences are depicted in fig. 1A and 1B, but await further clarification.

Our attentions were subsequently directed towards the treatment of the individual monosaccharide structual units of the saccharides used in this investigation, under similar conditions. The yield of the diacetal **4** (71.5%) from D-glucose was particularly gratifying. There are a number[22,23] of well-established syntheses of this well-known derivative, they all involve time-consuming neutralization and purification steps. There is frequently the need to remove considerable amounts of unreacted D-glucose and the monoacetal **9** from the product. Compound **4** and **9** are two of the most frequently employed carbohydrate synthons and have found numerous applications in both carbohydrate



Figuur 1A. Proposed mechanism for the iodine-catalyzed isopropylidenation of diol groups.



Figuur 1B. Acid-catalyzed hydrolysis of sucrose and isopropylidenation of the released monosaccharides.

and natural product chemistry. They also provide convenient routes to *inter alia* usefully protected derivatives of D-allose[24,25], D-gulose[26], D-ribose[27,28], and D-idose[29]. Compound **4** has recently[30] been employed as an intermediate in syntheses of D-ribulose and D-erythronic acid. The facile formation of either of the di-*O*-isopropylidene-D-fructopyranose derivatives **5** (81.5%) and **6** (70%) depending on the reaction conditions is noteworthy. Compound **5** is considered to be the thermodynamically controlled product from the normal acid-catalyzed condensation of D-fructose with acetone, whereas **6** is the kinetic product. The diacetal **6** is formed initially, but isomerizes to **5** at a rate depending upon the catalyst concentration. The use of zinc chloride is reported to favour the formation of **6**. A comprehensive study of the optimal conditions required for the isolation of the two components has been described[31] but it was reported that purification of the crude products by fractional crystallization was not readily achieved. The conditions described here now represent the most convenient reported hitherto.

The conventional acid-catalyzed condensation of acetone with D-galactose provides compound **11** in good yield[32] but the crude product needs to be freed from considerable quantities of acetone condensation products by distillation *in vacuo*. The procedure now described leads to essentially pure material in excellent yield (83.5%), without further purification. The syrupy product was characterized as the known[32] *p*-toluenesulphonate **17** in the usual manner.

For comparative purposes D-glucose was also treated with acetone containing iodine (0.21 equivs) under the conditions described by *Kartha*[17]. Although analysis (GLC) of the crude product indicated that the diacetal **4** was present in 77% yield difficulty was encountered in isolating the pure material (45%) because of the acetone condensation products present. When acetone alone was treated with the same quantity of iodine, dark oily material was isolated which on analysis (GLC) was shown to contain at least 11 constituents, whereas only trace amounts of these materials were detected when the lower quantity of iodine was employed.

Further examples of the use of this novel isopropylidenation procedure, and its application to other carbonyl derivatives are currently under investigation.

This investigation was carried out with the financial support of the Dutch National Innovation Program Carbohydrates (IOP-k).

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 pre-coated plates of silica gel (Merck) was performed with dichloromethane/methanol (4/1, v/v, solvent A) or hexane/ethyl acetate (1/1, v/v, solvent B). Detection was affected by spraying with 3% H_2SO_4 in ethanol and heating at 140°C. GLC was performed with a Hewlett–Packard 5790 gas chromatograph; a fused-silica capillary column (25 m) coated with HP-1 cross-linked methyl silicone gumphase operating at 100–150°C (t = 0 min 100°C isothermal; t = 5 min 5°C/min) and nitrogen as the carrier gas at 2 ml/min was used. Compounds were identified by co-injection with authentic samples. The percentages composition of the analysed mixtures are all relative. ^{1}H NMR spectra were recorded with a Bruker AC 100 (100 MHz) spectrometer on solutions in $CDCl_3$ (internal standard Me_4Si), and were used routinely to identify known products. Inulin, (ex dahlia tubers) purchased from Sigma Chemicals, and sucrose were powdered finely and dried *in vacuo* (80°C/15 mm) prior to use.

Reaction of acetone containing iodine

(a) With sucrose (1). A stirred suspension of sucrose (**1**, 10.0 g, 29.2 mmol) in acetone (500 ml) was treated with iodine (75 mg, 0.3 mmol, 0.01 equivs) and the mixture was heated under reflux for 4 h, whereon a clear solution was obtained. The cooled mixture was treated with 0.5M aqueous sodium thiosulphate solution until colourless, concentrated *in vacuo*, and the resultant product was dissolved in a mixture of dichloromethane (250 ml) and water (50 ml). The separated organic layer was washed with water (2 x 100 ml), 10% aqueous sodium chloride solution (100 ml), dried (Na_2SO_4), and concentrated *in vacuo* to give a colourless oil (14.44 g) which crystallized on standing.

The crude product was dissolved in 80% aqueous acetic acid (200 ml), set aside at room temperature for 22 h, and concentrated *in vacuo*. The residue was suspended in ether (100 ml), heated to boiling with stirring, and then stored overnight at 4°C. The resultant solid material (5.12 g, 80%) was collected by filtration, washed with cold ether (25 ml) and recrystallized from diisopropyl-ether/methanol to give 1,2-*O*-isopropylidene-α-D-glucofuranose (**9**, 4.03 g, 63%), m.p. 161–162°C, $[\alpha]_D$ $-11.6°$ (water); lit.[22] m.p. 160–161°C, $[\alpha]_D^{19}$ $-11.4°$ (water).

The combined filtrate and washings were washed with water (50 ml), dried ($CaCl_2$), concentrated *in vacuo*, and the crude product (5.41 g) was recrystallized from diisopropyl-ether/hexane to yield 2,3;4,5-di-*O*-isopropylidene-β-D-fructopyranose (**5**, 3.15 g). Treatment of the mother liquor with petroleum ether, b.p. 80–100°C, yielded more **5** (0.87 g); combined yield (4.02 g, 53%), m.p. 95–96°C, $[\alpha]_D$ $-38.5°$ (acetone); lit.[31] m.p. 97°C, $[\alpha]_D^{25}$ $-38.1°$ (acetone).

The above separated water washings were concentrated *in vacuo* and the crystalline residue recrystallized from diisopropyl-ether/ethanol to give the monoacetal **10** (0.22 g, 3.4%), m.p. 122–123°C, $[\alpha]_D$ − 160° (water); lit.[33] m.p. 120–121°C, $[\alpha]_D$ − 158.9° (water). The remainder of the material in the mother liquor was a mixture of compounds **9** and **10** which were not separated further.

(b) With inulin (7). A stirred mixture of inulin (**7**, 500 mg) suspended in acetone (50 ml) containing iodine (35 mg, 0.14 mmol, 0.05 equivs) was heated under reflux for 16 h and the resulting clear solution processed as described above in *(a)*. Recrystallization of the crude crystalline product (589 mg, 81%) from diisopropyl-ether/hexane gave pure **5** (419 mg, 58%), m.p. 94–95°C, $[\alpha]_D$ − 38.2° (acetone).

(c) With D-raffinose pentahydrate (8). A stirred suspension of **8** (1.003 g) in acetone (50 ml) containing iodine (21 mg, 0.08 mmol, 0.05 equivs) was heated under reflux for 72 h and processed as described in *(a)*. The resultant pale-yellow oil (1.036 g, 84%) was subjected to analysis (GLC), but it was not separated further.

In another experiment **8** (2.973 g, 5 mmol) suspended in acetone (120 ml) containing iodine (45 mg) was heated under reflux with stirring for 6 h. The resultant mixture was cooled to room temperature and the insoluble material was collected by filtration, washed with acetone (2 x 20 ml) and dried *in vacuo* over P_4O_{10}. The dried product (1.82 g) was added in small portions to a boiling mixture of anhydrous sodium acetate (0.5 g) in acetic anhydride (10 ml). On completion of the addition the mixture was maintained at 100°C for 15 min, cooled to room temperature, poured with stirring into ice water (200 ml), and stored at 0°C for 24 h. The water was decanted from the semi-solid material, which was dissolved in dichloromethane (75 ml) and the extract was washed successively with water (20 ml), saturated aqueous sodium hydrogen carbonate (20 ml), and water (10 ml). The dried (Na_2SO_4) washed extract was concentrated *in vacuo* and the residue recrystallized from ethanol to give β-D-melibiose octaacetate (**12**, 1.56 g, 46%), m.p. 173–176°C, $[\alpha]_D$ + 102° ($CHCl_3$); lit.[13] m.p. 177–178°C, $[\alpha]_D$ + 104° ($CHCl_3$).

(d) With D-melibiose (13), D-cellobiose (14), D-maltose (15) and D-lactose (16). The individual disaccharide, monohydrates (1.0 g) suspended in acetone (50 ml) containing iodine (40 mg, 0.05 equivs) were heated under reflux with stirring for 72 h. The resulting mixtures were cooled and the unreacted materials collected by filtration, washed with acetone (20 ml) and dried *in vacuo* (P_4O_{10}). The combined filtrate and washings were processed as described above in *(a)* and subjected to analysis (GLC). The results of these experiments are reported in Table I. The unreacted portion of the products were characterised by ^1H NMR spectroscopy (D_2O) in the usual manner by comparison with authentic samples of the disaccharides.

(e) With D-glucose. D-Glucose (10.0 g, 55.5 mmol) suspended in acetone (500 ml) containing iodine (700 mg, 2.76 mmol, 0.05 equivs) was heated under reflux with stirring for 2 h, and then processed as described in *(a)*. Recrystallization (petroleum ether, 80–100°C) of the resultant crude product (12.6 g, 87%) afforded **4** (10.32 g, 71.5%), m.p. 110°C, $[\alpha]_D$ − 18.8° (water); lit.[22] m.p. 110°C, $[\alpha]_D^{20}$ − 19.7° (water).

In another experiment treatment of D-glucose with iodine (140 mg, 0.01 equivs) in the same manner, but for 4 h, gave essentially the same result.

(f) With D-fructose. A stirred suspension of D-fructose (1.075 g, 5.96 mmol) in acetone (50 ml) containing iodine (71.7 mg, 0.28 mmol, 0.05 equivs) was heated under reflux for 3 h and processed as in *(a)*. Recrystallization of the crude product (1.265 g, 81.5%) from diisopropyl-ether/hexane gave **5** (965 mg, 62%), m.p. 94–95°C, $[\alpha]_D$ − 37.6° (acetone); lit.[31] m.p. 97°C, $[\alpha]_D$ − 33.6° (acetone).

In another experiment D-fructose (10.06 g, 55.5 mmol) suspended in acetone (250 ml) containing iodine (745 mg, 2.94 mmol, 0.05 equivs) was stirred at room temperature for 3 h and then processed as in *(a)*. The resultant crude product (10.20 g, 70%) was recrystallized from diisopropyl-ether/hexane to give **6** (6.24 g, 43%), m.p. 117–119°C, $[\alpha]_D$ − 158° (acetone); lit.[31] m.p. 119°C, $[\alpha]_D^{20}$ − 161° (acetone).

(g) With D-galactose. A stirred suspension of D-galactose (1.006 g, 5.55 mmol) in acetone (50 ml) containing iodine (70.5 mg, 0.28 mmol, 0.05 equivs) was heated under reflux for 45 min and then processed as described in *(a)* to give essentially pure **11** (1.206 g, 83.5%) as a pale yellow oil, $[\alpha]_D$ − 55.2° ($CHCl_3$); lit.[32] $[\alpha]_D^{29}$ − 55° ($CHCl_3$).

Treatment of the pure product with *p*-toluenesulphonyl chloride/pyridine in the usual manner gave the *p*-toluenesulphonate **17** (53%) after recrystallization from ethanol, m.p. 100–102°C, $[\alpha]_D$ − 64.5° ($CHCl_3$); lit.[32] m.p. 102–103°C, $[\alpha]_D$ − 66° ($CHCl_3$).

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