Synthesis of 6-deoxy-3-*C*-methyl-2-*O*-methyl-D-allose

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The preparation of 6-deoxy-3-*C*-methyl-2-*O*-methyl-D-allose is described. The compound was compared with L-vinelose, a new branched-chain sugar with the same constitution recently isolated, bound to cytidine 5′-pyrophosphate, from *Azotobacter vinelandii* strain O; the two sugars were shown to differ in configuration.

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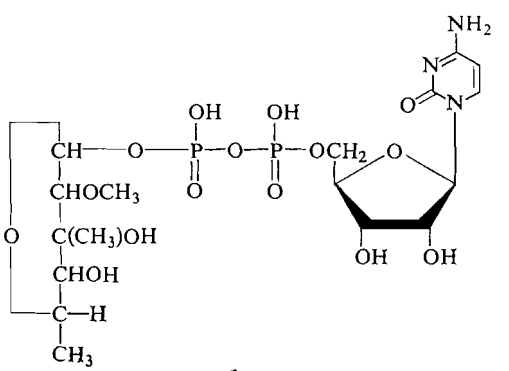
Introduction

Recently a new branched-chain sugar has been reported (1) to occur in a sugar nucleotide isolated from *Azotobacter vinelandii* strain O. This derivative, which has been shown to be cytidine 5′-(6-deoxy-3-*C*-methyl-2-*O*-methyl-L-aldohexopyranosyl dihydrogen pyrophosphate) (**1**), is the first sugar nucleotide isolated from living cells in which the sugar moiety is a branched-chain sugar. The trivial name vinelose has been suggested for this sugar.

It has been shown (2) that, in the biosynthesis of L-mycarose (2,6-dideoxy-3-*C*-methyl-L-*ribo*-hexose), L-cladinose(2,6-dideoxy-3-*C*-methyl-3-*O*-methyl-L-*ribo*-hexose), and L-noviose (6-deoxy-5-*C*-methyl-4-*O*-methyl-L-*lyxo*-hexose),D-glucose is utilized without intermediate breakdown and that the methyl branch is introduced into an unbranched hexose chain from methionine. Moreover, the *O*-methyl group of cladinose and noviose is supplied by methionine. The isolation of **1** from a natural source suggests that nucleotide-bound sugars probably are the actual intermediates which undergo the *C*- and *O*-methylation reactions (1). In continuation of our syntheses of branched-chain sugars we have now prepared 6-deoxy-3-*C*-methyl-2-*O*-methyl-D-allose (**15**)and compared it with an authentic sample of vinelose.[1] The two compounds are clearly distinguishable by gas–liquid chromatography of their 1,4-di-*O*-acetyl derivatives.



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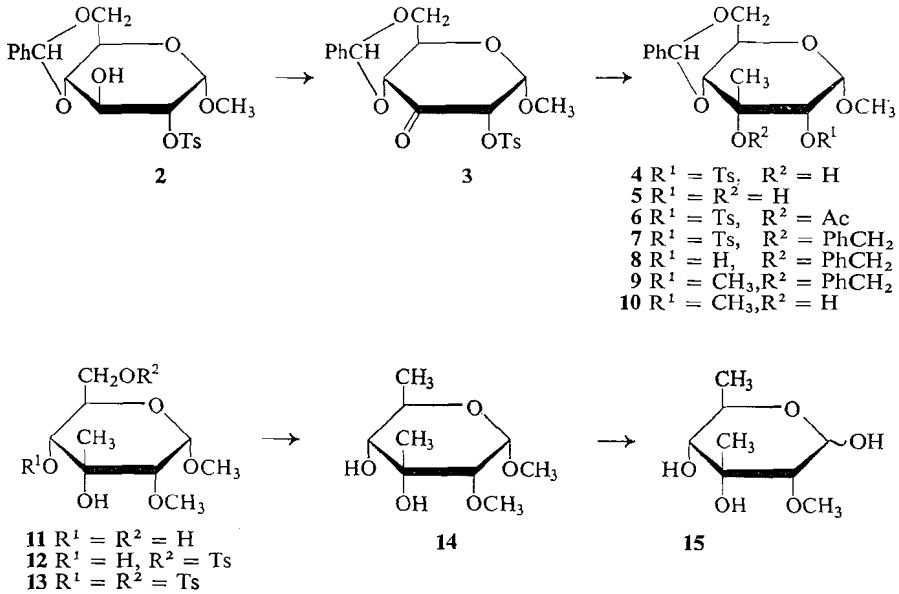
Results and Discussion

The preparation of methyl 4,6-*O*-benzylidene-3-*C*-methyl-2-*O*-*p*-tolylsulfonyl-α-D-allopyranoside (**4**) was readily achieved by the addition of methylmagnesium iodide to methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-*ribo*-hexopyranosid-3-ulose (**3**). A small amount of methyl 4,6-*O*-benzylidene-3-*C*-methyl-α-D-allopyranoside (**5**) was formed also in the Grignard reaction. Compound **3** was obtained in high yield by oxidation of methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (**2**) (3) with either the Pfitzner–Moffatt reagent (4) or ruthenium tetroxide (5). The addition product **4** was converted into the key intermediate, methyl 3-*C*-methyl-2-*O*-methyl-α-D-allopyranoside (**11**), by two routes. Treatment of **4** with sodium methoxide in dimethyl sulfoxide (6) gave in low yield the 2-*O*-methyl derivative **10**, amongst other products.[2] Catalytic de-*O*-benzylidenation of **10** then gave compound **11**. A higher overall yield of **11** was obtained by an alternative synthesis. Treatment of **4** with benzyl bromide and sodium hydroxide in tetrahydrofuran afforded methyl 3-*O*-benzyl-4,6-*O*-benzylidene-3-*C*-methyl-2-*O*-*p*-tolylsulfonyl-α-D-allopyranoside (**7**). This derivative was heated with sodium methoxide (7) to give methyl 3-*O*-benzyl-4,6-*O*-benzylidene-3-*C*-methyl-α-D-allopyranoside (**8**). Methylation of **8** with dimethyl sulfate and sodium hydroxide in tetrahydrofuran gave the crystalline 2-*O*-methyl ether **9**. Hydrogenation of compound **9** over palladium

[1]We thank Professor S. Suzuki for a gift of vinelose.

[2]A discussion of this reaction will be reported separately.



on carbon removed the benzyl and benzylidene groups to produce **11**.

Attempts to open the benzylidene ring in compound **9** by treatment with *N*-bromosuccinimide in boiling carbon tetrachloride to obtain the corresponding 6-bromo-4-benzoate were unsuccessful. This reaction was reported originally by Hanessian (8) and employed recently by us (5) in the synthesis of D-arcanose (2,6-dideoxy-3-*C*-methyl-3-*O*-methyl-D-*xylo*-hexose). Although **9** reacted rapidly with *N*-bromosuccinimide, several, as yet unidentified, products were formed, presumably due to the benzyl ether group.

Treatment of compound **11** with 1.1 moles of *p*-toluenesulfonyl chloride gave predominantly the 6-*O*-*p*-tolylsulfonyl derivative **12** and a small amount of the 4,6-di-*O*-*p*-tolylsulfonyl derivative **13**. Desulfonyloxylation of **12** with lithium aluminium hydride in tetrahydrofuran afforded methyl 6-deoxy-3-*C*-methyl-2-*O*-methyl-α-D-allopyranoside (**14**), which was converted to the free sugar (**15**) by acid-catalyzed hydrolysis. The nuclear magnetic resonance (n.m.r.) spectrum of **15** in deuterium oxide showed the presence of α and β anomers in the ratio 1:3, respectively. In chloroform-*d* an approximately 1:1 mixture was present. Gas–liquid chromatographic analysis of acetylation mixtures of **15** and authentic L-vinelose showed a major and a minor peak in each case (see Table I). In a preparative acetylation experiment, the compound giving rise to the major peak with **15** was isolated in crystalline form and assigned the 1,4-di-*O*-acetyl-6-deoxy-3-*C*-methyl-2-*O*-methyl-β-D-allopyranose structure on the basis of infrared and n.m.r. data. The data in Table I establish that vinelose does not possess the *allo* configuration.

TABLE I

Retention times of sugar components in acetylation mixture*

Sugar	Retention time	
	Major peak	Minor peak
L-Vinelose	1.20	0.94
6-Deoxy-3-*C*-methyl-2-*O*-methyl-D-allose (**15**)	1.63	1.18

*See Experimental section for details. Retention times given here are relative to erythritol tetraacetate (1.00).

We (5, 9) have shown previously that addition of methylmagnesium iodide to methyl 4,6-*O*-benzylidene-2-deoxy-α-D-hexopyranosid-3-uloses is highly stereoselective giving predominantly in each case the axially-oriented tertiary alcohol. In these compounds attack by the Grignard reagent from the side resulting in the formation of the axial alcohol is sterically more favorable than attack from the side resulting in the formation

of the equatorial alcohol. Although it is reasonable to expect the same considerations to obtain in compound **3**, we have assigned the configuration at the branching point by other methods. Lichtenthaler and Emig (10) have shown recently, from an n.m.r. study of *C*-methyl branched cyclanol acetates, that the configuration at the branching point can be deduced from the chemical shift of the *C*-methyl acetoxy group. The tertiary hydroxyl group in compound **4** failed to acetylate with acetic anhydride/pyridine, but acid-catalyzed acetylation (acetic anhydride/-*p*-toluenesulfonic acid) rapidly gave crystalline methyl 3-*O*-acetyl-4,6-*O*-benzylidene-3-*C*-methyl-2-*O*-*p*-tolylsulfonyl-α-D-allopyranoside (**6**) in high yield. The n.m.r. spectrum of **6** showed an acetyl signal at τ 8.03, a value in the range (τ 7.93–8.04) reported (10) for tertiary acetoxy groups possessing the axial orientation. With **4** in the C1 (D) conformation, these n.m.r. data support the assigned *allo* configuration.

Experimental

Solutions were concentrated below 50° under reduced pressure. Melting points were determined on a Fisher–Johns melting point apparatus and are uncorrected. Optical rotations were measured with a Bendix ETL-NPL Automatic Polarimeter, type 143A, at 20 ± 2°. Infrared spectra were measured on a Beckman-IR5A spectrophotometer. Nuclear magnetic resonance (n.m.r.) spectra were determined at 60 MHz in chloroform-*d* and tetramethylsilane as internal standard. Thin-layer chromatography (t.l.c.) was performed, unless otherwise stated, with Silica Gel G as the absorbent, and 2:3 ethyl acetate – petroleum ether (b.p. 60–80°) as the developing solvent. The developed plates were air dried, sprayed with 5% ethanolic sulfuric acid, and heated at about 150°. Paper chromatography was carried out by the descending method on Whatman No. 1 filter paper in the following solvent systems: 6:4:3 (v/v) butan-1-ol – pyridine – water (*a*); butan-1-ol saturated with water (*b*). The sugars were detected by spraying the chromatograms with a 1:1 mixture of vanillin (1% in ethanol) and perchloric acid (3% in water) and heating (11). Gas–liquid chromatography (g.l.c.) was performed on an F and M, model 402, high-efficiency gas chromatograph employing a flame-ionization detector. The liquid phase was supplied by Chromatographic Specialities, Brockville, Ontario, and was supported on acid-washed Chromosorb W (100–120 mesh). The conditions were as follows: 5% (w/w) LAC-4R-886 polyester wax (purged for 5 days at 200°), operated at 190° with a flow-rate setting of 3.0 at 30 p.s.i. of helium (50 ml/min).

Methyl 4,6-O-Benzylidene-2-O-p-tolylsulfonyl-α-D-ribo-hexopyranosid-3-ulose (3)

This compound was prepared from methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (**2**) (7.6 g) by the method of Baker and Buss (4). The crystalline product was recrystallized from ethanol to give white needles, (6 g, 80%), m.p. 163–164°, $[\alpha]_D$ +45° (*c*, 0.8 in chloroform). Baker and Buss report m.p. 165–167° and $[\alpha]_D^{25}$ +44.9 ± 0.9° (*N*,*N*-dimethyl formamide).

Methyl 4,6-O-Benzylidene-3-C-methyl-2-O-p-tolylsulfonyl-α-D-allopyranoside (4)

A solution of **3** (4.4 g) in dry benzene (250 ml) was added dropwise to a stirred solution of methylmagnesium iodide (prepared from magnesium (5 g) and methyl iodide (17 ml)) in ether (250 ml) at 0°. After standing at room temperature overnight, the reaction mixture was poured into ammonium chloride solution, and the aqueous layer was extracted with chloroform. Concentration of the dried extracts yielded a syrup which crystallized from chloroform–petroleum ether (b.p. 60–80°). Recrystallization from this solvent mixture gave **4** as white plates (3.6 g, 80%), m.p. 138–139°, $[\alpha]_D$ +45° (*c*, 2.0 in chloroform); λ_{max} (KBr) 2.84 (OH), 6.24, 7.48, 8.49 (sulfonate), 13.2, 14.3 μm (Ph); n.m.r. data: τ 2.0–2.8 (9-proton multiplet, aromatic H's), τ 4.48 (1-proton singlet, benzylidene-methine H), τ 5.2 (1-proton doublet, $J_{1,2}$ = 4Hz, H-1), τ 6.67 (3-proton singlet, OMe), τ 7.58 (3-proton singlet, aromatic Me), τ 8.8 (3-proton singlet, C-3 Me).

Anal. Calcd. for $C_{22}H_{26}O_8S$: C, 58.7; H, 5.8; S, 7.1. Found: C, 58.7; H, 5.8; S, 7.3.

Investigation of the mother liquors by t.l.c. showed the presence of **4** and a slower moving component. Fractionation on silica gel with ethyl acetate as eluent afforded the latter compound, which crystallized from chloroform–petroleum ether (b.p. 60–80°) as needles, m.p. 210–212°, $[\alpha]_D$ +95° (*c*, 0.3 in chloroform). The compound was identified as methyl 4,6-*O*-benzylidene-3-*C*-methyl-α-D-allopyranoside (**5**); λ_{max} (Nujol) 2.9, 2.98 (OH), 13.2, 14.2 μm (Ph), no absorption attributable to sulfonate; n.m.r. data: τ 2.5–2.8 (5-proton multiplet, Ph), τ 4.42 (1-proton singlet, benzylidene-methine H), τ 5.24 (1-proton doublet, $J_{1,2}$ = 4Hz, H-1), τ 6.5 (3-proton singlet, OMe), τ 8.6 (3-proton singlet, C-3 Me).

Anal. Calcd. for $C_{15}H_{20}O_6$: C, 60.8; H, 6.8. Found: C, 60.7; H, 6.7.

Methyl 3-O-Acetyl-4,6-O-benzylidene-3-C-methyl-2-O-p-tolylsulfonyl-α-D-allopyranoside (6)

A mixture of **4** (50 mg), *p*-toluenesulfonic acid (22 mg), and acetic anhydride (1.5 ml) was stirred at ambient temperature for 1h, and then poured into sodium bicarbonate solution. After effervescence had ceased, the mixture was extracted with chloroform (4 × 10 ml) and the combined extracts were washed with sodium bicarbonate solution and water. Concentration of the dried extracts afforded a clear syrup which crystallized spontaneously. Recrystallization from ether – petroleum ether (b.p. 60–80°) gave the acetate **6** as prisms (40 mg, 73%), m.p. 133–134°; λ_{max} (KBr) 5.68 (OAc), 6.24, 7.3, 8.45 μm (sulfonate), no absorption attributable to OH; n.m.r. data: τ 2.0–2.8 (9-proton multiplet, aromatic H's), τ 4.51 (1-proton singlet, benzylidene-methine H), τ 5.27 (1-proton doublet, $J_{1,2}$ = 4Hz, H-1), τ 6.7 (3-proton singlet, OMe), τ 7.6 (3-proton singlet, aromatic Me), τ 03 (3-8. proton singlet, OAc), τ 8.34 (3-proton singlet, C-3 Me).

Anal. Calcd. for $C_{24}H_{28}O_9S$: C, 53.6; H, 5.7. Found: C, 53.5; H, 5.6.

Methyl 3-O-Benzyl-4,6-O-benzylidene-3-C-methyl-2-O-p-tolylsulfonyl-α-D-allopyranoside (7)

A mixture of **4** (2.6 g), benzyl bromide (6 ml), and sodium hydroxide (12.5 g) was stirred in tetrahydrofuran at room temperature for 24 h. Thin-layer chromatography showed the presence of a compound with R_f 0.64 and the absence of starting material, R_f 0.48. The reaction mixture was freed from solid material by centrifugation and the clear liquid was concentrated to a mobile oil, which was purified by column chromatography on silica gel. Elution with benzene and then 2:3 ethyl acetate – petroleum ether (b.p. 60–80°) gave the 3-*O*-benzyl ether **7** as a syrup (3.04 g, 97%) which crystallized on standing, m.p. 49–50°, $[\alpha]_D$ +54° (*c*, 0.6 in methanol); λ_{max} (Film) 6.24, 7.3, 8.45 μm (sulfonate), no absorption attributable to OH; n.m.r. data: τ 2.1–3.0 (14-proton multiplet, aromatic H's), τ 4.65 (1-proton singlet, benzylidene-methine H), τ 6.8 (3-proton singlet, OMe), τ 7.64 (3-proton singlet, aromatic Me), τ 8.65 (3-proton singlet, C-3 Me). The region for the signals of the aromatic and benzyl–methylene protons was complex, but significantly no 2-proton singlet was evident.

Anal. Calcd. for $C_{29}H_{32}O_8S$: C, 64.4; H, 5.9; S, 5.9. Found: C, 64.8; H, 5.9; S, 5.8.

Methyl 3-O-Benzyl-4,6-O-benzylidene-3-C-methyl-α-D-allopyranoside (8)

A solution of the sulfonate **7** (3.1 g) in methanol (100 ml) containing sodium (2.6 g) was heated at reflux temperature for 3 h. Thin-layer chromatography showed that the starting material had all reacted. The product was isolated in the usual manner as a syrup (2.20 g, 99%), $[\alpha]_D$ +119° (*c*, 1.2 in tetrahydrofuran); R_f 0.52 (t.l.c.); λ_{max} (Film) 2.85 μm (OH), no absorption attributable to sulfonate; n.m.r. data: τ 2.5–2.8 (10-proton multiplet, aromatic H's), τ 4.56 (1-proton singlet, benzylidene-methine H), τ 6.55 (3-proton singlet, OMe), τ 8.42 (3-proton singlet, C-3 Me).

Anal. Calcd. for $C_{22}H_{26}O_6$: C, 68.4; H, 6.8. Found: C, 67.8; H, 6.8.

Methyl 3-O-Benzyl-4,6-O-benzylidene-3-C-methyl-2-O-methyl-α-D-allopyranoside (9)

Dimethyl sulfate (22 ml) was added dropwise with stirring to a slurry of **8** (2.2 g) and finely powdered sodium hydroxide (13 g) in tetrahydrofuran (50 ml). After the mixture was stirred at ambient temperature for 12 h, aqueous ammonia was added and the aqueous layer was extracted with chloroform. Concentration of the dried extracts yielded a crystalline product which was recrystallized from petroleum ether (b.p. 60–80°) to give white needles (1.835 g, 81%), m.p. 113–114°, $[\alpha]_D$ +108° (*c*, 0.7 in chloroform); R_f 0.65 (t.l.c.); n.m.r. data: τ 2.3–3.0 (10-proton multiplet, aromatic H's), τ 4.58 (1-proton singlet, benzylidene-methine H), τ 5.16 (3-proton broad signal, H-1 and benzyl-methylene), τ 6.54, 6.58 (3-proton singlets, C-1 OMe and C-2 OMe), τ 8.50 (3-proton singlet, C-3 Me).

Anal. Calcd. for $C_{23}H_{28}O_6$: C, 69.0; H, 7.0. Found: C, 69.3; H, 7.2.

Methyl 3-C-Methyl-2-O-methyl-α-D-allopyranoside (11)

A solution of **9** (1.27 g) in ethanol (25 ml) was hydrogenated over 10% palladium on carbon at atmospheric pressure for 12 h. Thin-layer chromatography showed complete conversion to a compound with R_f 0.07 (ether). The catalyst was removed by filtration, and the solution concentrated to give the triol **11** as a clear viscous syrup (710 mg, 97%), $[\alpha]_D$ +107° (*c*, 0.3 in chloroform); λ_{max} (Film) 2.9 (broad) μm (OH), no aromatic absorption; n.m.r. data: τ 5.02 (1-proton doublet, $J_{1,2}$ = 3.5 Hz, H-1), τ 6.48, 6.52 (3-proton singlets, C-1 OMe and C-2 OMe), τ 8.67 (3-proton singlet, C-3 Me).

Anal. Calcd. for $C_9H_{18}O_6$: C, 48.6; H, 8.1. Found: C, 48.2; H, 7.8.

Mono- and Di-O-p-tolylsulfonyl Derivatives of Methyl 3-C-methyl-2-O-methyl-α-D-allopyranoside

Syrupy methyl 3-*C*-methyl-2-*O*-methyl-α-D-allopyranoside (710 mg) in dry pyridine (10 ml) was treated with *p*-toluenesulfonyl chloride (670 mg, 1.1 moles) in pyridine (3 ml) below 0°. After the mixture was left at 5° for 24 h, t.l.c. showed the presence of the mono-*O*-*p*-tolylsulfonyl derivative (**12**), R_f 0.52 (ethyl acetate) and small amounts of the di-*O*-*p*-tolylsulfonyl derivative (**13**), R_f 0.73, and unchanged starting material. The solution was poured into water (50 ml) and the products were extracted with chloroform. Concentration of the extracts after they had been washed successively with sulfuric acid (3*N*), sodium bicarbonate solution, and water yielded a viscous syrup, which was chromatographed on silica gel, with 4:1 ethyl acetate – petroleum ether (b.p. 60–80°) as eluent. The 4,6-di-*O*-*p*-tolylsulfonyl derivative (**13**) was obtained as fine needles after recrystallization from chloroform – petroleum ether (240 mg, 14%), m.p. 129–130; λ_{max} (Film) 2.85 (OH), 6.25, 7.4, 8.45 μm (sulfonate); n.m.r. data: τ 2.0–2.8 (8-proton multiplet, aromatic H's), τ 5.1 (2-proton doublet, $J_{1,2}$ = 4 Hz, H-1), τ 6.52, 6.60 (3-proton singlets, C-1 OMe and C-2 OMe), τ 7.55 (6-proton singlet, aromatic Me's), τ 8.78 (3-proton singlet, C-3 Me).

Anal. Calcd. for $C_{23}H_{30}O_{10}S_2$: C, 52.0; H, 6.0; S, 12.0. Found: C, 51.9; H, 5.8; S, 11.7.

The mono-*O*-*p*-tolylsulfonyl derivative (**12**), was isolated as a syrup which crystallized as large prisms from chloroform – petroleum ether (870 mg, 72%), m.p. 116–118°, $[\alpha]_D$ +85° (*c*, 0.3 in chloroform); λ_{max} (KBr) 2.9 (OH), 6.25, 7.4, 8.4 μm (sulfonate); n.m.r. data: τ 2.0–2.8 (4-proton multiplet, aromatic H's), τ 5.12 (1-proton doublet, $J_{1,2}$ = 4Hz, H-1), τ 6.53, 6.61 (3-proton singlets, C-1 OMe, and C-2 OMe), τ 7.58 (3-proton singlet, aromatic Me), τ 8.73 (3-proton singlet, C-3 Me).

Anal. Calcd. for $C_{16}H_{24}O_8S$: C, 51.0; H, 6.4; S, 8.5. Found: C, 50.4; H, 6.3; S, 8.4.

Methyl 6-Deoxy-3-C-methyl-2-O-methyl-α-D-allopyranoside (14)

The 6-*O*-*p*-tolylsulfonyl derivative **12** (870 mg) was heated under reflux with lithium aluminium hydride (1 g) in tetrahydrofuran (25 ml) for 2 h. The reduced product was isolated in the usual manner as a colorless mobile liquid (445 mg, 94%), $[\alpha]_D$ +118° (*c*, 0.6 in chloroform); R_f 0.35 (ethyl acetate); n.m.r. data: τ 5.13 (1-proton doublet, $J_{1,2}$ = 4Hz, H-1), τ 6.5, 6.55 (3-proton singlets, C-1 OMe, and C-2 OMe), τ 6.93 (1-proton doublet,

$J_{2,1}$ = 4Hz, H-2), τ 8.7 (3-proton doublet, J = 6Hz, C-5 Me), τ 8.67 (3-proton singlet, C-3 Me).

*6-Deoxy-3-C-methyl-2-O-methyl-*D*-allose (15)*

A solution of the glycoside **14** (80 mg) in 2 *N* hydrochloric acid (4 ml) was heated at 90° for 2 h. The cooled solution was neutralized with Duolite A-4 (OH^-) ion-exchange resin and concentrated to a gummy residue which was extracted with hot chloroform. The extracts were concentrated to give the free sugar **15** as a clear viscous syrup (55 mg, 75%), $[\alpha]_{546}$ +5° (5 min), −5° (final) (*c*, 1.2 in water); n.m.r. data: τ 4.56 (doublet, $J_{1,2}$ = 4Hz, H-1 of α anomer), τ 4.97 (doublet, $J_{1,2}$ = 8Hz, H-1 of β anomer), τ 6.21 (singlet, C-2 OMe of β anomer), τ 6.35 (singlet, C-2 OMe of α anomer), τ 8.5–8.75 (C-3 Me and C-5 Me). For L-vinelose $[\alpha]_{546}$ +12° (*c*, 1.1 in water) has been reported (1). Paper chromatographic analysis of the syrupy product revealed only one component with R_{Rh} 1.68 in solvent *a* and 2.49 in solvent *b* (pink spot which changed to grayish blue within 24 h with vanillin–perchloric acid spray). Authentic L-vinelose had R_{Rh} 1.73 in solvent *a* and 2.50 in solvent *b*, and showed the same color change.

Gas–liquid Chromatographic Comparison of L*-Vinelose and 6-Deoxy-3-C-methyl-2-O-methyl-*D*-allose*

Acetylation of the two sugars was carried out by heating a small sample of each (< 1 mg) with 2 drops of 60% acetic anhydride in pyridine at 90° for 15 min. The solutions were examined by g.l.c. and the results are shown in Table I.

*1,4-Di-O-acetyl-6-deoxy-3-C-methyl-2-O-methyl-*β*-*D*-allopyranose*

A solution of **15** (50 mg) in 2:3 acetic anhydride and pyridine (2 ml) was heated at 90° for 1 h. The reaction mixture was poured into water (30 ml) and extracted with chloroform. Concentration of the extracts after they had been washed with sulfuric acid, sodium bicarbonate solution, and water gave a syrup which crystallized after several days. Recrystallization from chloroform–petroleum ether (b.p. 60–80°) gave prisms (40 mg, 55%), m.p. 108–110°; λ_{max} (KBr) 2.85 (OH), 5.75 μm (OAc); n.m.r. data: τ 4.13 (1-proton doublet, $J_{1,2}$ 8 Hz, H-1), τ 5.37 (1-proton doublet, $J_{4,5}$ = 9.5 Hz, H-4), τ 5.9 (1-proton multiplet, H-5), τ 6.4 (3-proton singlet, C-2 OMe), τ 6.95 (1-proton doublet, $J_{2,1}$ = 8 Hz, H-2), τ 7.83 (6-proton singlet, C-1 and C-4 OAc's), τ 8.33 (3-proton doublet, J = 9 Hz, C-5 Me), τ 8.82 (3-proton singlet, C-3 Me).

Anal. Calcd. for $C_{12}H_{20}O_7$: C, 52.2; H, 7.20. Found: C, 52.0; H, 7.1.

Acknowledgments

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