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Note

The stereoselective synthesis of novel 4-octulose derivatives[1]

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Abstract

Dihydroxylation of methyl (*E*)-2,3-dideoxy-4,5:6,8-di-*O*-isopropylidene-L-*xylo*-oct-2-ene-4-ulofuranosonate (**1**) with osmium tetraoxide took place with high diastereoselectivity to give a 7:1 mixture of methyl 4,5:6,8-di-*O*-isopropylidene-α-L-*glycero*-D-*galacto*- (**2**) and -D-*ido*-oct-4-ulofuranosonate (**3**). When **1** was dihydroxylated in the presence of dihydroquinine and dihydroquinidine *p*-chlorobenzoate, an appreciable increase and decrease, respectively, in the **2**/**3** ratio was observed. Compound **2** was transformed into its 2,3-di-*O*-methyl derivative **4** which was deisopropylidenated to methyl 2,3-di-*O*-methyl-α-L-*glycero*-D-*galacto*-oct-4-ulopyranosonate (**5**) and subsequently degraded to dimethyl 2,3-di-*O*-methyl-(+)-L-tartrate (**6**). On the other hand, compounds **2** and **3**, separately, were isopropylidenated to the corresponding 2,3:4,5:6,8-tri-*O*-isopropylidene derivatives **7** and **8**, which were reduced with $LiAlH_4$ to the related 2,3:4,5:6,8-tri-*O*-isopropylidene-α-L-*glycero*-D-*galacto*- (**9**) and -D-*ido*-oct-4-ulofuranose (**10**). Finally, compounds **9** and **10** were deisopropylidenated to the corresponding L-*glycero*-D-*galacto*- (**11**) and L-*glycero*-D-*ido*-oct-4-ulose (**12**). © 1998 Elsevier Science Ltd. All rights reserved

Keywords: 4-Octulose derivatives; Diastereoselective synthesis

In previous papers [1,2] we have reported on the use as starting chiral template of a common hexulose, D-fructose, in the synthesis of 4-octuloses and 2-deoxy-4-octuloses. On the other hand, 4-octuloses could be excellent chiral intermediates for the synthesis of potent glycosidase inhibitors such as polyhydroxyindolizidines [3]. We report in the present paper on the synthesis of some 4-octulose derivatives from L-sorbose and their configurational assignments.

1. Results and discussion

Dihydroxylation of **1** [4] with osmium tetraoxide afforded an approximate 7:1 mixture of methyl 4,5:6,8-di-*O*-isopropylidene-α-L-*glycero*-D-*galacto*- (**2**) and -L-*glycero*-D-*ido*-oct-4-ulofuranosonate (**3**) (GC) which could be resolved by cautious column chromatography.

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[1] Part III. For Part II, see ref. [1].

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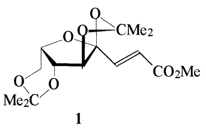

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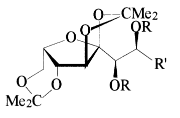
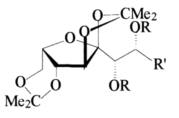


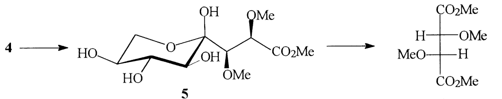
	R	R'
2	H	CO_2Me
4	Me	CO_2Me
7	CMe_2	CO_2Me
9	CMe_2	CH_2OH



	R	R'
3	H	CO_2Me
8	CMe_2	CO_2Me
10	CMe_2	CH_2OH

Configurational proof for the osmylation products was provided by conversion of **2** into dimethyl 2,3-di-*O*-methyl-(+)-L-tartrate (**7**) [5], involving methylation of **2** (→**4**), hydrolysis to methyl 2,3-di-*O*-methyl-α-L-*glycero*-D-*galacto*-oct-4-ulopyranosonate (**5**), oxidation with sodium periodate and treatment with diazomethane. The obtention of *R*,*R*-tartrate **6** clearly indicated a 2*R*,3*R* configuration for **2**.

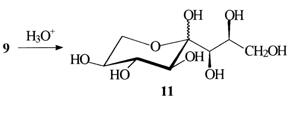
The pyranoid structure of **5** was assigned on the basis of its ^{13}C NMR spectrum, where resonance signals for only one pyranose anomer were present, according to the δ value [4] for C-4 (105.91). In addition, the α-configuration was tentatively assigned to the anomeric center, since it would be in accordance with stabilizing stereoelectronic (anomeric effect) and steric (the large substituent adopts an equatorial disposition) effects.



5 **6**

When dihydroxylation of **1** was carried out in the presence of chiral catalysts [6] such as dihydroquinine or dihydroquinidine *p*-chlorobenzoate, **2** and **3** were formed in a 9:1 and 2:1 ratio, respectively. The increase and decrease of stereoselectivity found (the **2**:**3** ratio changing from 7:1 to 9:1 and 2:1) in comparison with that observed without the presence of chiral catalysts, indicating a clear case of *matched* and *mismatched pair* double asymmetric induction [7].

Treatment of **2** and **3** with acetone–*p*-toluene sulfonic acid–cupric sulfate afforded crystalline methyl 2,3:4,5:6,8-tri-*O*-isopropylidene-α-L-*glycero*-D-*galacto*-oct-4-ulofuranosonate (**7**) and the -L-*glycero*-D-*ido*- isomer (**8**), respectively. Reduction of **7** and **8** with lithium aluminium hydride gave the corresponding octulose derivatives **9** and **10**, which were hydrolyzed to the respective free octuloses **11** and **12**.



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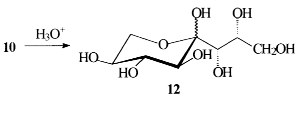

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2. Experimental

General methods.—See ref. [1]. In addition, GC analyses was performed on a Perkin-Elmer 8410 gas chromatograph equipped with a flame-ionisation detector and a steel column (2 m×3 mm i.d.) packed with 5% OV-17 on Chromosorb W (100–120 mesh): (A) at 190 °C; (B) 5 min at 190 °C, program to 230 °C, 15 °C/min; (C) at 230 °C; (D) 160 °C. The He flow rate was 30 mL/min, the injection port and the zone-detector temperatures were (A), (B) and (C) 250 °C, and (D) 200 °C.

Dihydroxylation of **1***: without chiral catalyst.*—To a stirred soln of **1** [4] (8.4 g, 27 mmol) in acetone (80 mL) was added a soln of $KClO_3$ (3.26 g, 27 mmol) in water (60 mL) and aq 1% OsO_4 (10 mL), and the mixture left at room temperature for 30 h. GC (C) then revealed the presence of two new products (t_R 7.17 and 8.89 min in a ~7:1 ratio). The mixture was concentrated to a residue that was extracted with EtOAc, then concentrated. Cautious column chromatography (2:1 ether–hexane→ether) afforded first methyl 4,5:6,8-di-*O*- isopropylidene-α-L-*glycero*-D-*galacto*-oct-4-ulofuranoso-nate as solid foam (**2**, 7.17 g, 52%), (t_R 7.17 min); $[\alpha]_D^{23}$ +8° (*c* 1.4, $CHCl_3$); IR (KBr): ν 3526 (OH), 1740 (C=O, ester), and 1385 cm^{-1} (CMe_2); ^1H NMR: δ 4.72 (s, 1 H, H-2), 4.68 (s, 1 H, H-3), 4.34 (d, 1 H, $J_{6,7}$ 1.5 Hz, H-6), 4.30 (s, 1 H, H-5), 4.11 (d, 1 H, H-7), 4.05 (s, 2 H, H-8,8), 3.80 (s, 3 H, OMe), 1.50, 1.42, 1.41, and 1.36 (4 s, 12 H, 2 CMe_2); ^{13}C NMR: δ 173.60 (C-1), 114.66 (C-4), 113.47 (*C*Me_2), 97.75 (*C*Me_2), 85.07 (C-5), 73.07 (C-6), 72.39 (C-7), 71.76 (C-3), 69.96 (C-2), 60.31 (C-8), 52.90 (OMe), 28.85 and 18.63 (C*Me*$_2$), 27.77 and 26.45 (C*Me*$_2$). Anal. Calcd for $C_{15}H_{24}O_9$: C, 51.72; H, 6.94. Found: C, 51.66; H, 7.21.

Eluted second was syrupy methyl 4,5:6,8-di-*O*-isopropylidene-α-L-*glycero*-D-*ido*-oct-4-ulofuranosonate (**3**, 1.14 g, 8.2%), (t_R 8.89 min); $[\alpha]_D^{25}$ −18° (*c* 1.2, $CHCl_3$); IR (neat): ν 3500 (OH), 1751 (C=O, ester), and 1385 cm^{-1} (CMe_2); ^1H NMR: δ 4.76 (s, 1 H, H-2), 4.65 (s, 1 H, H-3), 4.31 (d, 1 H, $J_{6,7}$ 1.8 Hz, H-6), 4.24 (s, 1 H, H-5), 4.12–4.05 (m, 3 H, H-7,8,8′), 3.79 (s, 3 H, OMe), 1.49, 1.44, 1.39, and 1.38 (4 s, 12 H, 2 CMe_2); ^{13}C NMR: δ 172.48 (C-1), 114.69 (C-4), 112.19 (*C*Me_2), 98.26 (*C*Me_2), 85.32 (C-5), 73.70 (C-6), 73.25 (C-7), 72.34 (C-3), 70.68 (C-2), 60.24 (C-8), 52.55 (OMe), 28.78 and 18.55 (C*Me*$_2$), 27.37 and 26.62 (C*Me*$_2$). Anal. Calcd for $C_{15}H_{24}O_9$: C, 51.72; H, 6.94. Found: C, 51.30; H, 6.93.

A small quantity (0.3 g) of a mixture of **2** and **3** was also obtained.

Dihydroxylation of **1***: with chiral catalyst*.—To a well-stirred and cooled (0 °C) soln of **1** (173 mg, 0.55 mmol), *N*-methylmorpholine *N*-oxide monohydrate (79 mg, 0.67 mmol) and dihydroquinine *p*-chlorobenzoate (70 mg, 0.15 mmol) in acetone–water (5:1 v/v, 1.6 mL), was added aq 0.04 M OsO_4 (0.15 mL) and the mixture left for 4 d at room temperature. GC (C) then showed the absence of **1** and the presence of **2** and **3** in ~9:1 ratio.

When dihydroxylation of **1** was performed in the presence of dihydroquinidine *p*-chlorobenzoate, as chiral catalyst, a ~2:1 ratio of **2** and **3** was obtained (GC analysis).

*Methyl 4,5:6,8-di-*O*-isopropylidene-2,3-di-*O*-methyl-α-*L-glycero-D-galacto*-oct-4-ulofuranosonate* (**4**).—To a stirred soln of NaH (80% oil dispersion) (500 mg, 16.7 mmol) in dry Me_2SO (5 mL) and imidazole (150 mg) under Ar, a soln of **2** (870 mg, 2.5 mmol) in dry THF (10 mL) was added dropwise and the mixture heated at 60 °C for 30 min. After cooling, iodomethane (3 mL, 54.5 mmol) was added and the mixture stirred for an additional 30 min. TLC (ether) then showed a faster-running product, the excess of hydride was destroyed by cautious addition of ether saturated with water, then water. The organic phase was separated and the aq phase extracted with ether. The extracts were washed with brine and concentrated. Column chromatography (1:3→1:1 ether–hexane) of the residue afforded crystalline **4** (810 mg, 86%), mp 81–83 °C; $[\alpha]_D^{23}$ +28° (*c* 1, $CHCl_3$); IR (KBr): ν 1757 (C=O, ester) and 1378 cm^{-1} (CMe_2); ^1H NMR: δ 4.49 (s, 1 H, H-5), 4.28 (d, 1 H, $J_{6,7}$ 2.3 Hz, H-6), 4.20 (d, 1 H, $J_{2,3}$ 5.7 Hz, H-2), 4.10 (m, 1 H, H-7), 4.02 (dd, 1 H, $J_{7,8}$ 2.5, $J_{8,8'}$ 13.4 Hz, H-8), 3.91 (d, 1 H, H-8′), 3.86 (d, 1 H, H-3), 3.78 (s, 3 H, CO_2Me), 3.56 and 3.48 (2 s, 6 H, 2 OMe), 1.49, 1.41, 1.40, and 1.39 (4 s, 12 H, 2 CMe_2); ^{13}C NMR: δ 171.38 (C-1), 114.72 (C-4), 113.16 (*C*Me_2), 97.41 (*C*Me_2), 85.49 (C-5), 81.61 (C-3), 81.00 (C-2), 73.00 (C-6), 72.86 (C-7), 60.34 (C-8), 61.30 and 58.80 (2 OMe), 51.95 (CO_2*Me*), 28.74 and 18.97 (C*Me*$_2$), 27.86 and 26.69 (C*Me*$_2$). Anal. Calcd for $C_{17}H_{28}O_9$: C, 54.24; H, 7.50. Found: C, 54.68; H, 7.52.

Degradation of **4** *to* **6**.—A soln of **4** (700 mg, 1.86 mmol) in aq 70% trifluoroacetic acid (7 mL) was left at room temperature overnight. TLC (10:1 $CHCl_3$–MeOH) then revealed a nonmobile compound. The mixture was concentrated and repeatedly co-distilled with water and the residue chromatographed (10:1 $CHCl_3$–MeOH) to afford methyl 2,3-di-*O*-methyl-*α*-L-*glycero*-D-*galacto*-oct-4-ulopyranosonate (**5**) as a colourless solid foam (500 mg, 91%). ^{13}C NMR: δ 171.28 (C-1), 105.91 (C-4), 87.44, 81.20, 74.40, 69.93, and 69.01 (C-2,3,5,6,7), 65.60 (C-8), 59.64, 59.53, and 59.14 (3 OMe). Anal. Calcd for $C_{11}H_{20}O_9$: C, 44.59; H, 6.80. Found: C, 44.25; H, 7.02.

Compound **5** (447 mg, 1.51 mmol) was oxidized in water (15 mL) with a soln of $NaIO_4$ (1.6 g, 7.5 mmol) in the same solvent (15 mL). The reaction was monitored by polarimetry to a constant rotation. The mixture was concentrated and the residue extracted with EtOAc. Concentration of the extracts gave a residue that was dissolved in dry MeOH (15 mL) and a stream of CH_2N_2 was passed through the soln until a slight yellow colour remained and the mixture left at room temperature for 30 min. GC (D) then revealed a main product with the same t_R as an authentic sample of **6**. The reaction mixture was concentrated and the residue chromatographed (1:2→1:1 ether–hexane) to afford **6** (113 mg) which had $[\alpha]_D^{28}$ +64° (*c* 1.5, MeOH) [lit. [5] $[\alpha]_D$ +81° (*c* 6.26, MeOH)] and spectral data were identical to those of an authentic sample.

*Methyl 2,3:4,5:6,8-tri-*O*-isopropylidene-α-*L-glycero-D-galacto*-oct-4-ulofuranosonate* (**7**).—To a stirred soln of a mixture of **2** (5 g, 14.4 mmol)] in dry acetone (60 mL), *p*-toluenesulfonic acid (950 mg) and anhyd $CuSO_4$ (6 g) were added at room temperature. The stirring was continued for 48 h. TLC (ether) then revealed a faster-running product. The mixture was neutralized (K_2CO_3), filtered through a Celite pad, and then concentrated. Column chromatography (1:2→1:1 ether–hexane) of the residue yielded crystalline **7** (3.6 g, 65%), mp 70–72 °C; $[\alpha]_D^{26}$ −15° (*c* 1.5, $CHCl_3$); IR (KBr): ν 1748 (C=O, ester), 1387, and 1378 cm^{-1} (CMe_2); ^1H NMR: δ 4.77 (d, 1 H, $J_{2,3}$ 7.0 Hz, H-2), 4.55 (d, 1 H, H-3), 4.49 (s, 1 H, H-5), 4.29 (d, 1 H, $J_{6,7}$ 2.4 Hz, H-6), 4.10 (m, 1 H, H-7), 4.01 (dd, 1 H, $J_{7,8}$ 2.4, $J_{8,8'}$ 13.4 Hz, H-8), 3.92 (bd, 1 H, H-8′), 3.77 (s, 3 H, CO_2Me), 1.50, 1.48, 1.46, 1.38, and 1.35 (5 s, 18 H, 3 CMe_2); ^{13}C NMR: δ 171.37 (C-1), 113.18 (C-4), 112.80 and 112.40 (2 *C*Me_2), 97.47 (*C*Me_2), 85.25 (C-5), 79.65 (C-3), 75.88 (C-2), 73.38 (C-6), 72.90 (C-7), 68.29 (C-8), 52.38 (OMe), 28.64 and 18.90 (C*Me*$_2$), 27.54, 26.60, 26.52, and 26.45 (2 C*Me*$_2$). Anal. Calcd for $C_{18}H_{28}O_9$: C, 55.66; H, 7.27. Found: C, 55.32; H, 7.25.

*Methyl 2,3:4,5:6,8-tri-*O*-isopropylidene-α-*L-glycero-D-ido-*oct-4-ulofuranosonate* (**8**).—Compound **3** (220 mg, 0.63 mmol) in dry acetone (5 mL), *p*-toluenesulfonic acid (90 mg) and anhyd $CuSO_4$ (250 mg) was isopropylidenated as above, to yield crystalline **8** (170 mg, 70%), mp 76–78 °C; $[\alpha]_D^{24}$ $+13°$ (c 1.3, $CHCl_3$); IR (KBr): ν 1749 (C=O, ester), 1392, 1384, and 1376 cm^{-1} (CMe_2); ^{1}H NMR data: δ 4.93 (d, 1 H, $J_{2,3}$ 6.0 Hz, H-2), 4.78 (d, 1 H, H-3), 4.51 (s, 1 H, H-5), 4.27 (d, 1 H, $J_{6,7}$ 2.5 Hz, H-6), 4.08 (m, 1 H, H-7), 4.04 (dd, 1 H, $J_{7,8}$ 2.8, $J_{8,8'}$ 13.1 Hz, H-8), 3.96 (dd, 1 H, $J_{7,8'}$ 1.2 Hz, H-8′), 3.77 (s, 3 H, CO_2Me), 1.51, 1.48, 1.40, and 1.36 (4 s, 18 H, 3 CMe_2); ^{13} C NMR: δ 171.57 (C-1), 114.89 (C-4), 112.35 and 112.12 (2 *C*Me$_2$), 97.71 (*C*Me$_2$), 84.95 (C-5), 78.43 (C-3), 75.61 (C-2), 73.78 (C-6), 72.49 (C-7), 60.13 (C-8), 52.46 (OMe), 28.25 and 19.06 (C*Me*$_2$), 27.82, 27.36, 26.88, and 25.80 (2 C*Me*$_2$). Anal. Calcd for $C_{18}H_{28}O_9$: C, 55.66; H, 7.27. Found: C, 55.25; H, 7.14.

*2,3:4,5:6,8-Tri-*O*-isopropylidene-α-*L-glycero-D-galacto-*oct-4-ulofuranose*(**9**).—To a stirred soln of **7** (3.4 g, 8.75 mmol) in dry ether (50 mL), $LiAlH_4$ (340 mg, 9 mmol) was added portionwise and the mixture left at room temperature for 15 min. TLC (ether) then showed the presence of a slower-running product. The excess of hydride was destroyed by cautious addition of ether saturated with water. The organic phase was separated and the aq phase extracted with ether. The combined extracts were washed with brine and then concentrated to crystalline **9** (3.05 g, quantitative), mp 105–107 °C (from hexane); $[\alpha]_D^{26}$ $-6°$ (c 1.4, $CHCl_3$); IR (KBr): ν 3487 (OH), 1387, and 1379 cm^{-1} (CMe_2); ^{1}H NMR: δ 4.46 (s, 1 H, H-5), 4.35 (dt, 1 H, $J_{1,2}$ = $J_{1',2}$ = 4.3, $J_{2,3}$ 8.3 Hz, H-2), 4.31 (d, 1 H, $J_{6,7}$ 2.3 Hz, H-6), 4.11 (d, 1 H, H-3), 4.09 (dd, 1 H, $J_{7,8}$ 2.2 Hz, H-7), 4.03 (dd, 1 H, $J_{8,8'}$ 13.5 Hz, H-8), 3.94 (bd, 1 H, H-8′), 3.87 (ddd, 1 H, $J_{1,1'}$ 11.8 Hz, H-1), 3.81 (dt, 1 H, H-1′), 2.33 (dd, 1 H, $J_{1,OH}$ 8.1, $J_{1',OH}$ 5.1 Hz, OH), 1.50, 1.43, 1.41, 1.40, 1.39, and 1.34 (6 s, 18 H, 3 CMe_2); ^{13} C NMR: δ 113.15 (C-4), 113.01 and 109.82 (2 *C*Me$_2$), 97.50 (*C*Me$_2$), 85.43 (C-5), 77.72 (C-2), 77.56 (C-3), 73.25 (C-6), 72.74 (C-7), 63.50 (C-1), 60.26 (C-8), 28.99 and 18.72 (C*Me*$_2$), 27.66, 27.52, 26.62, and 26.51 (2 C*Me*$_2$). Anal. Calcd for $C_{17}H_{28}O_8$: C, 56.65; H, 7.83. Found: C, 56.80; H, 8.03.

*2,3:4,5:6,8-Tri-*O*-isopropylidene-α-*L-glycero-D-ido-*oct-4-ulofuranose* (**10**).—Compound **8** (529 mg, 1.47 mmol) was reduced with $LiAlH_4$ (60 mg, 1.6 mmol) in dry ether (10 mL) as above to give crystalline **10** (516 mg, quantitative), mp 125–127 °C (from hexane); $[\alpha]_D^{23}$ $+6°$ (c 1, $CHCl_3$); IR (KBr): ν 3508 (OH), 1391, 1382, and 1375 cm^{-1} (CMe_2); ^{1}H NMR: δ 4.57 (s, 1 H, H-5), 4.40 (ddd, 1 H, $J_{1,2}$ 3.3, $J_{1',2}$ 4.8, $J_{2,3}$ 8.7 Hz, H-2), 4.24 (d, 1 H, $J_{6,7}$ 2.1 Hz, H-6), 4.21 (d, 1 H, H-3), 4.07 (dd, 1 H, $J_{7,8}$ 2.3, $J_{8,8'}$ 12.4 Hz, H-8), 4.05 (m, 1 H, H-7), 3.99 (bd, 1 H, H-8′), 3.93 (dd, 1 H, $J_{1,1'}$ 11.7 Hz, H-1), 3.77 (dd, 1 H, H-1′), 2.05 (bs, 1 H, OH), 1.47, 1.45, 1.43, 1.41, and 1.36 (5 s, 18 H, 3 CMe_2); ^{13}C NMR: δ 114.75 (C-4), 111.99 and 109.28 (2 *C*Me$_2$), 97.67 (*C*Me$_2$), 84.80 (C-5), 77.58 (C-2), 76.71 (C-3), 73.84 (C-6), 72.01 (C-7), 63.09 (C-1), 60.14 (C-8), 28.60 and 18.79 (C*Me*$_2$), 27.71, 27.31, 27.20, and 26.81 (2 C*Me*$_2$). Anal. Calcd for $C_{17}H_{28}O_8$: C, 56.65; H, 7.83. Found: C, 56.67; H, 7.97.

L-Glycero-D-galacto-*oct-4-ulose* (**11**).—A soln of **9** (80 mg, 0.22 mmol) in aq 50% TFA (3 mL) was left at room temperature for 4 d. TLC (EtOAc) revealed that **9** had disappeared and that a non-mobile substance was present. The mixture was concentrated and residual TFA removed by co-distillation with water. Column chromatography (3:1 $CHCl_3$–MeOH) of the residue afforded **11** (22 mg, 42%) that was homogeneous by TLC [R_f 0.33 (2:1 $CHCl_3$–MeOH) and had $[\alpha]_D^{25}$ $-7°$, $[\alpha]_{405}^{25}$ $-9°$ (c 1, MeOH).

L-Glycero-D-ido-*oct-4-ulose* (**12**).—Hydrolysis of **10** (80 mg, 0.22 mmol) in aq 50% TFA (3 mL), as described above yielded syrupy **12** (36 mg, 68%) that was homogeneous by TLC (as above) R_f 0.38, and had $[\alpha]_D^{25}$ $-18°$, $[\alpha]_{405}^{25}$ $-40°$ (c 1, MeOH).

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