SYNTHESIS OF 2-AMINO DERIVATIVES OF LEVOGLUCOSENONE

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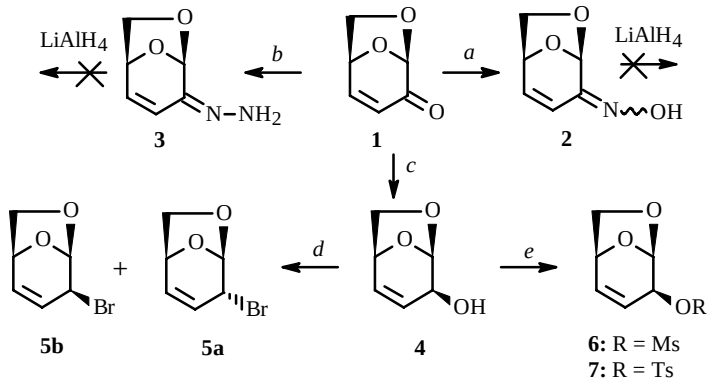
*2-Amino derivatives of levoglucosenone were prepared by reaction of the 2-methanesulfonyl (or p-toluenesulfonyl) derivatives with ammonia, methylamine, or octylamine under various conditions. The analogous reaction did not occur for saturated derivative **15**. The 2-amino-3,4-dihydro derivative was prepared by catalytic hydrogenation of unsaturated amine **9**.*

Key words: levoglucosenone, amino sugar, mucopolysaccharides, ketose oximes and hydrazone, nucleophilic substitution, aminolysis, 1,6-anhydro sugar sulfonates.

Amino sugars act as structural components of many natural compounds including such large groups as mucopolysaccharides and mixed biopolymers. However, they are rarely found in the free state. As a rule, amino sugars required for organic synthesis are obtained by aminolysis of halides, sulfonates, and anhydro derivatives of monosaccharides or reduction of ketose oximes and hydrazones [1, 2]. The carbohydrate levoglucosenone (**1**), which is prepared by cellulose pyrolysis [3], is promising for preparing unsaturated amino sugars and their derivatives. N-Containing derivatives of this sugar enone include heterocyclic products of tandem conversions [4-7], oxime **2** [8], and regioisomeric amines formed by hydroxyamination of 1,6-anhydro-3,4-dideoxy-β-D-threo-hex-3-enopyranose [9].

Oxime **2** was synthesized by the literature method [8]. Furthermore, reaction of levoglucosenone with hydrazine sulfate in pyridine produced a different azomethine, hydrazone **3**. Unfortunately, attempts to reduce azomethines **2** and **3** with $LiAlH_4$ gave products that were difficult to isolate from aqueous solutions.

Alernative approaches could be based on substitution reactions, which are known to proceed difficultly in six-membered pyranose rings [1]. Nevertheless, keeping in mind the allylic position of the reaction center and the pseudoequatorial orientation of the substituted group, we studied the possibility of this approach.



a. $NH_2OH \cdot HCl$, Py; *b*. $NH_2NH_2 \cdot H_2SO_4$, Py; *c*. $NaBH_4$, H_2O; *d*.PPh_3-CBr_4; *e*. TsCl, Py or MsCl, CH_2Cl_2, -10° C

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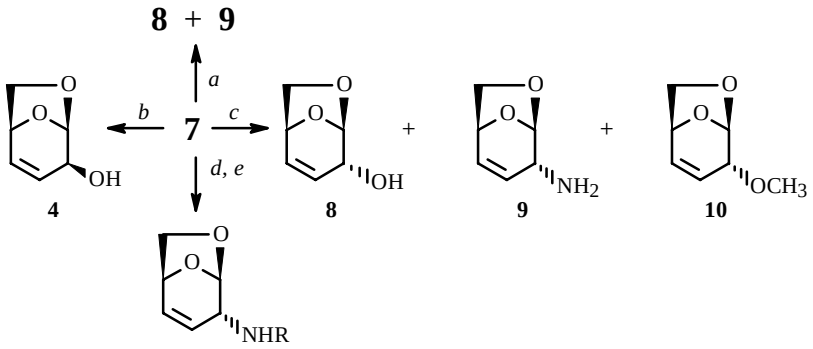
Reaction of levoglucosenone with $NaBH_4$ led stereospecifically to threo-alcohol **4** [10], bromination of which with PPh_3—CBr_4 gave a mixture of the epimeric bromides **5a** and **-b** (11%) in a 2:1 ratio. Considering that the substitution reaction in saturated sugars occurs via an S_N2 mechanism [1], the retention of the initial configuration in the minor product **5b** indicates that an allylic carbocationic intermediate formed.

The structures of the prepared compounds were established using PMR and ^{13}C NMR spectroscopy. Thus, the missing or very small $J_{1,2}$ for H-1 at 5.70 ppm in the PMR spectrum of erythro-bromide **5a** indicates that the H–C^1–C^2–H torsion angle is close to 90° and that the Br in **5a** has the α-orientation, in contrast with the doublet at 5.60 ppm with SSCC 2.9 Hz for H-1 in threo-bromide **5b**. The signals for C-1 and C-6 in the ^{13}C NMR spectrum of **5b** are shifted to strong field by 6.2 and 5.8 ppm, respectively, whereas that for C-5 undergoes a weak-field shift of 4.2 ppm compared with those in **5a**. This difference is probably a result of the syn-coupling of the substituents in **5b**.

The low yields of the epimeric bromides **5a** and **5b** prompted us to study the possible aminolysis of the corresponding sulfonates. Mesylate **6** and tosylate **7** that were required for this were prepared as before [10]. The presence of $J_{1,2}$ coupling in the PMR spectra of **6** and **7** indicate that C-2 has the threo configuration. For example, the signal for H-1 at 5.45 ppm in the spectrum of **7** is the same as in the starting threo-alcohol **4** and has $J_{1,2}$ = 2.3 Hz.

An attempt to substitute the sulfonate in the mesylate by boiling in acetone with NaBr with the hope that the stereochemical features and the allylic levoglucosenone would appear in this instance also did not give the desired result.

Treatment of **7** with aqueous ammonia at 100°C for 10 h in a sealed ampul caused stereospecific substitution of the tosyl group via an S_N2-mechanism. This is consistent with the two products, the desired amine **9** in 30% yield and erythro-alcohol **8** in 51% yield. Reaction in aqueous methylamine under analogous conditions gave the alcohol and the corresponding amine in yields of 56 and 40%.



9: R = H
11: R = CH_3
12: R = C_8H_{17}

a. 40% NH_4OH, ampul, 100°C; *b*. 40% NH_4OH, hv;
c. NH_3, MeOH, ampul; *d*. CH_3NH_2, ampul or NH_3, ampul;
e. $C_8H_{17}NH_2$, C_6H_6, boiling

In addition, irradiation with UV light of **7** in aqueous ammonia removed the tosyl group to form quantitatively **4** in a shorter time than by the known method [11].

Heating **7** in methanol saturated with ammonia in a sealed ampul [12] formed a mixture of the desired amine **9** (28.9%), the chromatographically less polar **8** (5%), and its methoxy ether **10** (51.2%).

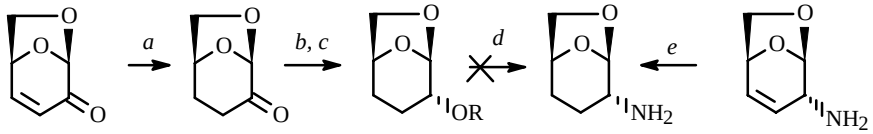
PMR spectra of **10** give a signal for H-1, in contrast with the known threo-epimer [10], with $J_{1,2}$ missing or very small. This indicates that the H–C^1–C^2–H torsion angle is close to 90° and, therefore, the new asymmetric center has the *R*-configuration.

Heating **6** and **7** in liquid NH_3 under analogous conditions formed **9** in yields of 70 and 63%, respectively. Reaction of **6** with liquid methylamine under these same conditions gave secondary amine **11** in 83.7% yield; conversion of 96.9%. In the case of tosylate **7** conversion - 80%. The high lability of **9** should be noted.

Prolonged contact of **6** and **7** with liquid ammonia or methylamine in sealed ampuls at room temperature gave amines **9** or **11**, respectively, in quantitative yields.

Boiling **7** with octylamine in benzene gave another secondary amine **12** in 85% yield.

Saturated tosylate **15**, which was prepared by hydrogenation of **1** and subsequent tosylation of dihydro derivative **14**, was subjected to aminolysis in order to estimate the magnitude of electronic and steric factors. However, heating a solution of **15** in liquid ammonia at 120°C for 15 h was unsuccessful. The equatorial orientation of the sulfonate probably prevents the substitution in this instance, assuming that the nucleophile attacks from inside the pyran ring. Saturated 2-amino derivative **16** was prepared in quantitative yield by hydrogenation of **9**.



1 **13** **14, 15** **16** **9**

14: R = H
15: R = OTs

a. 5% Pd/C, H_2; *b.*$NaBH_4$, H_2O; *c.* TsCl, Py; *d.* NH_3, ampul; *e.* 5% Pd/C, H_2, MeOH

Tosylate **7** was not aminolyzed by secondary amines diisopropylamine, benzylamine, urea, or thiourea.

Thus, levoglucosenone is a convenient substrate for preparing the corresponding unsaturated 2-amino derivatives and then the difficultly accessible saturated derivatives. This pathway is also promising for preparing 2-amino sugars modified at the 3- and 4-positions.

EXPERIMENTAL

IR spectra were recorded on UR-20 and Specord M-80 instruments (as films or in mineral oil). PMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer at working frequencies 300 and 75.47 mHz, respectively, with TMS internal standard and $CDCl_3$ solvent. TLC analysis used Silufol UV-254:366 (Czech Rep.) chromatographic plates. Optical rotation angles were measured on a Perkin—Elmer 141 instrument. Mass spectra were recorded in an MX-1306 instrument (70 eV ionizing potential, 30-50°C ionization-chamber temperature). Analytical data agreed with those calculated.

Syn- and anti-oximes of 1,6-anhydro-3,4-dideoxy-β-D-glycerohex-3-enopyranos-2-ylose (2) was prepared as before [7].

1,6-Anhydro-3,4-dideoxy-β-D-glycerohex-3-enopyranos-2-ylose hydrazone (3). A solution of **1** (1 g, 8 mmol) in Py (10 mL) was treated in portions with stirring at room temperature with $NH_2NH_2 \cdot H_2SO_4$ (1.42 g, 9 mmol). After the reaction was complete (TLC monitoring), the reaction mixture was evaporated. The solid was chromatographed over SiO_2 to afford **3** (1.025 g, 90%), R_f 0.26 (petroleum ether:ethylacetate, 2:1), mp 175-179°C, $[\alpha]_D^{20}$ -453° (*c* 1.0, $CHCl_3$).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 3.82 (1H, d, J = 6.6, H_{endo}-6), 3.88 (1H, dd, J = 6.6, J = 4.4, H_{exo}-6), 4.90 (1H, dd, J = 4.4, J = 4.3, H-5), 5.77 (1H, s, H-1), 6.70 (2H, m, H-3, H-4).

^{13}C NMR spectrum (δ, ppm): 68.63 (C-6), 72.07 (C-5), 101.59 (C-1), 118.16 (C-3), 139.49 (C-4), 155.25 (C-2).

1,6-Anhydro-3,4-dideoxy-β-D-threo-hex-3-enopyranose (9) was prepared as before [10].

1,6-Anhydro-2-C-bromo-2,3,4-trideoxy-β-D-erythro-hex-3-enopyranose (5a) and 1,6-Anhydro-2-C-bromo-2,3,4-trideoxy-β-D-threo-hex-3-enopyranose (5b). A solution of **4** (0.5 g, 3.9 mmol) in CH_2Cl_2 (5 mL) and triphenylphosphine (1.13 g, 4.3 mmol) at room temperature was treated in portions with stirring with CBr_4 (1.33 g, 4.0 mmol). After the reaction was complete (TLC monitoring), the reaction mixture was evaporated. The solid was chromatographed over SiO_2 to afford a mixture of **5a** and **5b** (0.087 g, 11%) in a 2:1 ratio, R_f 0.27 (petroleum ether), $[\alpha]_D^{20}$ -151.9° (*c* 1.0, $CHCl_3$).

Threo-bromide (5b). PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 3.58 (1H, dd, J = 8.3, J = 1.6, H_{exo}-6), 4.0 (1H, dd, J = 8.3, H_{endo}-6), 4.36 (1H, d, J = 3.4, H-2), 4.82 (1H, d, J = 6.5, J = 1.6, H-5), 5.2 (1H, d, J = 2.9, H-1), 5.90 (1H, m, H-4), 5.95 (1H, dd, J = 9.4, J = 3.0, H-3).

^{13}C NMR spectrum (δ, ppm): 44.15 (C-2), 65.48 (C-6), 76.77 (C-5), 95.60 (C-1), 126.04 (C-3), 128.61 (C-4).

Erythro-bromide (5a). PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 3.75 (1H, dd, J = 6.6, J = 4.7, H_{exo}-6), 3.83 (1H, d, J = 6.6, H_{endo}-6), 4.42 (1H, d, J = 3.8, H-2), 4.78 (1H, d, J = 4.7, H-5), 5.7 (1H, s, H-1), 5.90 (1H, dd, J = 9.7, J = 3.8, H-3), 6.1 (1H, dd, J = 7.9, J = 4.7, H-4).

^{13}C NMR spectrum (δ, ppm): 45.36 (C-2), 70.53 (C-5), 71.31 (C-6), 101.84 (C-1), 125.97 (C-4), 129.31 (C-3).

1,6-Anhydro-3,4-dideoxy-2-O-(methanesulfonyl)-β-D-threo-hex-3-enopyranose (6) and 1,6-anhydro-3,4-dideoxy-2-O-(*p*-toluenesulfonyl)-β-D-threo-hex-3-enopyranose (7) were prepared as before [10].

6: R_f 0.4 (petroleum ether:ethylacetate, 1:1).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 3.12 (3H, s, CH_3), 3.82 (1H, d, J = 6.8, J = 4.1, H_{exo}-6), 3.98 (1H, d, J = 6.8, H_{endo}-6), 4.72 (1H, dd, J = 4.2, J = 4.1, H-5), 5.41 (1H, d, J = 2.2, H-1), 5.68 (1H, ddd, J = 10.3, J = 2.4, J = 2.2, H-3), 5.7 (1H, t, J = 2.2, H-2), 6.28 (1H, dd, J = 10.3, J = 4.2, H-4).

^{13}C NMR spectrum (δ, ppm): 36.89 (CH_3), 71.21 (C-5), 71.37 (C-6), 76.26 (C-2), 99.02 (C-1), 123.63 (C-3), 134.20 (C-4).

7: R_f 0.7 (petroleum ether:ethylacetate, 1:1).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 2.46 (3H, s, CH_3), 3.78 (1H, dd, J = 6.7, J = 4.1, H_{exo}-6), 3.94 (1H, d, J = 6.7, H_{endo}-6), 4.65 (1H, dd, J = 4.1, J = 3.2, H-5), 5.20 (1H, d, J = 2.2, H-1), 5.45 (1H, t, J = 2.3, H-2), 5.52 (1H, dt, J = 10.0, J = 2.2, H-3), 6.20 (1H, dd, J = 10.0, J = 3.2, H-4), 7.32, 7.38 (2H, d, H3′, H-5′, Ph), 7.82, 7.86 (2H, d, H-2′, H-6′, Ph).

^{13}C NMR spectrum (δ, ppm): 21.51 (CH_3), 71.04 (C-5), 71.11 (C-6), 76.91 (C-2), 96.75 (C-1), 123.35 (C-4), 133.38 (C-3), 127.69, 133.38, 133.81, 145.05 (Ph).

Aminolysis of Sulfonates in Aqueous Ammonia and Methylamine. A sealed ampul containing a solution of **7** (0.1 g) in aqueous ammonia (10 mL, 40%) was heated for 7 h at 120°C. The ampul was cooled and opened. The reaction mixture was treated with saturated NaCl solution and extracted with ethylacetate (3 × 10 mL). The combined extracts were dried over $MgSO_4$ and evaporated. The solid was chromatographed over SiO_2 to afford **8** (0.034 g, 51%) and **9** (0.018 g, 30%).

1,6-Anhydro-3,4-dideoxy-β-D-erythro-hex-3-enopyranose (8): R_f 0.25 (petroleum ether:ethylacetate, 1:1), $[\alpha]_D^{20}$ -206.5° (*c* 1.0, CH_3OH).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 3.64 (1H, d, J = 6.8, H_{endo}-6), 3.68 (1H, dd, J = 6.8, J = 3.2, H_{exo}-6), 3.70 (1H, d, J = 3.7, H-2), 4.7 (1H, dd, J = 4.7, J = 3.2, H-5), 5.53 (1H, s, H-1), 5.82 (1H, dd, J = 9.8, J = 3.7, H-3), 6.18 (1H, dd, J = 9.8, J = 4.7, H-4).

^{13}C NMR spectrum (δ, ppm): 65.88 (C-2), 68.91 (C-6), 70.62 (C-5), 102.62 (C-1), 126.42 (C-3), 130.84 (C-4).

1,6-Anhydro-2-amino-2,3,4-trideoxy-β-D-erythro-hex-3-enopyranose (9): R_f 0.3 (ethylacetate), $[\alpha]_D^{20}$ -240° (*c* 1.0, $CHCl_3$).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.5 (2H, br.s, NH_2), 2.8 (1H, d, J = 3.7, H-2), 3.64 (1H, dd, J = 6.4, J = 4.7, H_{exo}-6), 3.72 (1H, d, J = 6.4, H_{endo}-6), 4.58 (1H, dd, J = 4.6, J = 4.4, H-5), 5.35 (1H, s, H-1), 5.68 (1H, dd, J = 9.8, J = 3.9, H-3), 6.0 (1H, dd, J = 9.8, J = 4.7, H-4).

^{13}C NMR spectrum (δ, ppm): 51.22 (C-2), 70.22 (C-6), 70.85 (C-5), 104.83 (C-1), 128.55 (C-3, C-4).

Aminolysis of **7** (0.1 g) in aqueous methylamine (40%) was performed under analogous conditions to afford **8** (0.034 g, 56.4%) and **11** (0.018 g, 40%).

1,6-Anhydro-2-aminomethyl-2,3,4-trideoxy-β-D-erythro-hex-3-enopyranose (11): R_f 0.2 (petroleum ether:ethylacetate, 1:1), $[\alpha]_D^{20}$ -89° (*c* 1.0, $CHCl_3$).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 2.53 (3H, s, CH_3), 2.89 (1H, d, J = 3.7, H-2), 3.6 (1H, br.s, $NHCH_3$), 3.7 (1H, dd, J = 6.2, J = 4.3, H_{exo}-6), 3.8 (1H, d, J = 6.2, H_{endo}-6), 4.68 (1H, t, J = 4.3, H-5), 5.6 (1H, s, H-1), 5.78 (1H, dd, J = 9.9, J = 3.7, H-3), 6.1 (1H, dd, J = 4.3, J = 3.9, H-4).

^{13}C NMR spectrum (δ, ppm): 33.78 (NCH_3), 51.78 (C-2), 70.15 (C-6), 70.65 (C-5), 101.08 (C-1), 126.28 (C-4), 129.05 (C-3).

Aminolysis of Sulfonates in Methanol. A solution of **7** (0.15 g) in methanol (5 mL) was saturated at 0°C with ammonia and heated for 7 h at 120°C in an autoclave. The reaction mixture was evaporated. The solid was chromatographed over SiO_2 to afford **10** (0.039 g, 51%), the amino derivative (0.020 g, 28.9%), and **8** (0.005 g, 5%).

1,6-Anhydro-2-O-methyl-3,4-trideoxy-β-D-erythro-hex-3-enopyranose (10): R_f 0.4 (petroleum ether:ethylacetate, 3:1), $[\alpha]_D^{20}$ -208° (*c* 1.0, $CHCl_3$).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 3.30 (1H, d, J = 3.8, H-2), 3.48 (3H, s, OMe), 3.68 (1H, dd, J = 6.7, J = 4.7, H_{exo}-6), 3.78 (1H, d, J = 6.7, H_{endo}-6), 4.72 (1H, dd, J = 4.7, H-5), 5.65 (1H, s, H-1), 5.68 (1H, dd, J = 9.8, J = 3.7, H-3), 6.25 (1H, dd, H-4, J = 9.8, J = 4.7, H-4).

Aminolysis in Liquid Ammonia and Methylamine. Compound **7** (0.28 g, 1 mmol) and liquid ammonia (5 mL) were placed into two thick-walled ampuls; **7** (0.28 g) and liquid methylamine (5 mL), into two others. The ampuls were sealed. One of each pair was held for 60 d at room temperature; the other, heated at 100°C for 10 h. After each period had expired, the ampuls were opened and volatile compounds were removed. The solid was chromatographed over silica gel. The reaction mixture from the heated ampuls gave **9** (0.082 g, 64.9%) and **11** (0.098 g, 70%). The reaction mixture from the long-term stored ampuls gave **9** (0.105 g, 83.7%) and **11** (0.130 g, 93%).

1,6-Anhydro-2-aminooctyl-2,3,4-trideoxy-β-D-erythro-hex-3-enopyranose (12). A solution of **7** (0.1 g) and octylamine (0.1 g) in benzene was boiled for 25 d. The reaction mixture was evaporated in a rotary evaporator. The solid was chromatographed over SiO_2 to afford **12** (0.065 g, 85%), R_f 0.4 (petroleum ether:ethylacetate, 1:1), $[\alpha]_D^{20}$ -72° (*c* 1.0, $CHCl_3$).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 0.88 (3H, t, CH_3, J = 7.0), 1.20 (10H, m, CH_2), 1.5 (2H, m, H-2′), 2.83 (1H, d, J = 3.8, H-2), 2.72 (1H, t, J = 6.6, H_b = 1′), 3.25 (1H, q, J = 6.6, H_a = 1′), 3.65 (1H, dd, J = 6.35, J = 4.4, H_{exo}-6), 3.8 (1H, d, J = 6.35, H_{endo}-6), 5.5 (1H, s, H-1), 5.75 (1H, dd, J = 9.8, J = 3.8, H-3), 6.07 (1H, dd, J = 9.8, J = 4.4, H-4), 8.15 (1H, br.s, NH).

^{13}C NMR spectrum (δ, ppm): 14.0, 22.63, 27.24, 29.19, 30.25, 31.82, 38.25, 47.16 ($8CH_2$), 56.43 (C-2), 70.44 (C-6), 70.89 (C-5), 101.61 (C-1), 126.39 (C-4), 129.47 (C-3).

1,6-Anhydro-β-D-glycerohexopyranos-2-ylose (13) was prepared as before [7].

1,6-Anhydro-β-D-glycerohexopyranos-2-ylose (14) and **1,6-anhydro-2-O-(*p*-toluenesulfonyl)-β-D-hexopyranose (15)** were prepared as before [10].

1,6-Anhydro-2-C-aminomethyl-2,3,4-trideoxy-β-D-erythro-hexopyranose (16). A solution of **9** (0.100 g, 0.78 mmol) in methanol (10 mL) was treated with Pd/C (0.005 g, 5%). The reaction mixture was stirred under a H_2 atmosphere with TLC monitoring. After 36 h the reaction mixture was filtered and concentrated. The solid was chromatographed over SiO_2 to afford **16** (0.075 g, 78%): R_f 0.20 (ethylacetate), $[\alpha]_D^{20}$ -39° (*c* 1.0, $CHCl_3$).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.36 (1H, m, CH_2^{eq}), 1.6 (1H, m, CH_2^{eq}), 1.7-2.0 (3H, m, H-2, CH_2^{ax}, CH_2^{ax}), 2.47 (2H, br.s, NH_2), 3.72 (1H, t, J = 6.2, H_{exo}-6), 3.88 (1H, d, J = 6.2, H_{endo}-6), 4.47 (1H, m, H-5), 5.35 (1H, s, H-1).

^{13}C NMR spectrum (δ, ppm): 19.09 (C-4), 25.10 (C-3), 57.10 (C-2), 66.90 (C-6), 73.26 (C-5), 102.25 (C-1).

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