

Preliminary communication

Identification and synthesis of vinelose

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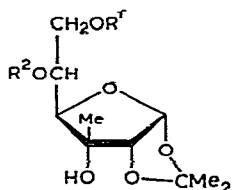
(Received September 17th, 1974; accepted for publication, September 30th, 1974)

The branched-chain sugar vinelose occurs as its 4-*O*-methylglycolate in two nucleotides present in a strain of *Azobacter vinelandii*¹⁻³. Vinelose has been identified as a 6-deoxy-3-*C*-methyl-2-*O*-methyl-L-aldohecopyranose possessing either the *altro*, *galacto*, or *talo* configuration on the basis of chemical and spectroscopic evidence^{2,3}. We have synthesised 6-deoxy-3-*C*-methyl-2-*O*-methyl-L-talopyranose (14), which proved to be identical with vinelose.

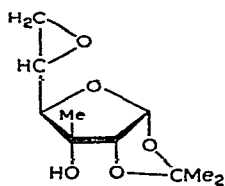
In essence, the required *L-talo* configuration is achieved by an inversion of configuration at C-5 of 1,2-*O*-isopropylidene-3-*C*-methyl- α -D-allofuranose⁴ (1). Thus, unimolar benzylation of the triol 1 gave the monobenzoate 2*, m.p. 112.5–113.5°, $[\alpha]_D +28^\circ$ (c 3, chloroform), and a small proportion of the dibenzoate 3, m.p. 155.5–156°, $[\alpha]_D +41^\circ$ (c 0.9, chloroform), which were cleanly separated by chromatography on silica gel. Sulphonylation of 2 furnished 6-*O*-benzoyl-1,2-*O*-isopropylidene-3-*C*-methyl-5-*O*-toluene-*p*-sulphonyl- α -D-allofuranose (4), m.p. 137–138°, $[\alpha]_D +45^\circ$ (c 1.1, chloroform), which on careful debenylation (sodium methoxide in methanol at –25°) afforded the 5-toluene-*p*-sulphonate 5, m.p. 73–74°, $[\alpha]_D +18^\circ$ (c 0.3, chloroform). On treatment with 1,5-diazabicyclo[5.4.0]undec-5-ene in benzene, the sulphonate 5 was smoothly converted into 5,6-anhydro-1,2-*O*-isopropylidene-3-*C*-methyl- β -L-talofuranose (6), m.p. 129–130°, $[\alpha]_D +30^\circ$ (c 0.7, chloroform), which with lithium aluminium hydride in ether gave 6-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl- β -L-talofuranose (7), m.p. 112.5–113°, $[\alpha]_D +14^\circ$ (c 2, chloroform). Benzylation of 7 afforded the monobenzoate 8, m.p. 136–137° (from ether–light petroleum), $[\alpha]_D \sim 0^\circ$ (c 0.6, chloroform), which could also be obtained by a benzoate-exchange reaction on 6-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-5-*O*-toluene-*p*-sulphonyl- α -D-allofuranose (9), m.p. 76.5–78.5° (from ether–light petroleum), $[\alpha]_D +27^\circ$ (c 1.5, chloroform). The sulphonate 9 was prepared by toluene-*p*-sulphonylation of 6-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl- α -D-allofuranose⁴; the benzoate-exchange route was less satisfactory than the one reported, since a number of other products were formed.

Benzylation (benzyl bromide, *N,N*-dimethylformamide, sodium hydride) of 7 gave 3,5-di-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl- β -L-talofuranose (10),

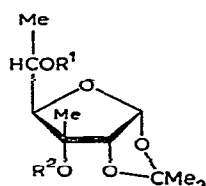
*Unless otherwise stated, dichloromethane–light petroleum (b.p. 60–80°) was used for recrystallizations.



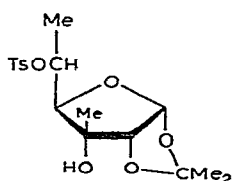
- 1 $R^1 = R^2 = H$
 2 $R^1 = Bz, R^2 = H$
 3 $R^1 = R^2 = Bz$
 4 $R^1 = Bz, R^2 = Ts$
 5 $R^1 = H, R^2 = Ts$



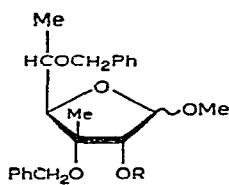
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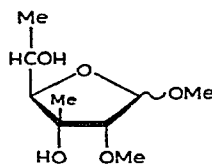
- 7 $R^1 = R^2 = H$
 8 $R^1 = Bz, R^2 = H$
 10 $R^1 = R^2 = CH_2Ph$



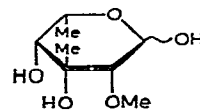
9



- 11 $R = H$
 12 $R = Me$



13



14

b.p. 140–145°(bath)/0.05 mmHg, $[\alpha]_D +27^\circ$ (c 0.4, chloroform). Successive methanolysis (2% methanolic hydrogen chloride), methylation (methyl iodide, *N,N*-dimethylformamide, sodium hydride), and debenzylation (hydrogen, 5% palladised charcoal) accomplished the sequence **10** → **11** → **12** → methyl 6-deoxy-3-*C*-methyl-2-*O*-methyl- $\alpha\beta$ -L-talofuranoside (**13**); these conversions were performed without separation of the anomeric glycosides. Finally, hydrolysis (*m* sulphuric acid, $\sim 100^\circ$) of **13** furnished syrupy 6-deoxy-3-*C*-methyl-2-*O*-methyl-L-talopyranose (**14**), $[\alpha]_{546} +13 \pm 1^\circ$ (equil., c 1, water); lit.² $[\alpha]_{546} +12^\circ$ (c 1, water). The i.r. (KBr disc) and mass spectra, and paper chromatographic (5 solvents) and electrophoretic (borate) mobilities of the synthetic sugar were shown to be indistinguishable from those of natural vinelose. Unfortunately, no crystalline derivatives of vinelose have been reported.

New compounds furnished elemental analyses and spectroscopic data compatible with the structures assigned.

ACKNOWLEDGMENTS

We thank the S.R.C. and the University of Dundee for financial assistance, and Professor S. Suzuki and Dr. S. Okuda for comparing the synthetic and natural sugars.

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