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IDENTITY OF L-VINELOSE AND 6-DEOXY-3-C-METHYL-2-O-METHYL-L-TALOSE

Masuo Funabashi*, Seiji Yamazaki and Juji Yoshimura
Laboratory of Chemistry for Natural Products, Faculty of Science,
Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan
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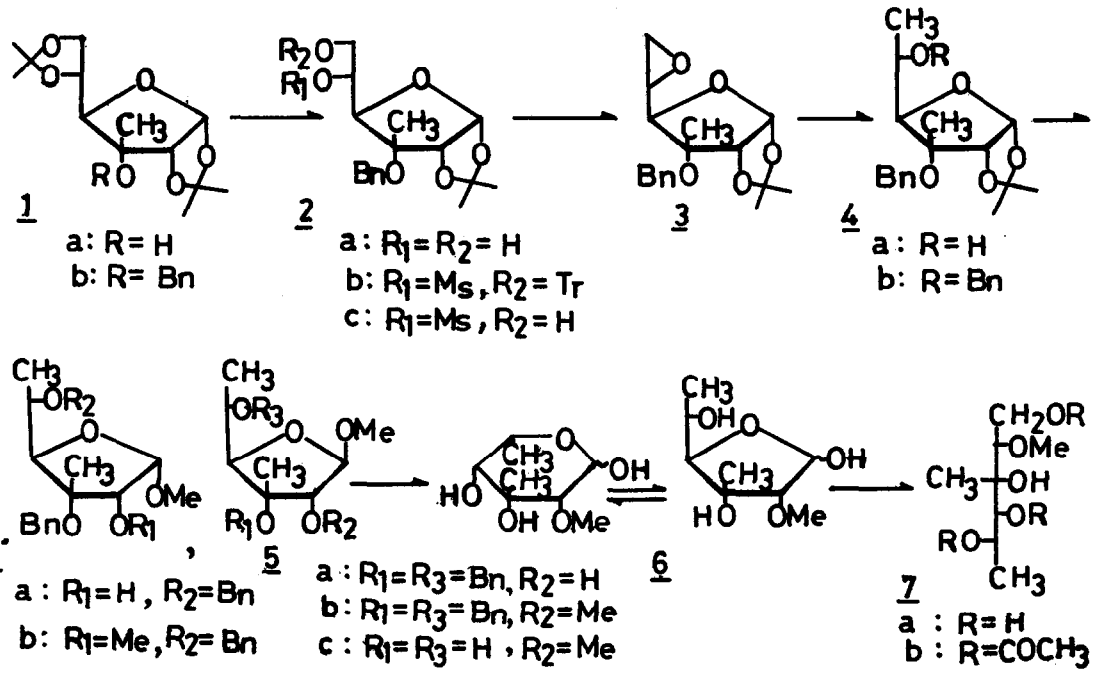
L-Vinelose, which has been isolated as a component of the first branched-chain sugar nucleotide ; cytidine diphosphate 6-deoxy-3-C-methyl-2-O-methyl-L-aldohexopyranoside[1] from *Azotobacter vinelandii* Strain O, has been proposed to have one of three possible configurations such as L-*talo*, L-*galacto* and L-*altro*.[2] L-*Talo* configuration, especially, has been suggested to be preferred, though the definite proof remains unavailable.

The present paper, therefore, affords an unambiguous answer to the above question by synthesizing for the first time the most probable 6-deoxy-3-C-methyl-2-O-methyl-L-talose 6 in eleven steps from 1,2;5,6-di-O-isopropylidene-3-C-methyl-α-D-allofuranose[3] 1a and by comparing the compound 6 with the authentic specimen of natural L-vinelose.[4]

The synthetic routes are briefly described in a following way: benzylation of 1a with benzylchloride in sodium hydride-dimethylsulfoxide system gave the corresponding 3-O-benzyl derivative 1b [m.p. 55-56°, $[\alpha]_D^{24}$+43.7° (c 1.0, methanol)] quantitatively. The compound 2a [m.p. 118-119°, $[\alpha]_D^{24}$ +53.3° (c 1.0, methanol)] obtained by partial hydrolysis of 1b with 70 % acetic acid was successively tritylated and mesylated in pyridine to give 1,2-O-isopropylidene-3-O-benzyl-3-C-methyl-5-O-mesyl-6-O-trityl-α-D-allofuranose 2b [syrup, $[\alpha]_D^{24}$+7.7° (c 1.0, methanol)] in 85 % yield. Detritylation of 2b was then effected in hot 70 % acetic acid to give the compound 2c [m.p. 86-86.5°, $[\alpha]_D^{24}$ +50.4° (c 1.0, methanol)] in 83 % yield. Treatment of 2c with sodium methoxide in methanol gave 5,6-anhydro-L-*talo* derivative 3 [syrup, $[\alpha]_D^{24}$+52.5° (c 1.0, methanol) in

85 % yield. The compound 4a [m.p. 90-91°, $[\alpha]_D^{24}$ +32° (c 1.0, methanol) obtained in high yield by reduction of 3 with $LiAlH_4$ was further benzylated to 4b [m.p. 115-117°, $[\alpha]_D^{24}$ +23.5° (c 1.0, methanol)] in a similar way as 1b. Methanolysis of 4b with 3 % hydrogen chloride in methanol gave the corresponding methyl α,β-L-talofuranosides (α:β = 2:1) , which were successively methylated in an usual manner to 2-O-methyl derivatives 5b and 5'b. The predominant α-anomer 5b [syrup, $[\alpha]_D^{24}$ -3.4° (c 1.0, methanol)] was hydrogenated in acetic acid in the presence of palladium on carbon (10 %) to 5c [syrup, $[\alpha]_D^{24}$ -15.0° (c 1.34, methanol)] quantitatively. Hydrolysis of 5c in 2N sufuric acid (90°, 2 hr), finally, gave the desired compound 6 [syrup, $[\alpha]_D^{24}$ +14.3° , $[\alpha]_{546}^{24}$ +16.4° (c 1.21, water) ; lit.[1], $[\alpha]_{546}^{14.5}$ +12.0° (c 1.0, water)] in good yield. The compound 6 was further reduced with $NaBH_4$ in water to the corresponding 6-deoxy-3-C-methyl-2-O-methyl-L-talitol 7a [syrup, $[\alpha]_D^{24}$ -6.5°, $[\alpha]_{546}^{24}$ -7.2° (c 1.5, water); lit.[1] , $[\alpha]_{546}^{24}$ -6.4° (c 1.0, water)], a part of which was acetylated with acetic anhydride in pyridine to the triacetate 7b [syrup, $[\alpha]_D^{22}$ -36.5°, $[\alpha]_{546}^{22}$ -44.2°(c 1.0, chloroform); lit.[1], $[\alpha]_{546}^{21}$ -45.7°(c 1.0, chloroform)].



There were no differences at all among the authentic L-vinelose, L-vinelitol[4] in addition to their acetates and each of the synthetic ones at our hand as far as the comparative analyses of them by PC, TLC, GLC and NMR are concerned.

The typical data of GLC analysis are shown in the following table 1, in which the relative retention times of the synthetic samples are in very good agreement with those of the authentic ones.

Table 1. GLC analysis of the synthetic and authentic specimens

Compounds		
Authentic L-vinelose diacetate	1.11, 1.19 (major)	0.89, 1.13 (major)
Synthetic L-vinelose diacetate	1.11, 1.20 (major)	0.89, 1.13 (major)
Authentic L-vinelitol triacetate	2.38	2.05
Synthetic L-vinelitol triacetate	2.40	2.03

A: 5 % NPGA, B: 5 % LAC-4R-886 (temperature = 180°)

Standard: erythritol tetraacetate (1.00)

NMR data (first order analysis) of synthetic L-vinelitol triacetate 7b are listed in the table 2 in comparison with those of the authentic specimen reported in the literature.[1]

Table 2. NMR data of L-vinelitol triacetate ($CDCl_3$)

	Synthetic (100 Mc)	Authentic (60 Mc)[1]
C_3-CH_3	δ 1.16, s	1.16, s
C_5-CH_3	1.20, d $J_{5,6}$ = 6.3 Hz	1.21, d $J_{5,6}$ = 6.0 Hz
O-$COCH_3$	2.05, 2.16	2.08, 2.17
OH	2.81	2.76
H_2	3.31, dd $J_{1,2}$ = 6.3	3.32, dd $J_{1,2}$ =6.4
	$J_{1',2}$ = 2.8	$J_{1',2}$ = 3.0
OCH_3	3.46, s	3.48, s
$H_{1'}$	4.03, dd $J_{1,1'}$ = 12.0	4.08, dd $J_{1,1'}$ = 11.7
H_1	4.53, dd	4.54, dd
H_4	5.04, d $J_{4,5}$ = 2.8	5.05, d $J_{4,5}$ = 3.0
H_5	5.35, qd	5.37, qd

Thus, the structure of L-vinelose can be concluded to be 6-deoxy-3-C-methyl-2-O-methyl-L-talose.

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4. We heartfully thank Dr. S. Okuda for a gift of the authentic L-vinelose and L-vinelitol.