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BRANCHED-CHAIN SUGARS

VII. DETERMINATION OF THE CONFIGURATION OF L-VINELOSE BY SYNTHESIS

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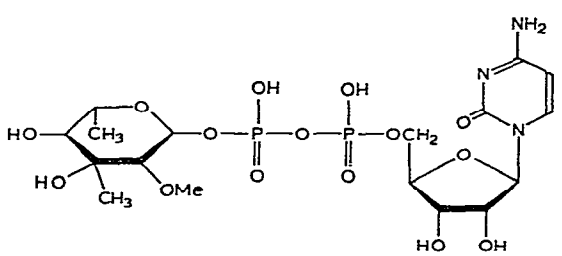
ABSTRACT

The configuration of L-vinelose was unequivocally determined to be 6-deoxy-3-*C*-methyl-2-*O*-methyl-L-talose by comparing an authentic specimen with the synthetic product obtained in eleven steps from 1,2:5,6-di-*O*-isopropylidene-3-*C*-methyl-α-D-allofuranose.

INTRODUCTION

L-Vinelose, a component of the first branched-chain sugar nucleotide to be described, cytidine 5′-(6-deoxy-3-*C*-methyl-2-*O*-methyl-L-aldohexopyranosyl diphosphate)[1], isolated from *Azotobacter vinelandii* Strain O, has been suggested as having one of three possible configurations, namely L-*talo*, L-*galacto*, and L-*altro*, from conformational considerations of n.m.r. data for β-L-vinelosyl phosphate.



Cytidine 5′-(6-deoxy-3-*C*-methyl-2-*O*-methyl-L-aldohexopyranosyl diphosphate)

As part of a synthetic and stereochemical program on branched-chain sugars we have recently reported[2] the stereoselective synthesis of 1,2:5,6-di-*O*-isopropylidene-3-*C*-methyl-α-D-glucofuranose and related compounds, potentially important precursors for synthesis of naturally occurring, branched-chain sugars. In a previous

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communication[3], we have confirmed the validity of the foregoing speculation for L-vinelose by synthesizing the most probable structure, 6-deoxy-3-*C*-methyl-2-*O*-methyl-L-talose (**6**), from 1,2:5,6-di-*O*-isopropylidene-3-*C*-methyl-α-D-allofuranose[4] (**1a**). Brimacombe *et al.** almost simultaneously reported[5] the synthesis of L-vinelose by a similar route.

We now describe in detail full data on the configuration and the synthesis of L-vinelose, and also report observations on the behavior of the sugar in solution.

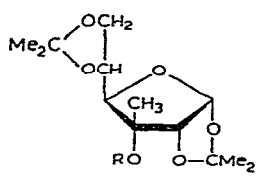
RESULTS AND DISCUSSION

The starting compound **1a** was initially benzylated in the conventional manner[6] with benzyl chloride–sodium hydride in methyl sulfoxide to give crystalline 3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-3-*C*-methyl-α-D-allofuranose (**1b**) in 80% yield. The 5,6-*O*-isopropylidene group of **1b** was then removed with 70% acetic acid to give the corresponding 5,6-diol **2a**, which was then successively tritylated and mesylated in pyridine to give 3-*O*-benzyl-1,2-*O*-isopropylidene-3-*C*-methyl-5-*O*-mesyl-6-*O*-trityl-α-D-allofuranose (**2b**) as a syrup in 85% yield. Detritylation of **2b** in 85% hot acetic acid gave crystalline 3-*O*-benzyl-1,2-*O*-isopropylidene-3-*C*-methyl-5-*O*-mesyl-α-D-allofuranose (**2c**), which was further converted into the syrupy 5,6-anhydro-β-L-talofuranose derivative **3** in 85% yield by treating **2c** with sodium methoxide in methanol. Proton n.m.r. spectra showed the presence of typical epoxymethylene signals at δ 2.71. Reduction of **3** with lithium aluminum hydride in ether gave a high yield of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-β-L-talofuranose (**4a**), and the free hydroxyl group at C-5 was then benzylated as effected with **1b**. Methanolysis of **4b** with 3% methanolic hydrogen chloride for 3 h at room temperature gave the corresponding methyl α,β-L-talofuranosides (**5a** and **5'a**) quantitatively in the ratio of 2:1. Methylation of the α,β mixture, followed by separation by preparative t.l.c., gave the 2-*O*-methyl derivatives (**5b** and **5'b**, respectively). These α,β-anomers were readily differentiated by their optical rotations and $J_{1,2}$ values (**5b**, 2.5 Hz; **5'b** 5.0 Hz). The latter values are considered diagnostic for anomeric assignment in such furanoid rings[7] and indicate that H-1 and H-2 of **5b** and **5'b** are *trans* and *cis*, respectively, in this instance. Therefore, **5b** is the α-anomer and **5'b** is the β-anomer. The preponderance of **5a** over **5'a** is understandable in view of the non-bonded interaction of 1,2-*cis* substituents of **5'a**.

Hydrogenation of compound **5b** over palladium on carbon (10%) removed the benzyl groups at C-3 and C-5 to give methyl 6-deoxy-3-*C*-methyl-2-*O*-methyl-α-L-talofuranoside (**5c**) in quantitative yield. Hydrolysis of **5c** was finally effected in M sulfuric acid for 2 h at 90° to convert it into the desired 6-deoxy-3-*C*-methyl-2-*O*-methyl-L-talose (**6**), obtained in good yield.

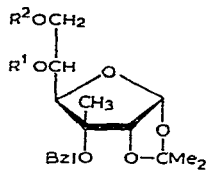
Interestingly, the proportion of furanose forms (~40%) of compound **6** in dry pyridine was higher than expected by comparison with D-talose[9]. Acetylation of **6**

*The pyranose form was assigned, without proof, to 6-deoxy-3-*C*-methyl-2-*O*-methyl-L-talose (**6**).



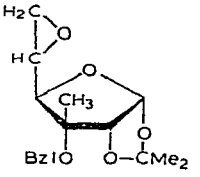
1

a R = H
b R = Bzl



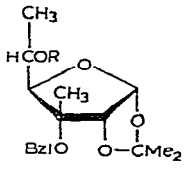
2

a $R^1 = R^2 = H$
b R^1 = Ms, R^2 = Tr
c R^1 = Ms, R^2 = H



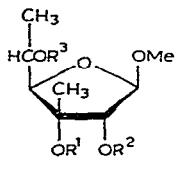
3

(Bzl = CH_2Ph)



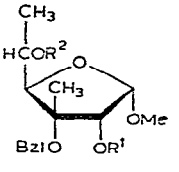
4

a R = H
b R = Bzl



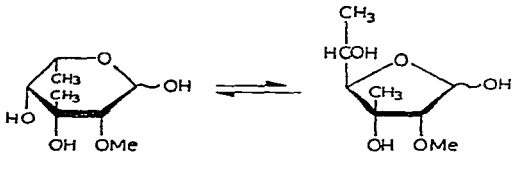
5

a $R^1 = R^3$ = Bzl, R^2 = H
b $R^1 = R^3$ = Bzl, R^2 = Me
c $R^1 = R^3$ = H, R^2 = Me

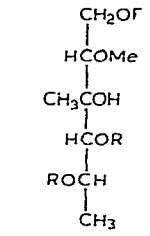


5'

a R^1 = H, R^2 = Bzl
b R^1 = Me, R^2 = Bzl



6



7

a R = H, b R = Ac

with acetic anhydride after keeping **6** in pyridine overnight at room temperature, revealed three spots on thin-layer chromatograms, although paper chromatography of **6** showed only one spot (Table I). The n.m.r. spectrum of the acetate also showed the presence of three components, for which proton signals could be completely assigned after separation; the products were 1,5-di-*O*-acetyl-6-deoxy-3-*C*-methyl-2-*O*-methyl-α-L-talofuranose (**8**) and 1,4-di-*O*-acetyl-6-deoxy-3-*C*-methyl-2-*O*-methyl-α- and -β-L-talopyranose (**9a** and **9b**), respectively. The ratio of these three components as isolated was about 2:2:1 (n.m.r., approximately 5:4:3 from the intensities of each H-1 signal). Diagnosis of the structures as **8**, **9a**, and **9b** by n.m.r. spectroscopy (Table II) was performed as follows: (*a*) **8** is a furanose form, as H-5 is more deshielded by an acetoxyl group than H-4, and the fact that $J_{1,2} = 0$ means that H-1 and H-2 are *trans* as already described; (*b*) **9a** and **9b** are pyranoses, as the H-4 signals are more deshielded than H-5. The anomeric assignment, which can not be made from the

$J_{1,2}$ value in this instance*, was made by observing the expected deshielding of the H-1 signal of **9a** in comparison with that of **9b** (H-1 of **9a** is 0.53 p.p.m. to lower field than that of **9b**). Therefore, H-1 of **9a** is equatorially oriented, whereas H-1 of **9b** is axially oriented. In other words, **9a** is the α-anomer and **9b** the β-anomer, and they both have the $^1C_4$(L) conformation. The deshielding of H-5 in **9a** can also be explained by the presence of an axial acetoxyl group at C-1.

TABLE I

PAPER CHROMATOGRAPHIC COMPARISON OF SYNTHETIC AND AUTHENTIC SPECIMENS OF L-VINELOSE AND L-VINELITOL

Sample	R_F (L-*rhamnose* = 1.00)[a]			
	A	*B*	*C*	*D*
Authentic L-vinelose	2.58	2.45	1.81	1.31
Synthetic L-vinelose (**6**)	2.57	2.47	1.80	1.29
Authentic L-vinelitol	2.23	2.25	1.79	
Synthetic L-vinelitol (**7a**)	2.28	2.32	1.79	

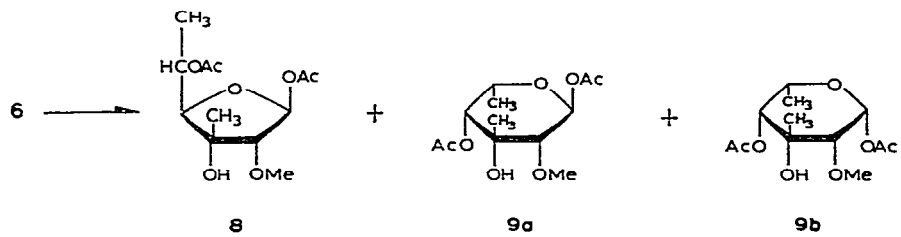
[a]Solvents: A, 3:1:3 Ethyl acetate–acetic acid–water; B, Butanol saturated with water (upper layer); C, 4:1:5 Butanol–ethanol–water; D, 6:4:3 Butanol–pyridine–water.

TABLE II

N.M.R. DATA FOR COMPOUNDS **8**, **9a**, AND **9b**

Compound		*H-1*	*H-2*	*H-4*	*H-5*	*OH*	*OMe*	*OAc*	CH_3-*C-5*	CH_3-*C-3*
8	δ	6.08	3.33	3.77	5.01	3.05	3.54	2.04, 2.08	1.28	1.33
		s	s	d	q[a]	s	s		d	s
		$J_{1,2} \doteqdot 0$, $J_{4,5} = J_{5,CH_3} = 6.7$ Hz								
9a	δ	6.29	3.37	4.80	4.15	2.93	3.54	2.10, 2.15	1.18	1.43
		d	d	d	qd	s	s		d	s
		$J_{1,2} \geqslant 1.0$ Hz, $J_{4,5} \geqslant 1.5$ Hz, $J_{5,CH_3} = 6.7$ Hz								
9b	δ	5.76	3.35	4.73	3.83	3.10	3.63	2.13, 2.15	1.20	1.38
		d	d	d	qd	s	s		d	s
		$J_{1,2} \geqslant 1.0$ Hz, $J_{4,5} \geqslant 1.5$ Hz, $J_{5,CH_3} = 6.5$ Hz								

[a]q = quintet.



8 **9a** **9b**

*N.m.r. data of some mannose derivatives are helpful for the anomeric assignment (see ref. 10).

Reduction of **6** with sodium borohydride in water gave the L-talitol derivative **7a**, and acetylation of **7a** with acetic anhydride in pyridine gave the triacetate **7b** quantitatively. Comparison of L-vinelose, L-vinelitol, and their acetates, with the synthetic samples was effected by paper chromatography (Table I), gas–liquid chromatography, n.m.r. data and optical rotations; some of these data were published in the preliminary communication[3].

From the good agreement of these data, it can be securely concluded that L-vinelose has the L-*talo* configuration.

It may be noted that a preliminary assignment of the possible configuration of L-vinelose should be possible indirectly by the following three criteria: (*a*) comparison of $J_{4,5}$ of talitol, galactitol, and altritol [the $J_{4,5}$ value (3.0 Hz) for L-vinelitol triacetate[1] is too small to accord with that for L-altritol in comparison with n.m.r. data for other alditols[8]]; (*b*) comparison of $J_{1,2}$ and $J_{4,5}$ of β-talopyranose, -galactopyranose, and -altropyranose [the small coupling constants for β-L-vinelosyl phosphate ($J_{1,2} = J_{4,5} = 2$ Hz)[1] seem to exclude the possibiiity of the *galacto* and *altro* configurations, in which either H-1 and H-2 or H-4 and H-5 must have the *trans*-diaxial orientation in their $^1C_4$(L) conformations, as pointed out by Okudà *et al.*[1]]; and (*c*) the pyranose–furanose ratio for L-vinelose in water [the relatively high furanose content[7b,9] of talose (31%) or altrose (33%) in water would not be expected for galactose (~0%) even after allowing for the methyl branch at C-3].

EXPERIMENTAL

General methods. — Melting points were determined on a Yanagimoto micro melting-point apparatus and are uncorrected. Solvents were evaporated off *in vacuo*. N.m.r. spectra were recorded with a JNM-4H-100 spectrometer with solutions in chloroform-*d* containing tetramethylsilane as the internal reference. G.l.c. analyses were performed on a Shimazu GC-5AP$_3$ gas chromatograph equipped with a hydrogen flame-ionization detector. The glass columns (2.5 m × 5 mm) were packed with (*a*) 5% neopentyl glycol adipate polyester, or (*b*) 5% LAC 4R-886 on 60–80 mesh Neosorb NC (Nishio Industry Ltd.). Analysis conditions and results are given in the previous paper[3]. T.l.c. and preparative t.l.c. was effected on plates of silica gel (Merck type 60) with the solvent systems: A, 10:1 benzene–methanol; B, 1:1 benzene–ethyl acetate; and C, 10:1 ethyl acetate–ethanol. Compounds were detected with iodine vapor or 5% methanolic sulfuric acid spray followed by heating on a hot plate. Paper chromatography was performed by the ascending technique on Toyo No. 51A filter paper, with the solvent systems shown in Table I. Compounds were detected by vanillin (1%)–perchloric acid (3%)[11] and or by the periodate–benzidine method[12].

3-O-Benzyl-1,2:5,6-di-O-isopropylidene-3-C-methyl-α-D-allofuranose (**1b**). — To a suspension of sodium hydride (100 mg) and 1,2;5,6-di-*O*-isopropylidene-3-*C*-methyl-α-D-allofuranose[4c] (**1a**) (550 mg, 2 mmol) in dry methyl sulfoxide (15 ml) was added gradually benzyl chloride (520 mg, 4 mmol). The mixture was then heated for

1 h at 70° on a water bath, and then poured into a mixture of ice and water and extracted with chloroform. The extract was washed with water, dried (anhydrous magnesium sulfate), and evaporated to give a crystalline residue, which was recrystallized from hexane to afford **1b** as needles (660 mg, 90%), m.p. 55–56°, $[\alpha]_D^{24}$ +43.7° (*c* 1.0, methanol).

Anal. Calc. for $C_{20}H_{28}O_6$: C, 65.91; H, 7.74. Found: C, 65.97; H, 7.80.

3-O-Benzyl-1,2-O-isopropylidene-3-C-methyl-α-D-allofuranose (**2a**). — A solution of **1b** (500 mg, 1.38 mmol) in 70% acetic acid (20 ml) was kept overnight at room temperature and then evaporated to yield a crystalline residue, which was recrystallized from ethanol to give needles (430 mg, 96%); m.p. 119–120°, $[\alpha]_D^{24}$ +53.3° (*c* 1.0, methanol).

Anal. Calc. for $C_{17}H_{24}O_6$: C, 62.95; H, 7.46. Found: C, 62.68; H, 7.47.

3-O-Benzyl-1,2-O-isopropylidene-5-O-mesyl-3-C-methyl-6-O-trityl-α-D-allofuranose (**2b**). — A solution of **2a** (500 mg, 1.54 mmol) and chlorotriphenylmethane (520 mg, 1.86 mmol) in dry pyridine (5 ml) was kept at room temperature until the starting material disappeared (t.l.c.) and methanesulfonyl chloride (210 mg, 1.86 mmol was then added. The mixture was kept overnight at room temperature and then poured into a mixture of ice and water, and the product extracted with chloroform. The extract was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to give a syrup that was purified by preparative t.l.c. to give amorphous powder (0.84 g, 85%); $[\alpha]_D^{24}$ +7.7° (*c* 1.0, methanol).

Anal. Calc. for $C_{37}H_{40}O_8S \cdot H_2O$: C, 67.05; H, 6.38. Found: C, 66.82; H, 6.67.

3-O-Benzyl-1,2-O-isopropylidene-5-O-mesyl-3-C-methyl-α-D-allofuranose (**2c**). — Compound **2b** (640 mg, 1 mmol) was heated in 85% acetic acid for 1.5 h at 80°. The mixture was then cooled in an ice–water bath and the precipitate filtered off. The filtrate was then concentrated to a syrup that was purified on a column of Wako Gel (C-200) by eluting with 5:1 benzene–ethyl acetate to yield crystals (330 mg); m.p. 85–86°, $[\alpha]_D^{24}$ +50.4° (*c* 1.0, methanol).

Anal. Calc. for $C_{18}H_{26}O_8S$: C, 53.72; H, 6.51. Found: C, 53.93; H, 6.62.

5,6-Anhydro-3-O-benzyl-1,2-O-isopropylidene-3-C-methyl-β-L-talofuranose (**3**).— To an ice-cooled solution of **2c** (400 mg, 1 mmol) in dry methanol (5 ml) was added a solution of sodium methoxide (30 mg of sodium metal in 3 ml of dry methanol), and the mixture was kept at 0° with stirring. The solution was then evaporated and the residue treated with chloroform and aqueous sodium chloride. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated to a syrup that was purified by preparative t.l.c. (solvent A) to give pure **3** as a syrup (270 mg); $[\alpha]_D^{24}$ +52.5° (*c* 1.0, methanol); n.m.r.: δ 1.33, 1.54 (isopropyl methyl), 2.71 m (H-6, H-6′), 3.05 q ($J_{5,6} = J_{5,6'} = J_{4,5} = 4.0$ Hz, H-5), 3.87 d (H-4), 4.33 d ($J_{1,2}$ 3.7 Hz, H-2), 4.58 s (–CH_2–Ph), 5.76 d (H-1), 7.35 (phenyl).

Anal. Calc. for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.45; H, 7.13.

3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-3-C-methyl-β-L-talofuranose (**4a**). — A suspension of **3** (1.93 g, 6.3 mmol) and lithium aluminum hydride (200 mg) in dry ether (50 ml) was boiled under reflux for 1 h. The mixture was then successively

treated with water and 15% sodium hydroxide, and the precipitate filtered off. The filtrate and washings were washed with water and dried over anhydrous magnesium sulfate. The washings were further extracted with chloroform, washed with aqueous sodium chloride, and dried over anhydrous magnesium sulfate. Both extracts were evaporated to yield crystals, which were recrystallized from hexane; yield, 1.52 g (80%), m.p. 90–91°, $[\alpha]_D^{24}$ +32° (*c* 1.0, methanol); n.m.r.: δ 1.22 (C–CH_3 at C-3 and C-5), 1.33, 1.57 (isopropyl methyl), 2.25 (OH), 3.86 m (H-4 and H-5), 4.34 d ($J_{1,2}$ 3.7 Hz, H-2), 4.60 (–CH_2Ph), 5.74 d (H-1), 7.34 (phenyl).

Anal. Calc. for $C_{17}H_{24}O_5$: C, 66.21; H, 7.85. Found: C, 66.49; H, 7.86.

3,5-Di-O-benzyl-6-deoxy-1,2-O-isopropylidene-3-C-methyl-β-L-talofuranose (**4b**). — To a suspension of sodium hydride (260 mg) and **4a** (850 mg, 2.75 mmol) in dry methyl sulfoxide (10 ml) was gradually added benzyl chloride (600 mg, 4.7 mmol) with stirring. The mixture was heated for 1.5 h at 70° on a water bath and then poured into ice–water and extracted with chloroform. The extract was washed with aqueous sodium chloride and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a crystalline residue, which was recrystallized from hexane; yield, 0.87 g, m.p. 115–117°, $[\alpha]_D^{24}$ +23.5° (*c* 1.0, methanol); n.m.r.: δ 1.20–1.28 (CH_3 at C-3 and C-5), 1.32, 1.57 (isopropyl), 3.65 (apparent quintet) ($J_{4,5} = J_{5,6} =$ 7.5 Hz, H-5), 4.03 d (H-4), 4.28 d (d, $J_{1,2}$ 4.0 Hz, H-2), 5.78 d (H-1), 7.32 (phenyl).

Anal. Calc. for $C_{24}H_{30}O_5$: C, 72.33; H, 7.59. Found: C, 72.50; H, 7.53.

Methyl 3,5-di-O-benzyl-6-deoxy-3-C-methyl-α,β-L-talofuranoside (**5a** *and* **5'a**). — A solution of **4b** (1 g, 2.45 mmol) in 3% methanolic hydrogen chloride (20 ml) was kept for 3 h at room temperature. Neutralization of the solution with silver carbonate, followed by evaporation, gave the syrupy α,β-L-talofuranoside derivative (0.95 g); $[\alpha]_D^{24}$ +15.7° (*c* 1.1, methanol).

Anal. Calc. for $C_{22}H_{28}O_5$: C, 70.94; H, 7.58. Found: C, 71.19; H, 7.61.

Methyl 3,5-di-O-benzyl-6-deoxy-3-C-methyl-2-O-methyl-α- and -β-L-talofuranoside (**5b** *and* **5'b**). — To a solution of **5** (0.81 g, 2.17 mmol) in dry methyl sulfoxide (10 ml) was added a suspension of sodium hydride (200 mg) in methyl sulfoxide (5 ml), and the mixture was heated at 60° with stirring on a water bath. Methyl iodide was then added to the mixture while maintaining the temperature at 60° for 10 min. The cooled solution was poured into ice–water, extracted with chloroform, and the extract was washed with aqueous sodium chloride and water. The organic layer, dried over anhydrous magnesium sulfate, was evaporated to a syrup (0.88 g). Preparative t.l.c. with 5:1 benzene–methanol gave the α-anomer (0.41 g) and β-anomer (0.18 g), respectively, as syrups; α-anomer, $[\alpha]_D^{24}$ −3.4° (*c* 1.34, methanol); β-anomer, $[\alpha]_D^{24}$ +66° (*c* 1.11, methanol); n.m.r.: (α-anomer, **5b**) δ 1.25 d ($J_{5,6}$ 6.3 Hz, CH_3 at C-5), 1.35 s (CH_3 at C-3), 3.43 s, 3.45 s (OCH_3), 3.54 d ($J_{1,2}$ 2.5 Hz, H-2), 3.58 q ($J_{4,5} = J_{5,6} = 6.3$ Hz, H-5), 3.98 d (H-4), 4.51 s, 4.61 q (OCH_2Ph×2), 4.98 d (H-1); (β-anomer; **5'b**) 1.28 d ($J_{5,6} = 6.3$ Hz, CH_3 at C-5), 1.38 s (CH_3 at C-3), ~3.4 (unresolved, H-5), 3.46 s, 3.50 s (OCH_3), 3.64 d ($J_{1,2}$ 5.0 Hz, H-2), 4.65 ($J_{4,5}$ 4.0 Hz, H-4), 4.54 s, 4.62 q (OCH_2Ph×2), 5.03 d (H-1).

Anal. Calc. for $C_{23}H_{30}O_5$: C, 71.48; H, 7.82. Found: (α-anomer); C, 71.09; H, 7.92. Found: (β-anomer); C, 71.21; H, 7.95.

Methyl 6-deoxy-3-C-methyl-2-O-methyl-α-L-talofuranoside (**5c**). — Compound **5b** (510 mg, 1.06 mmol) was hydrogenated in 70% acetic acid (14 ml) in the presence of palladium on carbon (10%) for 2 h. Filtration, followed by evaporation of the filtrate gave a pure syrup (200 mg); $[\alpha]_D^{24}$ −15° (*c*, 1.34, methanol).

Anal. Calc. for $C_9H_{18}O_5$: C, 52.41; H, 8.80. Found: C, 52.32; H, 8.56.

6-Deoxy-3-C-methyl-2-O-methyl-α,β-L-talose (**6**). — A solution of **5c** (110 mg, 0.54 mmol) in M sulfuric acid (6 ml) was heated for 2 h at 90°. The cooled solution was then neutralized with an excess of barium carbonate. After filtration from the precipitate, the filtrate was treated with Amberlite IR-120 (H^+) resin, and evaporated to a clear syrup (85 mg, 83%), $[\alpha]_D^{24}$ +14.3°, $[\alpha]_{546}^{24}$ +16.4° (*c* 1.21, water) [lit.[11], $[\alpha]_{546}^{14,5}$ +12.0° (*c* 1.0, water)].

Anal. Calc. for $C_8H_{16}O_5$: C, 49.99; H, 8.39. Found: C, 49.53; H, 8.72.

Acetylation of compound **6**. — To a solution of **6** (40 mg) in dry pyridine (2 ml), which had been kept for 12 h at room temperature, was added acetic anhydride (2 ml). The solution was again kept overnight at room temperature, and then poured into ice–water and extracted with chloroform. The extract was washed with aqueous sodium hydrogen carbonate and water, dried over anhydrous magnesium sulfate, and evaporated to give a syrup (57 mg). The latter was subjected to preparative t.l.c. (Solvent B) to give three pure components, namely 1,5-di-*O*-acetyl-6-deoxy-3-*C*-methyl-2-*O*-methyl-α-L-talofuranose (**8**) [21 mg, syrup from the upper band, $[\alpha]_D^{23}$ −25.4° (*c* 1.05, methanol)], 1,4-di-*O*-acetyl-6-deoxy-3-*C*-methyl-2-*O*-methyl-α-L-talopyranose (**9a**) [21 mg, syrup from the middle band, $[\alpha]_D^{23}$ −53.9° (*c* 1.05, methanol)], and 1,4-di-*O*-acetyl-6-deoxy-3-*C*-methyl-2-*O*-methyl-β-L-talopyranose (**9b**) [11 mg, needles from the lowest band, m.p. 119–120°, $[\alpha]_D^{23}$ +9.8° (*c* 0.55, methanol)].

Anal. Calc. for $C_{12}H_{20}O_7$: C, 52.16; H, 7.30. Found: (for **8**); C, 51.83; H, 7.62; (for **9a**); C, 51.95; H, 7.58; (for **9b**); C, 51.96; H, 7.35.

6-Deoxy-3-C-methyl-2-O-methyl-L-talitol (**7a**). — *A*. A mixture of compound **6** (41 mg) and sodium borohydride (100 mg) in aqueous sodium hydrogen carbonate (20 mg in 10 ml) was kept for 3 h at room temperature. After acidification with acetic acid, the solution was treated successively with Amberlite IR-120 (H^+) and Amberlite IRA-400 (OH^-) resins, and evaporated in the presence of methanol to a syrup that was further extracted with acetone. Evaporation of dry ethanol from the product gave a clear syrup (37 mg); $[\alpha]_D^{24}$ −6.5°, $[\alpha]_{546}^{24}$ −7.2° (*c* 1.5, water) [lit.[1], $[\alpha]_{546}^{18,8}$ −6.4° (*c* 1.0, water)].

B. A solution of the triacetate **7b** (45 mg) in methanol (5 ml) saturated with ammonia was kept for 2 h at room temperature and then evaporated to a syrup, which was further treated as already described. A clear syrup (22 mg) was obtained.

Anal. Calc. for $C_8H_{18}O_5$: C, 49.47; H, 9.34. Found: C, 49.23; H, 9.55.

1,4,5-Tri-O-acetyl-6-deoxy-3-C-methyl-2-O-methyl-L-talitol (**7b**). — A solution of **7a** (30 mg) in dry pyridine (2 ml) and acetic anhydride (2 ml) was kept overnight

at room temperature, and evaporated to a syrup that was further purified by preparative t.l.c. (1:1 benzene–methanol) to give the pure acetate **7b** (40 mg); $[\alpha]_D^{22}$ −36.5°, $[\alpha]_{546}^{22}$ −44.2° (*c* 1.0, chloroform) [lit.[1] $[\alpha]_{546}^{21}$ −45.7° (*c* 1.0, chloroform)]; n.m.r.: δ 1.16 s (CH_3 at C-3), 1.20 d ($J_{5,6}$ 6.3 Hz, CH_3 at C-5), 2.05 s, 1.26 s (6-H and 3 H, OAc), 2.81 broad s (OH), 3.31 dd ($J_{1,2}$ 6.3, $J_{1',2}$ 2.8 Hz, H-2), 4.53 dd (H-1), 5.04 d ($J_{4,5}$ 2.8, H-4), 5.35 qd ($J_{5,6}$ 6.3 Hz, H-5).

Anal. Calc. for $C_{14}H_{24}O_8$: C, 52.49; H, 7.55. Found: C, 52.31; H, 7.82.

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REFERENCES

1 S. Okuda, N. Suzuki, and S. Suzuki, *J. Biol. Chem.*, 242 (1967) 958–966; 243 (1968) 6453–6460.
2 M. Funabashi, H. Sato, and J. Yoshimura, *Chem. Lett.*, (1974) 803–804.
3 M. Funabashi, S. Yamazaki, and J. Yoshimura, *Tetrahedron Lett.*, (1974) 4331–4334.
4 (*a*) A.-M. Sepulchre, G. Vass, and S. D. Gero, *Compt. Rend.*, (C), 274 (1972) 1077–1080; (*b*) H. Paulsen, V. Sinnwell, and P. Stadler, *Chem. Ber.*, 105 (1972) 1978–1988; (*c*) J. S. Brimacombe, A. J. Rollins, and S. W. Thompson, *Carbohydr. Res.*, 31 (1973) 108–113.
5 J. S. Brimacombe, S. Mahmood, and A. J. Rollins, *Carbohydr. Res.*, 38 (1974) C7–C8.
6 (*a*) J. Yoshimura, M. Funabashi, S. Ishige, and T. Sato, *Bull. Chem. Soc. Japan*, 39 (1966) 1760–1764; (*b*) J. S. Brimacombe, B. D. Jones, M. Stacey, and J. J. Willard, *Carbohydr. Res.*, 2 (1966) 167–169.
7 (*a*) L. D. Hall, *Chem. Ind.* (London), (1963) 950–951; (*b*) M. Rudrum and D. F. Shaw, *J. Chem. Soc.*, (1965) 52–57; (*c*) J. D. Stevens and H. G. Fletcher, Jr., *J. Org. Chem.*, 33 (1968) 1799–1805; (*d*) J. Alfordi, C. Peciar, R. Palovčík, and P. Kováč, *Carbohydr. Res.*, 25 (1972) 249–252; (*e*) H. Maehr, T. H. Williams, M. Leach, and A. Stempel, *Helv. Chim. Acta*, 57 (1974) 212–213.
8 (*a*) J. B. Lee and B. F. Scanlon, *Tetrahedron*, 25 (1969) 3413–3428; (*b*) D. Horton and J. D. Wander, *Carbohydr. Res.*, 10 (1969) 279–288; (*c*) S. J. Angyal, R. Le Fur, and D. Gagnaire, *ibid.*, 23 (1972) 125–138.
9 S. J. Angyal and V. A. Pickles, *Carbohydr. Res.*, 4 (1967) 269–270; *Aust. J. Chem.*, 25 (1972) 1695–1710.
10 G. Descotes, F. Chizat, and J. C. Martin, *Bull. Soc. Chim. Fr.*, (1970) 2305–2309; E. Hemmerand and S. Liaaen-Jensen, *Acta Chem. Scand.*, 24 (1970) 3019–3023.
11 A. P. Maclennan and H. M. Randall, *Anal. Chem.*, 31 (1959) 2020–2022.
12 H. T. Gordon, W. Thornburg, and L. N. Werum, *Anal. Chem.*, 28 (1956) 849–855.