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NEW SYNTHESES OF METHYL 4,6-*O*-BENZYLIDENE-2-DEOXY-3-*C*-METHYL-α-D-*arabino*-HEXOPYRANOSIDE AND ITS CONVERSION INTO D-EVERMICOSE*

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ABSTRACT

Methyl 4,6-*O*-benzylidene-2-deoxy-3-*C*-methyl-α-D-*arabino*-hexopyranoside (**4**) was prepared from methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-methylene-β-D-*erythro*-hexopyranoside (**1b**) and from methyl 4,6-*O*-benzylidene-3 *C*-methyl-α-D-*gluco*-hexopyranoside (**6a**) by two different methods Synthesis of D-evermicose‡ (**10**) (2,6-dideoxy-3-*C*-methyl-D-*arabino*-hexose) was then achieved in four steps from **4**

INTRODUCTION

Such 2,6-dideoxy-3-*C*-methyl-D- or -L-hexoses as L-mycarose[2a], L-cladinose[2a], L-olivomycose[2a], L-chromose B[2a], L-arcanose[2a], D-evermicose[2b] and L-axenose[2c] are examples of important, naturally occurring, branched-chain sugars The general introduction of the desired *C*-methyl branching at C-3 of hexoses has been achieved primarily by the action of such reagents as methylmagnesium bromide and diazomethane with the corresponding hexos-3-uloses

In a previous paper[3], we proposed a simple method for introducing methyl-branching via epoxidation of *C*-methylene sugars, followed by reduction with lithium aluminum hydride instead of reaction with diazomethane, as the latter may cause undesired ring-expansion acco ding to the solvent or the structure of the starting material[4]

RESULTS AND DISCUSSION

We therefore extended our epoxidation method to prepare the title compound, methyl 4,6-*O*-benzylidene-2-deoxy-3-*C*-methyl-β-D-*arabino*-hexopyranoside (**4**) from

*Part X of the series ' Branched-Chain Sugars"

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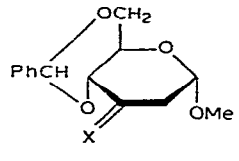
‡A synthesis of D-evermicose via resolution of *trans*-3-hydroxy-3-*C*-methyl-DL-*glycero*-hex-4-enoic acids has recently been reported by Dyong *et al* [1]

methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-methylene-α-D-*erythro*-hexopyranoside* (**1b**) Compound **4** was also prepared by another route, from methyl 4,6-*O*-benzylidene-3-*C*-methyl-α-D-glucopyranoside[6] (**6a**)



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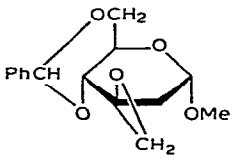
b X = CH_2



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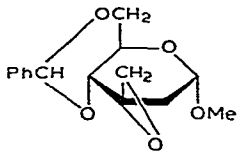

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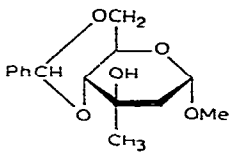

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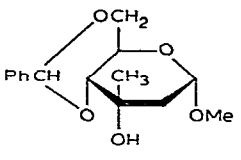

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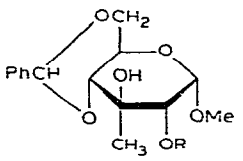
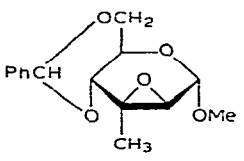


6 a R = H
b R = Ms



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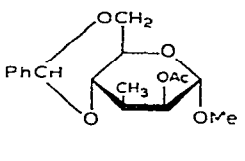

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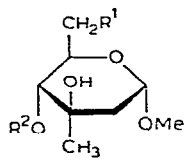
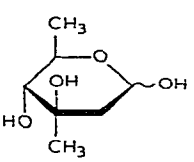


9 a R^1 = Br R^2 = Bz
b R^1 = H R^2 = Bz



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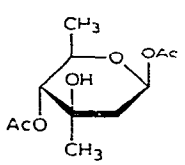

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Compound **4** is a potential precursor to most of the naturally occurring branched-chain sugars just mentioned Although it has already been synthesized by treating methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose (**1a**) with diazomethane[4d] followed by reduction with lithium aluminum hydride, the yield was unsatisfactorily low and the procedure seems to be impractical for further reaction steps

We prepared the starting material **1b** from the corresponding glycos-3-ulose **1a**

*After the completion of this paper, another description of the synthesis of **1b** appeared[5]

The former was readily oxidized with *m*-chloroperoxybenzoic acid in 1,2-dichlororoethane to give two epoxides, which could be separated by column chromatography in yields of 61 and 18%, respectively The desired epoxide (**2**) was the predominant product as expected, as the electrophilic attack of the reagent on the carbon–carbon double bond of **1b** occurred from the side opposite the methoxyl group The configuration of each was determined by comparison of the physical data with data found in the literature[4] Reduction of the unseparated epoxides gave a mixture of the desired compound **4** and its C-3 epimer **5** Separation of the compounds by column chromatography gave **4** and **5** in yields of 65 and 20%, respectively* The physical data were in good agreement with values given in the literature

Compound **4** was also prepared by a different route Methyl 4,6-*O*-benzylidene-3-*C*-methyl-α-D-glucopyranoside (**6a**) was converted into the methanesulfonate **6b** in 86% yield Compound **6b** was then treated with sodium methoxide in methanol to give methyl 2,3-anhydro-4,6-*O*-benzylidene-3-*C*-methyl-α-D-mannopyranoside (**7**) in 93% yield

It is commonly recognized that nucleophilic attack on methyl 2,3-anhydro-α-D-mannopyranoside gives exclusively the product of diaxial ring-opening[8] (the methyl γ-D-altropyranoside derivative) Diequatorial ring-opening, however, may also be expected in the case of the branched-chain sugar **7**, as the presence of an axial methyl group at C-3 might impede the nucleophile from approaching C-3 In fact, reduction of **7** with lithium aluminum hydride gave a 1 1 mixture of methyl 4,6-*O*-benzylidene-3-deoxy-3-*C*-methyl-α-D-mannopyranoside (**8**) (diaxial ring-opening) and **4** (diequatorial ring-opening) The compounds have identical R_F values in t l c treatment of the mixture of **8** and **4** with acetic anhydride in pyridine was, therefore necessary to effect separation The less-polar acetate **8** could then be readily separated from **4** in 47% yield by column chromatography The yield of **4** was 40% from **7** The *manno* configuration of **8** was readily confirmed by ^{1}H-n m r spectroscopy ($J_{1,2} = 1\ 0$, $J_{2,3} = 3\ 0$ Hz)

Compound **4** was converted into D-evermicose in four steps in the following manner treatment with *N*-bromosuccinimide in carbon tetrachloride gave methyl 4-*O*-benzoyl-6-bromo-2 6-dideoxy-3-*C*-methyl-α-D-*arabino*-hexopyranoside(**9a**) quantitatively Reduction of **9a** with tributylstannane in benzene in the presence of γ,γ′-azobis(isobutanonitrile) gave the corresponding 2,6-dideoxy derivative **9b** also quantitatively After debenzoylation of **9b** in methanolic ammonia, the compound was hydrolyzed with 0 1*M* hydrochloric acid to give crystalline 2,6-dideoxy-3-*C*-methyl-α,β-D-*arabino*-hexose (D-evermicose) The physical data of **10** were in good agreement with those of D-evermicose[2b]**

*In the synthesis of L-oliyomycose Jones *et al*[7] obtained the enantiomer of **4** in 72% yield by oxymercuration of the corresponding 3-*C*-methylene sugar followed by reduction, the C-3 epimer was not described

Although the melting point and optical rotation of the synthetic diacetate **11 differ from the reported values for D-evermicose diacetate (see Experimental section), the n m r data are in good agreement Authentic samples were unfortunately not available

EXPERIMENTAL

General methods — Melting points were determined on a Yanagimoto micro melting-point apparatus and are uncorrected Solvents were evaporated *in vacuo* N m r spectra were recorded with a JNM-PS-100 spectrometer for solutions in chloroform-*d* containing tetramethylsilane as the internal reference Optical rotations were measured with a Carl Zeiss LEP Al spectrophotometer using an 0 5-dm tube

Methyl 4,6-O-benzylidene-2,3-dideoxy-3-C-methylene-α-D-erythro-hexopyranoside (**1b**) — A solution of butyllithium (10%, 8 7 ml, 13 6 mmol) in hexane was gradually added to a cold suspension of methyltriphenylphosphonium bromide (6 g, 16 8 mmol) in dry tetrahydrofuran (20 ml) cooled in an ice–water bath A solution of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose[9] (**1a**, 3 g, 11 4 mmol) dissolved in tetrahydrofuran (90 ml) was then rapidly added with vigorous stirring to the yellow–orange suspension The mixture was stirred at room temperature for 30 min, and the reaction was monitored by t l c After addition of acetone (10 ml) and ether (200 ml), the precipitate was collected by filtration The filtrate was evaporated and the residue was placed on a column of silica gel (Wako-gel C-200, 100 g) Elution with benzene gave white crystals (1 8 g, 60%) Recrystallization from ethanol gave **1b**, m p 121–122°, $[\alpha]_D^{25}$ +146° (*c* 1 0, carbon tetrachloride) [lit [5] m p 121–122 5°, and $[\alpha]^{23}$ +163° (*c* 1 04, chloroform)] (Found C, 68 75, H, 6 98 Calc for $C_{15}H_{18}O_4$ C, 68 69, H, 6 92%), n m r δ 2 60 (broad, 2 H, H-2a, H-2e), 3 39 (s, 3 H, OCH_3) 3 68–4 4 (m, 4 H, H-4 H-5, H-6a, H-6e), 4 80 (q, 1 H, $J_{1,2}$ 3 0 and 2 0 Hz H-1), 4 95 and 5 18 (m 2 H, exo-methylene), and 7 3–7 65 (m, 5 H phenyl)

Methyl 3,3[1]-anhydro-[4,6-O-benzylidene-3-C-(hydroxymethyl)-α-D-arabino-hexopyranoside] (**2**) *and methyl 3,3[1]-anhydro-4,6-O-benzylidene-2-deoxy-3-C-(hydroxymethyl)-α-D-ribo-hexopyranoside* (**3**) — A solution of **1b** (11 g 42 mmol) and *m*-chloroperoxybenzoic acid (85% purity, 16 5 g, 81 mmol) dissolved in 1,2-dichloroethane (500 ml) was stirred overnight at room temperature The precipitate was removed by filtration, and the filtrate was washed with 0 1M sodium hydroxide and water, and dried (magnesium sulfate) The organic layer was evaporated to a crystalline mass, a part (1 g) of which was placed on a column of silica gel (20 g), and eluted with benzene to give **2** (650 mg, 61%) as the less polar portion and **3** (190 mg, 18%) as the more polar portion Compound **2** had m p 113–114°, $[\alpha]_D^{22}$ 110° (*c* 1 0, ethyl acetate) [lit [4d] m p 116 5–117°, $[\alpha]_D$ +119° (*c* 0 5, ethyl acetate)] Compound **3** had m p 123–125°, $[\alpha]_D$ +140° *c* 1 0, ethyl acetate) [lit [4c] m p 123–124°, $[\alpha]_D$ +154° (ethyl acetate)] (Found for **2** C, 64 85, H, 6 47, **3**, C, 64 68, H, 6 52, Calc for $C_{15}H_{18}O_5$ C, 64 73, H, 6 52%), n m r of **2** δ 1 68 (d, 1 H, J_{gem} 13 2 Hz, H-2e), 2 40 (q, 1 H, $J_{1,2a}$ 4 0, $J_{2a,3}$ 1 5 Hz, H-2a), 2 78 (d, 1 H, $J_{3,3}$ 5 0 Hz, H-3″), 3 22 (q, 1 H, H-3′), 3 36 (s, 3 H, OCH_3), 3 68–4 4 (m, 4 H, H-4, H-5, H-6, and H-6′), 4 86 (d, 1 H, H-1), 5 52 (s, 1 H C*H*Ph), and 7 2–7 52 (m, 5 H, phenyl), n m r of **3**, δ 1 65 (d, 1 H, J_{gem} 14 Hz, H-2e), 2 48 (q, 1 H, $J_{1,2a}$ 4 0 Hz, H-2a), 2 52 (d, 1 H, J_{gem} 5 0 Hz, H-3′), 3 04 (d, 1 H, H-3″), 3 41 (s, 3 H, OCH_3), 3 7–4 4 (m, 4 H, H-4,

H-5, H-6, H-6'), 4.82 (d, 1 H, H-1), 5.52 (s, 1 H, C*H*Ph), and 7.2–7.5 (m, 5 H, phenyl)

*Methyl 4,6-*O*-benzylidene-2-deoxy-3-*C*-methyl-α-*D*-arabino-hexopyranoside* (**4**) *and methyl 4,6-*O*-benzylidene-2-deoxy-3-*C*-methyl-α-*D*-ribo-hexopyranoside* (**5**) — Lithium aluminum hydride (6.5 g) was gradually added to a solution of the crude epoxide (10 g), already described, in dry tetrahydrofuran (200 ml). The mixture was boiled for 30 min under reflux. Ethyl acetate and water were successively added to the mixture, and the precipitate was removed by filtration and washed with ether. The filtrate and washings were evaporated to a crystalline mass, which was placed on a column of silica gel (Wako-gel C-200, 100 g) that was eluted with benzene to give **5** (2.0 g, 20%) as the less-polar component and **4** (6.5 g, 65%) as the more-polar component. Compound **4** had m.p. 75–77°, $[\alpha]_D^{22}$ +87° (*c* 1.0, ethanol)* [lit.[4a] m.p. 79–79.5°, $[\alpha]_D$ +122° (*c* 1.0, ethanol)]. Compound **5** had m.p. 124–125°, $[\alpha]_D^{22}$ +137° (*c* 1.0, ethanol) [lit.[4d] m.p. 125.5–126°, $[\alpha]_D$ +121° (*c* 0.2, ethanol)]. (Found, for **4**: C, 64.35; H, 7.22. **5**: C, 64.21; H, 7.21. Calc. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19%). N.m.r. of **4**, δ 1.50 (s, 3 H, C–CH_3), 1.8–2.18 (m, 2 H, H-2a, H-2e), 2.28 (s, OH), 3.32 (s, 3 H, OCH_3), 3.52–3.90 (m, 3 H, H-4, H-6, H-6'), 4.1–4.4 (m, 1 H, H-5), 4.76 (q, 1 H, $J_{1,2a}$ 2.0, $J_{1,2e}$ 3.4 Hz, H-1), 5.56 (s, 1 H, C*H*Ph), and 7.28–7.6 (m, 5 H, phenyl). N.m.r. of **5**: δ 1.30 (s, 3 H, C–CH_3), 1.88 (q, 1 H, $J_{1,2e}$ 4.0 Hz, H-2e), 2.04 (q, 1 H, $J_{1,2a}$ 1.0 Hz, H-2a), 3.20 (s, 3 H, OCH_3), 3.72 (t, 1 H, $J_{5,6a} = J_{6,6} = 9.0$ Hz, H-6a), 4.06 (q, 1 H, $J_{5,6e}$ 4.5 Hz, H-6e), 4.12–4.40 (m, 2 H, H-4, and H-5), 4.76 (q, H-1), 5.56 (s, 1 H, C*H*Ph), and 7.2–7.56 (m, 5 H, phenyl).

*Methyl 4,6-*O*-benzylidene-3-*C*-methyl-2-*O*-(methylsulfonyl)-α-*D*-glucopyranoside* (**6b**) — Methanesulfonyl chloride (0.88 g, 7.75 mmol) was added to a solution of methyl 4,6-*O*-benzylidene-3-*C*-methyl-α-*D*-glucopyranoside (**6a**, 1.2 g, 4.12 mmol) in dry pyridine (50 ml) cooled in an ice–water bath. The solution was kept for 24 h at room temperature, and then poured into ice–water. The aqueous solution was extracted with chloroform (2 × 100 ml). The extracts were washed with saturated aqueous sodium hydrogencarbonate and with water. Evaporation of the dried extract gave a residue (1.4 g) that was recrystallized from ethanol (10 ml) to give **6b** (1.2 g, 85%), m.p. 110–112°, $[\alpha]_D^{25}$ +48° (*c* 1.0, chloroform) (Found: C, 51.49; H, 5.98. Calc. for $C_{16}H_{22}O_8S$: C, 51.33; H, 5.92 %). N.m.r. δ 1.48 (s, 3 H, C–CH_3), 2.55 (broad, 1 H, OH), 3.10 (s, 3 H, OSO_2CH_3), 3.40 (s, 3 H, OCH_3), 3.45–3.85 (m, H-4, H-5, and H-6a), 4.27 (q, 1 H, $J_{5,6e}$ 2.5, $J_{6a,6e}$ 7.5 Hz, H-6e), 4.51 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-2), 4.87 (d, 1 H, H-1), 5.50 (s, 1 H, C*H*Ph), and 7.1–7.51 (m, 5 H, phenyl).

*Methyl 2,3-anhydro-4,6-*O*-benzylidene-3-*C*-methyl-α-*D*-mannopyranoside* (**7**) — A solution of **6b** (6.4 g, 17 mmol) and sodium methoxide (0.6 g, 26 mmol) in abs. methanol (100 ml) was boiled under reflux until the starting material disappeared.

*There is a discrepancy between the literature value and the experimental value for the optical rotation of **4**. Similar values (87°, +84°) for **4** were obtained, however, when the compound was produced by different routes.

The cooled solution was then concentrated to yield a precipitate that was recrystallized from ethanol (100 ml) to give pure **7** (4 41 g, 93%), m p 142–143°, $[\alpha]_D^{25}$ +76° (*c* 1 0, chloroform) (Found C, 64 46, H, 6 44 Calc for $C_{15}H_{18}O_5$ C, 64 73, H, 6 52), n m r δ 1 45 (s, 3 H, C–CH_3), 2 92 (s, 1 H, H-2), 3 42 (s, 3 H, O–CH_3), 3 5–3 8 (m, 3 H, H-4, H-5, and H-6), 4 27 (q, 1 H, $J_{5\,6e}$ 2 5, $J_{6e\,6a}$ 5 0 Hz, H-6e), 4 81 (s 1 H, H-1), 5 50 (s, 1 H, C*H*Ph), and 7 2–7 6 (m, 5 H, phenyl)

Reduction of the epoxide **7** — Lithium aluminum hydride (1 25 g, 32 9 mmol) was carefully added to a stirred solution of **7** (4 59 g, 16 5 mmol) in dry 1,4-dioxane (110 ml) The mixture was boiled for 6 h under reflux, and cooled to room temperature The excess of lithium aluminum hydride was decomposed by successive addition of ethyl acetate and water, and the precipitate was removed by filtration The filtrate was extracted with chloroform (2 × 100 ml) The extracts were washed with water, dried (magnesium sulfate), and evaporated to a colorless syrup (4 2 g) which showed two spots having the same R_F value in t l c (R_F 0 43, 8 1 benzene–methanol) Acetylation of the syrup with acetic anhydride (30 ml) and pyridine (30 ml), followed by conventional processing gave a residue that was fractionated on a column of silica gel (Wako-gel C-200, 40 g) by eluting with benzene White crystals of **4** (1 85 g, 40% from **7**) were obtained together with a syrupy monoacetate corresponding to **8** (methyl 2-*O*-acetyl-4 6-*O*-benzylidene-3-deoxy-3-*C*-methyl-α-D-mannopyranoside 2 53 g 47%) Compound **4** had m p 74–75°, $[\alpha]_D^{25}$ +84° (*c* 1 0 chloroform) **8** had $[\alpha]^{25}$ −47° (*c* 1 0 carbon tetrachloride) (Found for **8** C, 63 26, H, 6 91 Calc for $C_{17}H_{22}O_6$ C 63 34, H, 6 88%) n m r δ 1 04 (d, 3 H, *J* 7 0 Hz, C–CH_3), 2 16 (s, 3 H, OAc), 2 34 (oct, 1 H, $J_{2\,3}$ 3 0, $J_{3\,4}$ 10 Hz, H-3), 3 41 (s, 3 H, OCH_3), 3 5–3 9 (m, 3 H, H-4 H-6 and H-6′). 4 26 (m, 1 H, H-5), 4 58 (d, 1 H, $J_{1\,2}$ 1 Hz, H-1), 4 95 (q 1 H, H-2), and 7 2–7 6 (m 5 H, phenyl)

Methyl 4-O-benzoyl-6-bromo-2,6-dideoxy-3-C-methyl-α-D-arabino-hexopyranoside (**9a**) — A mixture of **4** (230 mg, 0 82 mmol) barium carbonate (350 mg), and *N*-bromosuccinimide (175 mg, 0 98 mmol) in dry carbon tetrachloride (45 ml) was boiled for 2 h under reflux with stirring Insoluble materials were removed by filtration and the filtrate was washed with aqueous sodium hydrogencarbonate and with water Evaporation of the dried filtrate gave white needles (275 mg 93%) m p 119–120°, $[\alpha]_D^{25}$ +82° (*c* 1 0, carbon tetraiodide) (Found C, 50 73, H, 5 47 Calc for $C_{15}H_{19}BrO_5$ C, 50 34, H, 5 29%), ν_{max} 1730 cm^{-1} (C=O), n m r δ 1 48 (s 3 H, C–CH_3), 2 08 (m, 2 H, H-2a, and H-2e), 2 6 (broad, 1 H, OH), 3 40 (s, 3 H OCH_3), 3 4–3 7 (m, 2 H, H-6, H-6′), 4 01 (oct, 1 H, $J_{5\,6}$ 3 7, $J_{5\,6}$ 10 Hz, H-5), 4 85 (q, 1 H, $J_{1\,2e}$ 2 5 $J_{1\,2a}$ 3 7 Hz, H-1), 5 0 (d 1 H, $J_{4\,5}$ 10 Hz H-4), and 7 3–7 7 and 7 9–8 2 (m, 5 H, phenyl)

Methyl 4-O-benzoyl-2 6-dideoxy-3-C-methyl-α-D-arabino-hexopyranoside (**9b**) — A solution of **9a** (300 mg, 0 83 mmol) and tributylstannane (480 mg, 1 65 mmol) in dry benzene (15 ml) was boiled under reflux in the presence of α,α′-azobis(isobutanonitrile) for 3 h The solution was then concentrated and placed on a column of silica gel that was eluted with benzene to give **9b** quantitatively as white crystals, m p 93–94°, $[\alpha]_D^{25}$ +60° (*c* 1 0, carbon tetrachloride) (Found C, 64 11, H, 7 08,

Calc for $C_{15}H_{20}O_5$, C, 64 28, H, 7 14%), n m r δ 1 22 (s, 3 H, $J_{5,6}$ 6 0 Hz, CH–CH_3), 1 45 (s, 3 H, C–CH_3), 2 04 (m, 2 H, H-2e and H-2a), 2 65 (broad, 1 H, OH), 3 30 (s, 3 H, OCH_3), 3 90 (oct, 1 H, $J_{4,5}$ 10 Hz, H-5), 4 71 (q, 1 H, $J_{1,2e}$ 1 9, $J_{1,2a}$ 3 8 Hz, H-1), 4 86 (d, 1 H, H-4), and 7 2–7 7 and 7 9–8 1 (m, 5 H, phenyl)

2,6-Dideoxy-3-C-methyl-D-arabino-*hexose* (**10**) *and 1,4-di*-O-*acetyl-2,6-dideoxy-3-C-methyl-β*-D-arabino-*hexopyranose* (**11**) — A solution of **9b** (450 mg, 1 6 mmol) in methanol saturated with ammonia (30 ml) was kept for 4 h at room temperature and then evaporated to a syrup The syrup was hydrolyzed in 0 05M sulfuric acid (25 ml) for 30 min at 90° The solution was then neutralised with barium carbonate, and the precipitate was removed by filtration The filtrate was finally deionized with Amberlite IR-120(H^+) resin and evaporated to a residue that crystallized from acetone to give white needles [(**10** 130 mg) having m p 105–109° $[\alpha]_D^{25}$ +20 8° (*c* 1 0, water 24 h)] [lit [2b] m p 108–112°, $[\alpha]_D$ +20 7° (water 24 h)] (Found C 72 24, H, 5 12 Calc for $C_7H_{14}O_4$ C, 72 33 H, 5 00%) Acetylation of **10** (70 mg) with acetic anhydride (3 ml) and pyridine (3 ml) gave white needles (55 mg) m p 115–117° $[\alpha]_D^{22}$ +28° (*c* 1 0, carbon tetrachloride) [lit [2b] m p 73°, $[\alpha]_D$ +39 5°] (Found C, 53 23, H, 7 29 Calc for $C_{11}H_{18}O_6$ C, 53 65 H, 7 37%) n m r of **11** δ 1 22 (d, 3 H, $J_{5,6}$ 6 0 Hz CH–CH_3), 1 32 (s, 3 H, C–CH_3), 2 10 and 2 13 (s, 3 H × 2, $COCH_3$) 3 62 (oct 1 H, $J_{4,5}$ 10 Hz H-5) 4 61 (d 1 H H-4) 5 75 (q 1 H, $J_{ax} = 8\ 8$ $J_{ae} = 3\ 2$ Hz, H-1), and 2 9 (broad, 1 H, OH)

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