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SYNTHESIS OF 5-*O*-α- AND -β-D-GLUCOPYRANOSYL-D-GLUCOFURANOSE AND 5-*O*-α-D-GLUCOPYRANOSYL-D-FRUCTOPYRANOSE (LEUCROSE)

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ABSTRACT

Reaction of 1,2-*O*-cyclopentylidene-α-D-glucofuranurono-6,3-lactone (**2**) with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**1**) gave 1,2-*O*-cyclopentylidene-5-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-glucofuranurono-6,3-lactone (**3**, 45%) and 1,2-*O*-cyclopentylidene-5-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucofuranurono-6,3-lactone (**4**, 38%). Reduction of **3** and **4** with lithium aluminium hydride, followed by removal of the cyclopentylidene group, afforded 5-*O*-α- (**9**) and -β-D-glucopyranosyl-D-glucofuranose (**12**), respectively. Base-catalysed isomerization of **9** yielded crystalline 5-*O*-α-D-glucopyranosyl-D-fructopyranose (leucrose, 53%).

INTRODUCTION

The disaccharide leucrose (**13**) has been isolated from dextran-producing cultures of *L. mesenteroides*[1] and *S. bovis*[2,3]. The latter bacterium also produces 5-*O*-α-isomaltosyl-D-fructopyranose[3]. In addition, 5-*O*-α-D-glucopyranosyl-D-glucofuranose (**9**), which is closely related structurally to **13**, was erroneously believed to be present in manioc flour[4–6].

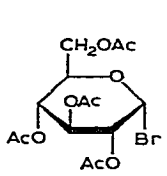
We have prepared[6] 5-*O*-(2-acetamido-2-deoxy-α-D-glucopyranosyl)-β-D-glucofuranose (**11**) *via* condensation of dimeric 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride with 1,2-*O*-isopropylidene-α-D-glucofuranurono-6,3-lactone. However, attempted preparation of **9** by a similar route failed. The cyclopentylidene acetal is a better protecting group for the glucofuranose residue than is the isopropylidene acetal[7], and we now report the synthesis of **9**, **12**, and **13** using 1,2-*O*-cyclopentylidene-α-D-glucofuranurono-6,3-lactone[7] (**2**) as the aglycon precursor.

RESULTS AND DISCUSSION

Condensation of **1** with **2**[7] in acetonitrile in the presence of mercuric cyanide and bromide was poorly stereospecific. However, the yield of products was high in comparison with that (10–11%) from 3,6-di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose[8,9]. The coupling products **3** (45%) and **4** (38%) were readily separated

by fractional crystallization from ethanol. Reduction of **3** and **4** with lithium aluminium hydride in 1,2-dimethoxyethane afforded the cyclopentylidene-protected disaccharides, which were isolated and characterized as the hexa-acetates **5** and **6**, respectively. Deacetylation of **5** and **6** in methanolic sodium methoxide gave 1,2-*O*-cyclopentylidene-5-*O*-α- (**7**) and -β-D-glucopyranosyl-α-D-glucofuranose (**8**), respectively. The ^{1}H-n.m.r. spectra obtained at various stages of the preparation of **7** and **8** were in agreement with the structures assigned. The anomeric configuration of the acetates **3**–**6** was established on the basis of the chemical shift of H-5′; H-5 in 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosides resonates at higher field than in the α anomers. The interglycosidic, anomeric proton resonances were discernible after deacetylation.

The removal of the cyclopentylidene group from **7** and **8** was effected with 0.52M sulphuric acid[7], yielding the free sugars **9** and **12** (~96%), respectively. The change in optical rotation accompanying the hydrolyses was consistent with the presence of a (1 → 5)-linkage[7] in both **9** and **12**. Compound **12** was characterized as its known toluene-*p*-sulphonylhydrazone[9,10]. The g.l.c. data (Table I) for the



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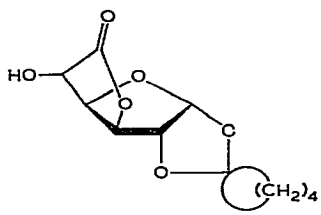

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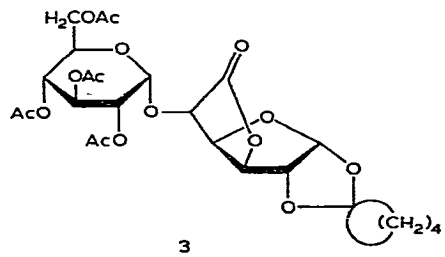

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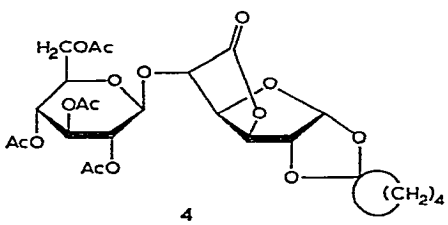

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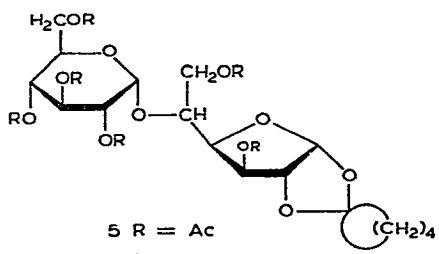

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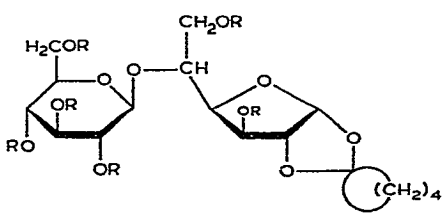
7 R = H



6 R = Ac
8 R = H

TABLE I

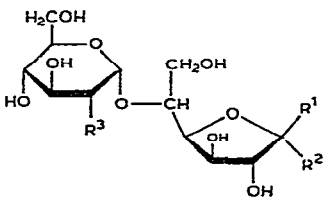
G.L.C. DATA[a] FOR THE *O*-TRIMETHYLSILYL DERIVATIVES OF **9**, **12**, AND **13**, AND THE RESPECTIVE ALDITOLS[b] (IN PARENTHESES)

	SE-30 (3.8%) T_S	*OV-17 (3%)* T_S
12	1.12 1.24 (1.58)	1.15 1.26 (1.61)
9	1.13 1.22 (1.98)	1.13 1.23 (2.01)
synthetic **13**	1.46 1.67 (1.98)[c]	1.47 1.73 (2.01)[c]
authentic **13**	1.46 1.67 (1.98)[c]	1.47 1.73 (2.01)[c]

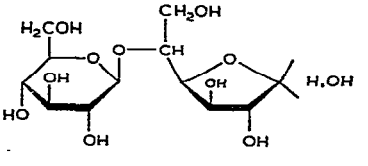
[a]The retention times (T_S) are given relative to per-*O*-Me_3Si-sucrose; error ±0.03. [b]Prepared by sodium borohydride reduction of the respective disaccharides. [c]A shoulder attributable to per-*O*-Me_3Si-5-*O*-α-D-glucopyranosyl-D-mannitol was observed on the positive slope of the peak.

trimethylsilylated disaccharide alditols derived from **9** and authentic leucrose were identical. The $J_{1,2}$ values for the furanose moieties in **9** and **12** accorded with those observed[6] for **10**.

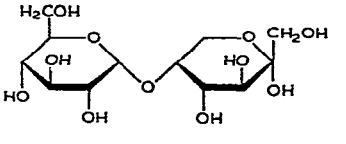
The isomerization of **9** in saturated, oxygen-free calcium hydroxide solution was monitored directly by t.l.c., and by g.l.c. of the trimethylsilylated derivatives, polarimetry, and ^{1}H-n.m.r. spectroscopy [$Ca(OD)_2$ in deuterium oxide]. The ^{1}H-n.m.r. spectrum immediately recorded after dissolution of **9** revealed the α-furanoid form exclusively, presumably because of complex formation with calcium ions at O-1 and O-2, which are *cis* in the α-form. A similar phenomenon has been observed for 5-*O*-methyl-D-ribofuranose[11]. In the isomerization reaction, no anomeric protons attributable to mannofuranose were observed, and **9** was almost quantitatively consumed within 3 h, yielding mainly **13**. At intermediate reaction times, the ^{1}H-n.m.r. spectra and g.l.c. traces were those of **9** and **13** superimposed. However, longer reaction times produced other components (t.l.c.) which were not further investigated. No mannose could be detected after methanolysis of crude **13** and subsequent g.l.c. analysis[12].



9 R^1, R^2 = H,OH ; R^3 = OH
10 R^1, R^2 = H,OH ; R^3 = NHAc
11 R^1 = OH, R^2 = H, R^3 = NHAc



12



13

Thus, the formation of the 1,2-enediol from **9** is extremely rapid in comparison to its back-formation from **13**. The anomerisation of **11** (*cf.* **9**) is instantaneous in water[6], indicating that the furanose hemiacetal is in rapid equilibrium with the corresponding pseudo-acyclic intermediate, which was postulated[13] to be the immediate precursor for the 1,2-enediol produced in alkaline media. Conversely, the anomerization of fructose has been ascribed largely to pyranose–furanose interconversion rather than to $\alpha \rightarrow \beta$ pyranose change[14]. The slow mutarotations of leucrose[1] and other 5-substituted fructopyranoses[14,15] have been cited to support this hypothesis. The apparently negligible back-formation of the 1,2-enediol from **13** substantiates the concept that the main factor controlling the rate of enolization is the concentration of an intermediate pseudo-acyclic form[13].

Selection of optimal reaction conditions permitted the isolation of a product (53%) which was identical with authentic **13** (see also the data in Table I).

The foregoing procedure offers an attractive route for the preparation of leucrose-type oligosaccharides[3], and increases the utility of D-glucofuranurono-6,3-lactone[6,7,16] for the preparation of (1 → 5)-linked disaccharides.

EXPERIMENTAL

Materials. — Leucrose was a gift from Dr. F. H. Stodola (Peoria, Illinois).

General methods. — Melting points were determined on a Mettler FP5/FP51 photoelectric apparatus. Specific rotations were determined at ambient temperature with a Perkin–Elmer 141 Polarimeter. Half-lives of the cyclopentylidene acetals were determined as described earlier[7]. ^{1}H-N.m.r. spectra (internal Me_4Si or sodium 2,2-dimethyl-2-silapentane-5-sulphonate, as appropriate) were recorded with a Varian EM390 (90 MHz) spectrometer, and i.r. spectra with a Pye Unicam SP1100 spectrophotometer. Solutions were concentrated at 40° (bath)/~14 mmHg. T.l.c. was performed on silica gel (Schleicher & Schüll TLC Ready Plastic Foil FR-1500) with conventional detection by charring with sulphuric acid. Column chromatography was performed on silica gel (Merck Kieselgel 60, 230–400 mesh) with *A*, chloroform; *B*, chloroform–methanol (25:1); *C*, propan-2-ol–ethyl acetate–water (2:2:1); and *D*, acetic acid–ethyl acetate–water–butan-1-ol (6:3:1:8). G.l.c. of trimethylsilylated derivatives[17] of sugars was carried out on a Pye 104 instrument equipped with flame-ionization detector and glass columns (1.60 m × 4 mm) packed with 3.8% of SE-30 or 3% of OV-17 on Chromosorb W-AW DMCS (80–100 mesh) (oven temperature, 227°; nitrogen flow-rate, 40 ml/min). The retention times (T_S) are given relative to that of trimethylsilylated sucrose.

1,2-O-Cyclopentylidene-5-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-α-D-glucofuranurono-6,3-lactone (**3**) *and 1,2-O-cyclopentylidene-5-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-glucofuranurono-6,3-lactone* (**4**). — A mixture of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**1**; 16.4 g, 40 mmol), mercuric cyanide (5.04 g, 20 mmol), mercuric bromide (7.2 g, 20 mmol), 1,2-*O*-cyclopentylidene-α-D-glucofuranurono-6,3-lactone[7] (**2**; 10 g, 41.3 mmol), and dry acetonitrile

(100 ml) was kept at room temperature for 1.5 h in the dark, and then concentrated. The residue was extracted with chloroform (4 × 50 ml), and the combined extracts were shaken with M potassium bromide (3 × 100 ml), dried (Na_2SO_4), and concentrated to a syrup. Addition of ether afforded a crystalline 1 : 1 mixture (16 g) of **3** and **4**. The remaining mother liquor was subjected to column chromatography (solvent *A*) and gave an additional crop of **3** + **4** (6 g) (Found: C, 51.08; H, 5.36. $C_{25}H_{32}O_{15}$ calc.: C, 52.45; H, 5.63%).

Fractional crystallization of **3** + **4** from ethanol (2 g/100 ml), in which the former was more soluble, was monitored by t.l.c. (solvent *B*) and yielded **3** (10.6 g, 45%; R_F 0.6), m.p. 129–131°, $[\alpha]_D$ +136° (*c* 2.5, chloroform), ν_{max}^{KBr} 1820 (C=O, lactone) and 1750 cm^{-1} (C=O, acetyl). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.6–1.9 (m, 8 H, cyclopentylidene-CH_2); 2.00, 2.03, 2.06, and 2.09 (4 s, 12 H, 4 AcO); 5.97 (d, $J_{1,2}$ 3.8 Hz, H-1); 4.74 (d, $J_{2,1}$ 3.8 Hz, H-2); 4.53 (d, $J_{5,4}$ 4.4 Hz, H-5); 5.36 (d, $J_{1',2'}$ 3.9 Hz, H-1'); and 4.0–5.7 (m, 8 H, other protons) (Found: C, 52.40; H, 5.59%). Compound **4** (9.0 g, 38%; R_F 0.5) had m.p. 108–110°, $[\alpha]_D$ +6.5° (*c* 2.5, chloroform), ν_{max}^{KBr} as for **3**. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.6–1.9 (m, 8 H, cyclopentylidene-CH_2); 2.00, 2.02, 2.06, and 2.08 (4 s, 12 H, 4 AcO); 5.96 (d, $J_{1,2}$ 3.8 Hz, H-1); 4.71 (d, $J_{2,1}$ 3.8, $J_{2,3}$ ~0 Hz, H-2); 4.79 (d, $J_{3,4}$ 3.0 Hz, H-3); 5.59 (d, $J_{5,4}$ 4.4 Hz, H-5); 4.20 (d, 2 H, $J_{6a',5'} = J_{6b',5'} = 3.6$ Hz, H-6a'b'); 3.73 (m, 1 H, H-5'β); and 4.9–5.2 (m, 5 H, other protons) (Found: C, 52.30; H, 5.61%).

*3,6-Di-*O*-acetyl-1,2-*O*-cyclopentylidene-5-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-α-*D*-glucofuranose* (**6**). — A solution of **4** (5.1 g, 8.9 mmol) in 1,2-dimethoxyethane (180 ml) was flushed with nitrogen, and lithium aluminium hydride (2.2 g, 58 mmol) was added in portions with stirring. The mixture was then stirred for 3 h at 45–50°, and cooled to 10°, and the excess of hydride was decomposed with ethyl acetate (27 ml). The addition of 50% aqueous methanol (220 ml) gave a precipitate that was collected over diatomaceous earth and thoroughly washed with methanol. The filtrates were combined, the pH was adjusted to 5–6 with hydrochloric acid, and the solution was concentrated. A solution of the residue in water (1 litre) was freeze-dried, and the residue was conventionally acetylated with pyridine (80 ml) and acetic anhydride (40 ml) for 16 h at 5°, and 6 h at room temperature, to yield **6** (3.46 g, 59%), m.p. 111–113° (from ether), $[\alpha]_D$ −16° (*c* 3, chloroform), ν_{max}^{KBr} 1750 cm^{-1} (C=O, acetyl); no lactone absorption was observed (Found: C, 52.86; H, 6.07. $C_{29}H_{40}O_{17}$ calc.: C, 52.73; H, 6.10%).

*3,6-Di-*O*-acetyl-1,2-*O*-cyclopentylidene-5-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-α-*D*-glucofuranose* (**5**). — Compound **3** (4.6 g, 8.0 mmol) was reduced with lithium aluminium hydride and acetylated as described above for **4**. The resulting, viscous syrup was eluted from a column (15 × 5 cm) of silica gel with solvent *A* to afford **5** (4.6 g, 86%), as a brittle foam, $[\alpha]_D$ +50° (*c* 2.5, chloroform), ν_{max}^{film} as for **6** (Found: C, 52.95; H, 6.15%).

*1,2-*O*-Cyclopentylidene-5-*O*-α-*D*-glucopyranosyl-α-*D*-glucofuranose* (**7**). — A solution of **5** (5 g, 7.6 mmol) in 0.02M methanolic sodium methoxide (200 ml) was monitored by t.l.c. (solvents *B* and *C*) until reaction was complete, neutralized with

Amberlite IR-120 (H^+) resin, and then treated with a mixed-bed (H^+, HO^-) resin (100 mg), filtered, and concentrated. A solution of the residue in water (500 ml) was passed through a fine sintered-glass funnel and freeze-dried, affording amorphous **7** (3.0 g, 97%), $[\alpha]_D$ +81° (*c* 1.5, water). ^{1}H-N.m.r. data (D_2O): δ 6.10 (d, $J_{1,2}$ 3.9 Hz, H-1α), 5.25 (d, $J_{1',2'}$ 3.8 Hz, H-1'α), and 4.75 (d, $J_{1,2}$ 3.9 Hz, H-2) (Found: C, 49.77; H, 6.80, $C_{17}H_{28}O_{11}$ calc. C, 50.00; H, 6.91%).

1,2-O-Cyclopentylidene-5-O-β-D-glucopyranosyl-α-D-glucofuranose (**8**). — Treatment of **6** (3.4 g, 5.2 mmol) as described above for **5** yielded **8** (2.0 g, 95%), $[\alpha]_D$ +3° (*c* 1.5, water). ^{1}H-N.m.r. data (D_2O): δ 6.01 (d, $J_{1,2}$ 3.8 Hz, H-1α), 4.64 (d, $J_{2,1}$ 3.8 Hz, H-2), and 4.66 (d, $J_{1',2'}$ 7.5 Hz, H-1'β) (Found: C, 49.88; H, 6.80%).

5-O-α-D-Glucopyranosyl- (**9**) *and 5-O-β-D-glucopyranosyl-D-glucofuranose* (**12**). — The hydrolyses of **7** and **8** (1.5 g, 3.7 mmol) in 0.52M sulphuric acid (75 ml) were monitored at 20° by t.l.c. (solvent *D*) and polarimetry[7] [$t_{0.5}$ ~1.7 h, $\partial\alpha/\partial t < 0$, consistent with a (1 → 5)-linkage[7] in **7** and **8**; Freudenberg[9] reported $\partial\alpha/\partial t < 0$ for the isopropylidene analogue of **8**]. After 9.5–10 h, the reaction was quenched with ice and subsequent neutralization with Dowex 1 X2 (HCO_3^-) resin. Each mixture was filtered and freeze-dried to yield **9** (95%), $[\alpha]_D$ +69.5° (*c* 2, water), and **12** (94%), $[\alpha]_D$ −25° (*c* 2, water). Each product was subjected to ion-exchange chromatography[18] on a column (1.5 m × 2 cm) of Dowex 50 X4 (K^+) resin to remove any traces of glucose and **7** or **8**, and isolated by freeze-drying.

Compound **9** had $[\alpha]_D$ +71° (*c* 2, water); for g.l.c. data, see Table I. The ^{1}H-n.m.r. spectrum was similar to that of **10**[6] and indicated a 1:1 $\alpha\beta$-mixture: δ 5.51 (d, $J_{1,2}$ 4.0 Hz, furanoid H-1α), 5.14 (d, $J_{1',2'}$ 3.6 Hz, H-1α'), 5.24 (d, $J_{1,2}$ 0.8 Hz, furanoid H-1β), and 5.18 (d, $J_{1',2'}$ 3.6 Hz, H-1'α). Compound **9** is best characterized by its facile conversion into crystalline **13**.

Compound **12** had $[\alpha]_D$ −28° (*c* 2, water); lit.[9,10] $[\alpha]_D$ −22° and −23° (*c* 1, water) for syrupy **12**. For g.l.c. data, see Table I. The ^{1}H-n.m.r. spectrum (D_2O) was consistent with a 1:1 $\alpha\beta$-mixture: δ 5.53 (d, $J_{1,2}$ 3.6 Hz, furanoid H-1α), 4.66 (d, $J_{1',2'}$ 7.5 Hz, H-1'β), 5.22 (d, $J_{1,2}$ < 0.5 Hz, furanoid H-1β), and 4.70 (d, $J_{1',2'}$ 7.5 Hz, H-1'β). Treatment[9] of **12** with toluene-*p*-sulphonylhydrazine gave the hydrazone, m.p. 178–179° (dec.), $[\alpha]_D$ −21° (*c* 1, 4:1 pyridine–water); lit.[10] m.p. 180–181° (dec.), $[\alpha]_D$ −22°.

5-O-α-D-Glucopyranosyl-D-fructopyranose (*leucrose*, **13**). — Compound **9** (630 mg, 1.84 mmol) was treated in an atmosphere of nitrogen with oxygen-free 0.044M calcium hydroxide[19] (7 ml) at 35°. The $[\alpha]_{546}$ value rapidly dropped from +7° (extrapolated t_0 value) to ~0.5° in 3 h. At intervals, aliquots (5 µl) were neutralized with 50% aqueous acetic acid and subjected to t.l.c. [solvent *C*; **9** (R_F 0.4) → **13** (R_F 0.23)] and g.l.c. analysis (trimethylsilyl derivatives, Table I). After 3 h, the ratio of **9** and **13** was ~1:9. The reaction mixture was quenched with ice and the required amount of Amberlite IR-120 (H^+) resin, and then filtered and freeze-dried. The product was subjected to ion-exchange chromatography[18] as described above, isolated by freeze-drying, and crystallized from methanol–ethanol to give **13** (331 mg, 53%), m.p. and mixture m.p. 156–157.5°, $[\alpha]_D$ −7° (*c* 2, water); lit.[1] m.p. 156–157°,

$[\alpha]_D$ −7.6° (*c* 4, water) (Found: C, 41.70; H, 6.50. $C_{12}H_{22}O_{11}$ calc.: C, 42.11; H, 6.48%). The ^{1}H-n.m.r. data (D_2O) [δ 5.13 (d, $J_{1',2'}$ 3.9 Hz, H-1'α) and 3.2–4.2 (13 H, other protons)] for synthetic and authentic **13** were indistinguishable.

Compound **9** (50 mg) was treated with an oxygen-free, saturated solution (0.6 ml) of calcium deuteroxide in deuterium oxide[19]. ^{1}H-N.m.r. spectroscopy [1,4-dioxane (δ 3.56) as internal reference] revealed the α form of **9** exclusively: δ 5.18 (d, 1 H, $J_{1,2}$ 2.3 Hz, H-1α) and 4.94 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1'α). Both doublets disappeared during 3 h, and a new doublet at δ 4.89 ($J_{1',2'}$ 3.8 Hz, H-1'α in **13**) reached maximum intensity. No other signals were observed in the anomeric region of the spectra. The reaction was quenched as described above, and a sample (1 mg) of crude **13** was subjected to methanolysis and g.l.c. analysis as devised by Clamp *et al.*[12]; no mannose was detected.

ACKNOWLEDGMENTS

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