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SYNTHESIS OF D-AMICETOSE AND L-RHODINOSE FROM L-GLUTAMIC ACID

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ABSTRACT

L-Glutamic acid has been converted into a separable mixture of D-amicetono- and L-rhodinono-γ-lactones by a sequence involving transformation into (*S*)-γ-carboxy-γ-butyrolactone (**2**), conversion of **2** into the corresponding methyl ketone by the diazoketone route, and selective reduction with zinc borohydride or borane–methyl sulfide. Reduction of the two lactones with di-isobutylaluminium hydride gave the corresponding deoxy sugars. In spite of some improvements in the preparation of **2**, the optical yield of this step was only ~80%, but one crystallisation from chloroform raised the optical purity to 96%. The subsequent steps produced a loss in optical purity of only 4%.

INTRODUCTION

The two diastereomeric 2,3,6-trideoxyhexoses, amicetose *(erythro)* and rhodinose *(threo)*, are constituents of several antibiotics[1] and have been prepared in their optically active forms by lengthy reaction-sequences starting from abundant natural sugars[2], or in the racemic form by simple routes[3]. The ready availability of their enantiomeric forms would make them useful as starting materials for the synthesis of other biologically important sugars, for example, the 3,6-dideoxyhexoses[4] and, possibly, the aminodeoxy sugars.

We have therefore investigated a synthesis of D-amicetose (**5**) and L-rhodinose (**6**) from inexpensive L-glutamic acid (**1**) by a simple route. The success of this approach depended on there being no substantial loss of optical purity during the reaction sequence and that the separation of amicetose from rhodinose could be effected simply.

RESULTS AND DISCUSSION

The conversion of L-glutamic acid (**1**) into (*S*)-(+)-γ-carboxy-γ-butyrolactone (**2**) with nitrous acid, first described by Wolff[5], has been repeatedly reported to give yields of up to 90%, and to proceed with retention of configuration. The

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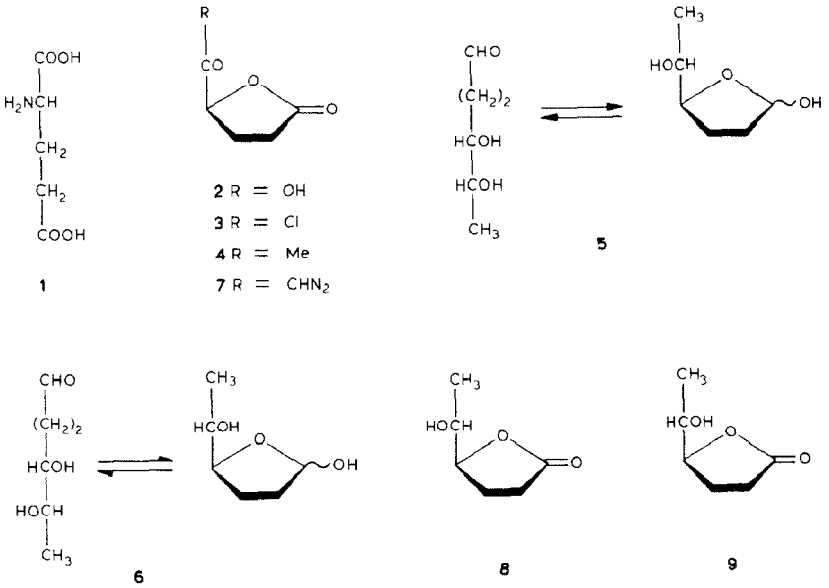
highest reported $[\alpha]_D$ value for a recrystallised product, which probably was optically pure, is +15.2° (methanol)[6] (*cf.* +10.6° for a distilled but not recrystallised product[7]), and there is a report[8] on the formation of optically inactive **2** from **1**. The crude deamination product was reported[9] to be almost optically pure, but some racemisation occurs during distillation. We found that, starting from optically pure **1**, the optical purity of the distilled product **2** varied in the range 60–80%. Some racemisation probably occurs during concentration of the strongly acidic reaction-solution, which can be diminished by prior neutralisation of hydrogen chloride; even so, the optical purity of the distilled product did not exceed 80%, probably because of the high temperature required for distillation. However, one crystallisation of the distillate from chloroform afforded a product of 96% optical purity. Compound **2** probably crystallises as a conglomerate (the m.p. of the enantiomer is 20° higher than that of the racemate) and therefore can be obtained optically pure by recrystallisation of the partially enriched mixture[10]. Furthermore, the optical purity of the liquid portion of a partially solidified distillate was very low. Evidently, the more abundant enantiomer crystallises first and only at the end of the crystallisation does the conglomerate deposit. This finding explains the reported formation of racemic **2** from L-glutamic acid[8], and other inconsistencies in the literature on the optical activity of **2**. It was also important to avoid the use of ethyl acetate or chloroform stabilised with ethanol in the isolation of **2**, because of the possibility of ethyl ester formation. Tetrahydrofuran was preferred for the extraction.

The conversion of **2** into the acid chloride **3**, using oxalyl chloride, was expected to proceed with little, if any, loss of optical purity, since an enantiomeric ex-



cess (e.e.) of 88.4% was established[11] for a compound obtained by conversion of **2** (of 86% optical purity according to the specific optical rotation of its methyl ester) into **3**, followed by reaction with an alkylcadmium and reduction of the product to the secondary alcohol[11]. We obtained **2** with an optical purity of 96% and with an optical rotation higher than the literature value[12] for a product prepared by using thionyl chloride. An attempt to assess the optical purity by the conversion of **3** into the methyl ester failed because treatment with methanol produced a mixture of methyl ester and dimethyl 2-hydroxyglutarate, even when the esterification was carried out in the presence of solid sodium hydrogencarbonate. In seeking to effect the conversion **3**→**4**, methylmagnesium bromide in tetrahydrofuran at −78° was used (*cf.* ref. 13). This reagent, which has been applied successfully to chlorides containing ester groups[14], gave poor results with **3**; the yield of **4** was <50% and the product was contaminated with less-volatile products, probably formed by attack of the reagent on the lactone carbonyl group. Conversion of **3** into the diazoketone **7** using diazomethane, followed by reduction with hydriodic acid under carefully controlled conditions, in order to avoid reaction of the lactone group, gave ~70% of **4**.

Treatment of **4** with 2 equiv. of di-isobutylaluminium hydride (DIBAL) gave a mixture of amicetose (**5**) and rhodinose (**6**). The n.m.r. spectrum of the crude reaction-product was the sum of the reported spectra[15,16] of the two deoxy sugars. Owing to the presence of α and β pyranose and furanose forms, which caused extensive overlapping of peaks, it was not possible to determine the precise ratio, but amicetose was the main component. This conclusion was confirmed by conversion of the mixture into the 2,4-dinitrophenylhydrazones (DNP). The derivatives of **5** and **6**, isolated by preparative t.l.c., had broad melting-points in rough agreement with the literature values, and specific rotations (−9° for **5**-DNP, −11° for **6**-DNP) that accorded with the D and L configurations, respectively, but did not indicate the optical purities. Values of −9.2°[17] for D-**5**-DNP and +12°[18] for L-**5**-DNP, and +13.7° for D-**6**-DNP[19] and −17.7°[2b] for L-**6**-DNP have been reported, and Haines[2b] has pointed out that the m.p. of L-**6**-DNP varies in an unsystematic way on recrystallisation, because of the presence of two components (t.l.c.).

Attempts to isolate **5** and **6** by chromatography failed, possibly because of the presence of tautomeric forms. Separation of the lactones **8** and **9** was therefore investigated. Selective reduction of the ketonic group of **4** with sodium borohydride in ethanol gave only 30–40% of **8** + **9**, substantial amounts of higher boiling products being formed concomitantly by ethanolysis of the lactone ring (ethyl signals in the n.m.r. spectrum) and probably by some reduction of the lactone group. *p*-Nitrobenzoylation of the crude product followed by preparative t.l.c. gave a mixture of the *p*-nitrobenzoates of **8** and **9**, from which the more abundant isomer was obtained pure. Since ketones having negative substituents α to the carbonyl function give preferentially the *erythro* alcohol[20], the pure ester was probably the *p*-nitrobenzoate of **8**.

In order to avoid ethanolysis, the reduction of **4** was carried out with zinc

borohydride in ether[21] and with the borane–methyl sulfide complex[22] in tetrahydrofuran. These reagents gave high yields of **8** + **9**, in ratios of 56:44 and 70:30, respectively. The low stereoselectivity of the zinc borohydride reaction was unexpected, since this reagent was reported to strongly favour formation of *erythro* hydroxy derivatives in the reduction of acyclic β-keto esters[21] and α,β-epoxy ketones[23]. Probably, the cyclic transition-state models involving chelation of the metal, proposed to explain the *erythro* selectivity in the above reactions, cannot be applied to **4**.

Separation of **8** from **9** on a limited preparative scale was achieved by medium-pressure (2 atm.) chromatography on silica gel and provided the pure diastereoisomers having the reported n.m.r. spectra[15,16]. The optical rotation of **8** corresponded to ~92% optical purity. Reduction of **8** and **9** with DIBAL gave D-amicetose (**5**), $[\alpha]_D$ +40°, and L-rhodinose (**6**), $[\alpha]_D^{20}$ −8°. According to the literature value[17] for the specific optical rotation of amicetose from natural sources, the observed rotation corresponded to 92% optical purity, thus confirming the value obtained for the lactone **8**. No evaluation of the optical purity of the rhodinose was possible, because of the variation in the reported specific rotations of the enantiomers: −6.7°[2b], −9.0°[15], +10.2°[17], −11°[19]. However, since **5** and **6** were obtained from **4** through reactions not involving its chiral centre, their optical purities must be the same.

The present method provides a simple approach to amicetose and rhodinose of high optical purity, but in limited amounts. Its use on a larger scale will require a more efficient technique for the separation of **8** from **9**, or a more stereoselective reduction of **4**.

EXPERIMENTAL

General. — Melting points (Kofler apparatus) and boiling points are uncorrected. N.m.r. spectra were recorded for ~10% solutions in $CDCl_3$ (internal Me_4Si) with Varian EM-360 A (60 MHz) and CFT-20 (79.9 MHz) spectrometers. G.l.c. was performed with glass columns (2.5 mm i.d × 2 m) fitted in a Carlo Erba Fractovap G.V. equipped with flame-ionisation detectors, under the following conditions: 10% of Carbowax 20M on silanised Chromosorb W(80–100 mesh); N_2 at 30 mL/min; temperature programme, 120→195° at 4°/min; injection-block temperature, 210°. Analytical and preparative t.l.c. was carried out on silica gel plates (Merck, PSC Fertigplatten Kieselgel 60 F_{254}). Optical rotations were determined with a Perkin–Elmer 241 photoelectric polarimeter. Microanalyses were performed on a Carlo Erba Elemental Analyzer Model 1106. Refractive indexes were determined with an Abbe Refractometer.

(S)-(+)-γ-*Carboxy-γ-butyrolactone* (**2**). — A solution of sodium nitrite (30 g, 0.43 mol) in water (210 mL) was added dropwise with vigorous stirring during 2 h to a solution of (*S*)-(+)-glutamic acid (50 g, 0.34 mol) in 4M hydrochloric acid (200 mL), the temperature being maintained below 5°. Stirring was continued over-

night at room temperature, and the mixture was neutralised with aqueous 15% sodium hydroxide (66 mL) and concentrated to dryness at 40–50°. The residue was extracted with boiling, peroxide-free tetrahydrofuran (3 × 200 mL), and the combined extracts were dried ($MgSO_4$) and concentrated. The oily residue (46 g) was distilled to yield **2** (36 g, 82%), b.p. 170–174°/0.6 mmHg, $[\alpha]_D^{20}$ +12.1 ±0.2° (*c* 2.2, ethanol); optical purity, 78%[24]. One crystallisation from chloroform at 0° gave needles, m.p. 72–74°, $[\alpha]_D^{20}$ +14.6 ±0.1° (*c* 5.8, methanol); lit.[6] m.p. 71–72°, $[\alpha]_D^{20}$ +15.2° (*c* 5, methanol). Optical rotations should be determined on freshly prepared solutions, since methanol slowly reacts with **2** and the optical activity decreases (formation of esters of hydroxyglutaric acid?). The optical purity of the crystallised acid was confirmed by conversion into its methyl ester with an excess of diazomethane in ether. The distilled ester (Kugelrohr, b.p. 60–70°/0.4 mmHg) had $[\alpha]_D^{20}$ +16.9 ±0.1° (*c* 3, methanol); λ_{max} 1760 and 1720 cm^{-1} (C=O). N.m.r. data: δ 2.3–2.8 (m, 4 H, H-2,3), 3.82 (s, 3 H, Me), and 4.9–5.1 (m, 1 H, H-4).

When ethyl acetate was used instead of tetrahydrofuran for the extraction, distillation of the extracted product gave an abundant forerun (b.p. 100–125°/0.8 mmHg) of the ethyl ester of **2**. N.m.r. data: δ 1.3 (t, 3 H, *J* 7 Hz, Me), 2.15–2.90 (m, 4 H, H-2,3), 4.35 (q, 2 H, *J* 7 Hz, CH_2), and 4.95–5.25 (m, 1 H, H-4).

A solution of **2** (0.2 g) in ethyl acetate (5 mL) containing conc. hydrochloric acid (0.2 mL) was left at room temperature for 48 h and then concentrated. N.m.r. spectroscopy indicated the residue to be **2** ethyl ester.

(S)-(+)-*γ-Chlorocarbonyl-γ-butyrolactone* (**3**). — A solution of **2** (optical purity, 96%; 9.6 g, 73.8 mmol) and oxalyl chloride (13 mL, 153 mmol) in benzene (40 mL) was heated for 1 h at 50° and then kept for 24 h at room temperature. Evaporation of the solvent and of excess of oxalyl chloride, followed by distillation of the residue, gave **3** (10.1 g, 92%), b.p. 82–84°/0.4 mmHg, n_D^{29} 1.4780, $[\alpha]_D^{20}$ +49 ±0.3° (*c* 1.2, benzene); λ_{max} 1760 cm^{-1} (C=O); lit.[8] b.p. 136–137°/12 mmHg, n_D^{22} 1.4812; lit.[12], for the (*R*)-enantiomer, $[\alpha]_D^{20}$ −44.5° (*c* 3.7, benzene). N.m.r. data: δ 2.28–3.00 (m, 4 H, H-2,3) and 4.87–5.17 (m, 1 H, H-4).

When a solution of **3** in methanol was concentrated, the residue contained two products (g.l.c.) in a ratio that changed with contact time. N.m.r. data for the mixture indicated the components to be the methyl ester of **2** and dimethyl 2-hydroxyglutarate[5].

(S)-(−)-*γ-Diazoacetyl-γ-butyrolactone* (**7**). — To an ethanol-free solution[25] of diazomethane (4.9 g, 0.117 mol) in ether (200 mL) at −10° was added slowly, with efficient stirring, a solution of **3** (6.8 g, 46 mmol) in anhydrous ether (150 mL). The mixture was left at room temperature overnight, and the excess of diazomethane and the ether were removed in a stream of dry air at room temperature, to give a residual yellow oil (6 g, 85%) of practically pure **7**. An analytical sample, obtained by Kugelrohr distillation [b.p. 50–60° (bath)/0.1 mmHg], had $[\alpha]_D^{25}$ −91.5 ±0.4° (*c* 0.8, chloroform); λ_{max} 2100 (N_2), 1760, 1720 (C=O), and 1610 cm^{-1} (C=N). N.m.r. data: δ 2.03–3.00 (m, 4 H, H-2,3), 4.75–5.00 (m, 1 H, H-4), and 5.81 (s, 1 H, CHN_2). The spectra of the crude and purified products were practically identical.

Anal. Calc. for $C_6H_6N_2O_3$: C, 46.76; H, 3.92. Found: C, 47.06; H, 4.14.

γ-Acetyl-γ-butyrolactone (**4**). — (*a*) *From* **7**. A solution of crude **7** (3.6 g, 23.4 mmol) in chloroform (150 mL) was treated dropwise with freshly distilled hydriodic acid (57%; 6.1 mL, 47 mmol) at room temperature with vigorous shaking. After 10 min, the solution was washed with aqueous 10% sodium thiosulphate, the organic layer was separated, the aqueous layer was washed with chloroform (3 × 20 mL), and the combined organic solutions were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified, either by elution from a short column of silica gel with ethyl acetate, or by distillation, to give **7** (2.5 g, 83%), b.p. 102–104°/1.5 mmHg, $[\alpha]_D^{20}$ +16.5 ±0.3° (*c* 0.25, methanol); λ_{max} 1755 and 1715 cm^{-1} (C=O); lit.[26] b.p. 83°/0.2 mmHg, $[\alpha]_D^{25}$ +13.4° (*c* 0.25, methanol). N.m.r. data: δ 2.27 (s, 3 H, Me), 2.00–2.70 (m, 4 H, H-2,3), and 4.70–5.00 (m, 1 H, H-4). The semicarbazone, prepared according to the method of Vogel[27], had m.p. 169–171° (from benzene–ethanol); λ_{max} 3430 (NH), 1725 (broad C=O), and 1560 cm^{-1} (C=N).

Anal. Calc. for $C_7H_{11}N_3O_3$: C, 45.40; H, 5.99; N, 22.69. Found: C, 45.18; H, 6.00; N, 22.44.

(*b*) *From* **3**. A solution of crude **3** [prepared from 7.5 g (58 mmol) of **2**] in anhydrous tetrahydrofuran at −78° was treated dropwise, with stirring under nitrogen, with a Grignard reagent prepared from magnesium (1.44 g, 60 mmol) and methyl bromide (6.7 g, 70 mmol) in dry ether (15 mL), and stirring was continued for 1 h at −78°. After storage overnight at room temperature, saturated aqueous ammonium chloride (9.0 mL) was added dropwise. The mixture was filtered, insoluble material was washed with ether, and the combined filtrate and washings were dried ($MgSO_4$) and concentrated. The residue was contaminated with by-products (n.m.r. data and g.l.c.). Fractional distillation gave **4** (3.53 g, 48% yield), b.p. 80–82°/0.2 mmHg, $[\alpha]_D^{20}$ +12.9 ±0.3° (*c* 0.35, methanol).

D-*Amicetose and* L-*rhodinose*. — To a solution of **4** (1.17 g, 9 mmol) in tetrahydrofuran (50 mL, freshly distilled from lithium aluminium hydride) at −30° under nitrogen was added dropwise, with a syringe through a rubber septum, a M solution of di-isobutylaluminium hydride (DIBAL; 20 mL, 20 mmol) in tetrahydrofuran. After 1 h at −20°, saturated aqueous ammonium chloride (5 mL) and then ether (330 mL) were added. The aqueous layer was absorbed with magnesium sulphate, the solids were filtered off and washed with chloroform, and the combined filtrate and washings were concentrated to dryness *in vacuo*, to yield an oil, the n.m.r. spectrum of which was a summation of the spectra of amicetose[16] (**5**) and rhodinose[15] (**6**).

The crude mixture was treated with 2,4-dinitrophenylhydrazine in methanol containing sulphuric acid. T.l.c. (dichloromethane–methanol, 9:1) showed two main spots with R_F 0.41 and 0.70, and some minor spots. Preparative t.l.c. gave D-amicetose 2,4-dinitrophenylhydrazone (R_F 0.41), m.p. 145–150°, $[\alpha]_D^{20}$ −8.9 ±0.3° (*c* 0.76, pyridine); lit.[17] m.p. 156–156.5°.

The component of R_F 0.70 was somewhat impure L-rhodinose 2,4-dinitrophenylhydrazone, m.p. 105–110°, $[\alpha]_D^{20}$ −11.0 ±0.3° (*c* 0.7, pyridine); lit.[17] m.p. 121–122°.

D-(+)-*Amicetono- and* L-(+)-*rhodinono-γ-lactones* (**8** *and* **9**). — (*a*) A solution of **4** (2.5 g, 20 mmol) in ethanol (50 mL) at 0° was treated with sodium borohydride (0.24 g, 6.34 mmol) and, after 4 h at 0°, adjusted to pH 5 with aqueous 10% hydrochloric acid, neutralised with solid sodium hydrogencarbonate, diluted with ether, filtered, dried ($MgSO_4$), and concentrated. The residue contained **8** and **9** together with a large proportion of by-products showing strong n.m.r. signals for ethoxyl groups. Treatment of the mixture with *p*-nitrobenzoyl chloride in pyridine, followed by preparative t.l.c. (ethyl acetate), produced, from the slower-moving band, a mixture of the *p*-nitrobenzoates of **8** and **9** in the ratio of ~60:40 (n.m.r. data: 2 d for Me at δ 1.47 and 1.44). Two crystallisations of this mixture from benzene–pentane gave a pure *p*-nitrobenzoate, m.p. 130–132° (presumably the derivative of **8**); λ_{max} 1696 and 1730 cm^{-1} (C=O). N.m.r. data: δ 1.44 (d, 3 H, Me), 2.0-2.8 (m, 4 H, H-2,3), 4.4–4.8 (m, 1 H, H-4), 5.08–5.52 (m, 1 H, H-5), and 8.3 (m, 4 H, C_6H_4).

Anal. Calc. for $C_{13}H_{13}NO_6$: C, 55.91; H, 4.70; N, 5.02. Found: C, 55.89; H, 4.82; N, 4.73.

(*b*) A solution of **4** (2.0 g, 15.6 mmol) in dry ether (15 mL) at 0° was treated slowly, under nitrogen, with an ethereal solution of zinc borohydride[28] (10 mmol in 40 mL). After 1 h at 0°, water was added, the water was absorbed with dry magnesium sulphate, insoluble material was collected and washed with ether, and the combined filtrate and washings were concentrated *in vacuo*, to give a liquid (1.9 g, 92%), g.l.c. of which showed that it was composed of 56% of **8** and 44% of **9**, without any by-products. This mixture (500 mg) was eluted from a column (3 × 20 cm) of silica gel at 2 atm. with light petroleum containing increasing amounts of ether. With a 70:30 solvent ratio, pure **8** was eluted, followed by mixture of **8** and **9**, and then pure **9**. Repetition of the chromatography on the intermediate fraction effected complete separation.

D-(+)-Amicetono-γ-lactone (**8**) had $[\alpha]_D^{25}$ +9.2 ±0.2° (*c* 1.3, chloroform); lit.[29] $[\alpha]_D^{20}$ −9.4° (*c* 1, chloroform; for a ~95% pure sample of the L-lactone). N.m.r. data: δ 1.20 (d, 3 H, Me), 1.9–2.8 (m, 4 H, H-2,3), 2.95 (s, 1 H, OH), 3.82–4.26 (m, 1 H, H-5), and 4.26–4.58 (m, 1 H, H-4).

L-(+)-Rhodinono-γ-lactone (**9**) had $[\alpha]_D^{25}$ +51.6 ±0.3° (*c* 2.5, chloroform); lit.[15] $[\alpha]_D^{25}$ +56.1° (*c* 2, chloroform). N.m.r. data: δ 1.25 (d, 3 H, Me), 1.9–2.7 (m, 4 H, H-2,3), 2.88 (s, 1 H, OH), 3.5–3.9 (m, 1 H, H-5), and 4.2–4.5 (m, 1 H, H-4). These data are in good agreement with those published[15,16].

(*c*) To a solution of **4** (1.0 g, 7.8 mmol) in dry tetrahydrofuran (10 mL, freshly distilled from lithium aluminium hydride) was added, at 0° under nitrogen, borane–methyl sulfide complex[22] (0.38 mL, 3.8 mmol). After 1 h at 0°, water (0.5 mL) was added, and the solution was diluted with ether (50 mL), dried ($MgSO_4$), and concentrated, to give a mixture of **8** and **9** in the ratio of 70:30.

D-(+)-*Amicetose* (**5**). — Lactone **8** (620 mg, 4.8 mmol) was reduced with M DIBAL (10.2 mL, 10.2 mmol), as described above for the reduction of **4**. The crude reduction-product was purified by elution from a column of silica gel with

chloroform–ether (1:1). The resulting, colorless oil (**5**, 85%) had $[\alpha]_D^{20}$ +40.1 ±0.3° (*c* 0.93, acetone); lit.[17] $[\alpha]_D^{22}$ +43.6° (*c* 1, acetone).

L-(−)-*Rhodinose* (**6**). — Lactone **9** was reduced, as described above, to give **6** (75%), $[\alpha]_D^{20}$ −8 ±0.3° (*c* 1, acetone). The n.m.r. spectra of **5** and **6** were in agreement with their structures; both exhibited several partly overlapping methyl-doublets and a bm at δ ~1.9, two overlapping bm at δ 3.0–4.3, and three anomeric proton signals at δ 4.9, 5.3, and 5.5, reflecting the equilibrium of furanose and pyranose forms.

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