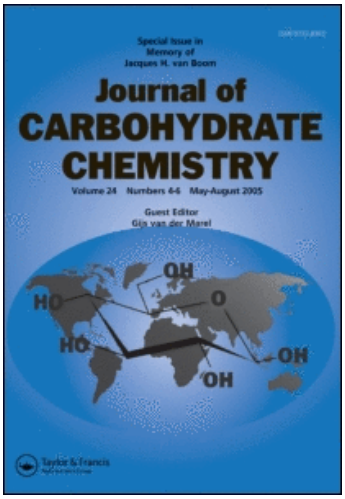

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OXIDATION PRODUCTS OF C-4 AND C-7 HYDROXYLS IN THE METHYL α-GLYCOSIDE DERIVATIVES OF KDN[1]

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ABSTRACT

A regioselective protection of hydroxyl groups in the methyl ester-methyl α-glycoside derivative of KDN was demonstrated. Isopropylidenation of methyl (methyl 3-deoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (**1**) gave mono- (8,9) and di- (5,7:8,9) *O*-isopropylidene derivatives. Benzoylation of methyl (methyl 3-deoxy-8, 9-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (**7**) gave di- (4,5) and tri- (4,5,7) *O*-benzoates. Through these reactions, it was found that the reactivity of the hydroxyl groups was different from that of methyl β-glycoside of KDN. Oxidation products of C-4 and C-7 hydroxyl groups (**6** and **11**) were synthesized from these compounds.

INTRODUCTION

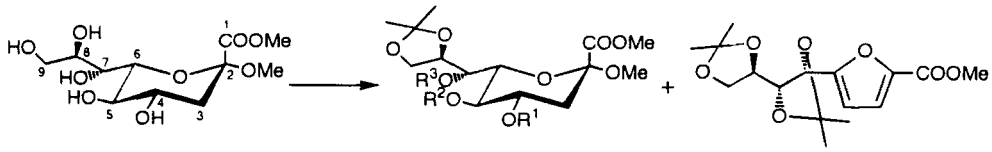
KDN, 3-deoxy-D-*glycero*-D-*galacto*-2-nonulosonic acid, isolated from polysialoglycoprotein (PSGP) of rainbow trout eggs,[2] has been prepared by large scale chemical synthesis based on the base-catalyzed aldol condensation of oxalacetic acid with D-mannose.[3,4] We have also synthesized various derivatives of KDN.[5-7]

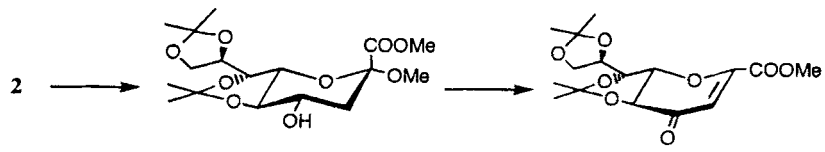
As a part of our investigations of the chemistry of KDN derivatives, we previously reported the regioselective protection of various hydroxyl groups on the methyl ester-methyl β-glycoside derivative of KDN by isopropylidenation and benzoylation reactions, and

synthesis of oxime derivatives from those protected compounds.[8] We have now examined protection of hydroxyl groups of the methyl ester-methyl α-glycoside derivative of KDN (**1**). In this paper, we report the synthesis of partially protected derivatives of **1** using isopropylidenation or benzoylation reactions. We then investigated the oxidation of unprotected C-4 or C-7 from the isopropylidenation or benzoylation, respectively.

RESULTS AND DISCUSSION

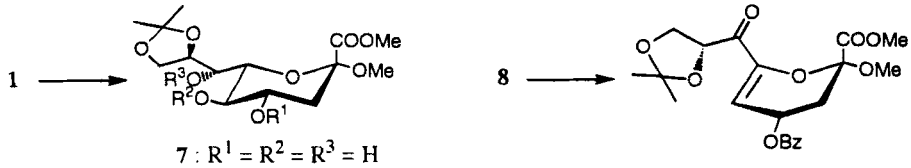
Treatment of **1** with an excess amount of 2,2-dimethoxypropane and *p*-toluenesulfonic acid monohydrate in acetone for 16 h at room temperature, and then acetylation with acetic anhydride and pyridine gave crystalline di-*O*-isopropylidene derivative, methyl (methyl 4-*O*-acetyl-3-deoxy-5, 7 : 8, 9-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-2-nonulopyranosid)-onate (**2**) in good yield as a major product. In addition, mono-*O*-isopropylidene derivative, methyl (methyl 4,5,7-tri-*O*-acetyl-3-deoxy-8,9-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (**3**) and furan derivative, methyl 2,5-anhydro-2,3,4-trideoxy-6,7:8,9-di-*O*-isopropylidene-D-*arabino*-non-2,4-dienonate (**4**) were isolated from the reaction mixture by silica gel column chromatography. The furan derivative (**4**) was the same product as the compound obtained by treatment of the methyl ester-methyl β-glycoside of KDN with 2,2-dimethoxypropane and *p*-toluenesulfonic acid monohydrate, based on its ^{1}H NMR spectrum which was identical with that reported previously.[8] Deacetylation of **2** with sodium methoxide in methanol gave C-4 hydroxy derivative (**5**). Ruthenium oxidation of **5** afforded unexpectedly the β-elimination product, 2-deoxy-4-keto derivative (**6**) in good yield. The structure of **6** was elucidated by ^{1}H NMR spectral analysis. The C-3 proton signal was observed as an olefinic proton at 6.24 ppm singlet, and the C4-H and C2-OMe





protons were absent. Furthermore, the positions of the isopropylidene groups methyl protons of **6** were found to be different from those of the di-*O*-isopropylidene derivative of the methyl ester-methyl β-glycoside of KDN [8] based on an NOE experiment. For the 5,7-*O*-isopropylidene group, on irradiation of the isopropylidene methyl protons at 1.38 ppm, an NOE was observed at H-5 (2.9%), and on irradiation at 1.56 ppm, an NOE was observed at H-7(2.3%). For the 8, 9-*O*-isopropylidene group, on irradiation at 1.44 ppm, an NOE was observed at H-8 and H-9 (2.3%), on irradiation at 1.46 ppm, an NOE was observed at H-9(1.0%). These experiment supported the structure of **6**. The formation of the alkene bond of **6** results from β-elimination of the C2-OMe group.

Isopropylidenation of **1** with a 1.2 equivalent amount of 2,2-dimethoxypropane in the presence of a catalytic amount of *p*-toluenesulfonic acid monohydrate gave mono-*O*-isopropylidene derivative, methyl (methyl 3-deoxy-8,9-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-2-nonulopyranosid) onate (**7**) in 91% yield. Benzoylation of **7** with an excess amount of benzoic anhydride and pyridine afforded 4,5-di-*O*-benzoate (**8**) as a major product, and 4,7-di-*O*-benzoate (**9**) and 4,5,7-tri-*O*-benzoate (**10**) as minor products isolated by silica gel chromatography. The structure of **8** was elucidated by ^{1}H NMR spectral analysis. The benzoylated positions of **8** were confirmed to be at C-4 and C-5 by a downfield shift of signals for H-4 and H-5 due to *O*-acylation. Previously, we carried out a similar experiment for benzoylation using the 8,9-*O*-isopropylidene derivative of the methyl ester-methyl β-glycoside of KDN.[8] The 4,7-di-*O*-benzoate was the major product. Therefore, we found that there was a difference in the reactivity of hydroxyl groups towards benzoylation between the α- and β-isomers of 8,9-*O*-isopropylidene derivatives of KDN. Oxidation at the C-7 hydroxyl group of **8** by use of ruthenium tetraoxide gave also β-elimination product, 5-deoxy-7-keto derivative (**11**). The structure of **11** was elucidated from its ^{1}H NMR spectrum. The signal of the C-5 proton was observed as an olefinic proton at 6.33 ppm singlet. The formation of the 5-deoxy-5-ene derivative (**11**) is considered to occur by the same process as that of the 2-deoxy-2-ene derivative (**6**).



7 : $R^1 = R^2 = R^3 = H$
8 : $R^1 = R^2 = Bz$, $R^3 = H$
9 : $R^1 = R^3 = Bz$, $R^2 = H$
10 : $R^1 = R^2 = R^3 = Bz$

11

In conclusion, we demonstrated the regioselective protection of hydroxyl groups on the methyl ester-methyl α-glycoside derivatives of KDN, and synthesized the C-4 or C-7 keto

derivative from those protected compounds. We also found a difference in reactivity of hydroxyl groups between methyl ester-methyl α- and β-glycoside derivatives of KDN.

EXPERIMENTAL

General methods. Melting points were measured with a YAZAWA BY-10 melting point apparatus without correction. Optical rotations were measured with a JASCO DIP-370 digital polarimeter. Fast atom bombardment mass spectra (FAB-MS) and high resolution mass spectra (HRMS) were measured with a JEOL JMS-DX300 and a JEOL JMS-AX505 HA, respectively. Infrared (IR) spectra were recorded as a film with a JASCO A-102 spectrometer. The NMR spectra were measured with a Varian VXR-300 (300 MHz) spectrometer using tetramethylsilane (TMS) as an internal reference. Thin-layer chromatography (TLC) was performed on Silica gel 60 F_{254} (Merck) plates, and spots were detected by ultraviolet (UV) irradiation or by spraying with 5% sulfuric acid solution. Column chromatography was conducted on Silica gel 60 (70–230 mesh, Merck). Solvent evaporations were conducted *in vacuo*.

Methyl (Methyl 4-*O*-Acetyl-3-deoxy-5, 7 : 8, 9-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (2). 2, 2-Dimethoxypropane (2.5 g, 24 mmol) and *p*-toluenesulfonic acid (3 mg) were added to a solution of **1** (450 mg, 1.52 mmol) in acetone (20 mL). The mixture was stirred for 16 h at room temperature, then pyridine (2 mL) was added to the solution. The mixture was concentrated, the residue was dissolved in pyridine (5 mL), and to this solution acetic anhydride (2 mL) was added. The mixture was stirred for 16 h at room temperature, poured into saturated sodium hydrogen carbonate solution, and extracted with ethyl acetate (30 mL × 3). The extract was washed with brine, dried over sodium sulfate, and concentrated to dryness. The residue was chromatographed on a column of silica gel with *n*-hexane– ethyl acetate (3 : 1) to give **2** (350 mg, 55%) as colorless crystals, methyl (methyl 4, 5, 7-tri-*O*-acetyl-3-deoxy-8, 9-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (**3**, 94 mg, 13%) and methyl 2, 5-anhydro-2, 3, 4-trideoxy-6, 7 : 8, 9-di-*O*-isopropylidene-D-*arabino*-non-2, 4-dienonate (**4**, 18 mg, 4%).

2 : mp 117 – 119 °C; $[\alpha]_D^{26}$ -36.0° (*c* 0.97, MeOH); IR ν_{max} 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28, 1.29, 1.42, 1.47 (4s, 12H, $2CMe_2$), 1.76 (dd, 1H, $J_{3ax,4}$ = 11.5 Hz, $J_{3ax,3eq}$ = 12.5 Hz, H-3_{ax}), 2.04 (s, 3H, OAc), 2.68 (dd, 1H, $J_{3eq,4}$ = 5.0 Hz, H-3_{eq}), 3.36 (s, 3H, OMe), 3.60–3.79 (m, 6H, H-5~9), 3.83 (s, 3H, COOMe), 4.94 (ddd, 1H, $J_{4,5}$ = 9.0 Hz, H-4); FAB-MS *m/z* 419 ($M^+ + 1$).

Anal. Calcd for $C_{19}H_{30}O_{10}$: C, 54.54; H, 7.23. Found: C, 54.26; H, 7.19.

3 : $[\alpha]_D^{25}$ -15.6° (*c* 1.03, MeOH); IR ν_{max} 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33, 1.35 (2s, 6H, CMe_2), 1.91 (dd, 1H, $J_{3ax,4}$ = 11.0 Hz, $J_{3ax,3eq}$ = 12.5 Hz, H-3_{ax}), 2.00, 2.00,

2.11 (3s, 9H, OAc), 2.68 (dd, 1H, $J_{3eq,4}$ = 5.0 Hz, H-3_{eq}), 3.35 (s, 3H, OMe), 3.85 (s, 3H, COOMe), 3.94 (dd, 1H, $J_{6,7}$ = 2.0 Hz, $J_{5,6}$ = 9.0 Hz, H-6), 4.01 (dd, 1H, $J_{8,9}$ = 6.5 Hz, $J_{9,9'}$ = 8.5 Hz, H-9), 4.10 (dd, 1H, $J_{8,9'}$ = 6.5, 8.5 Hz, H-9'), 4.38 (dt, 1H, $J_{7,8}$ = 3.5 Hz, H-8), 4.89 (t, 1H, $J_{4,5}$ = 9.0 Hz, H-5), 4.95 (ddd, 1H, H-4), 5.44 (dd, 1H, H-7); FAB-MS *m/z* 463 (M^+ + 1).

Anal. Calcd for $C_{20}H_{30}O_{12}$: C, 51.95; H, 6.54. Found: C, 51.72; H, 6.42.

Methyl (Methyl 3-Deoxy-5,7 : 8,9-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (5). A 28% sodium methoxide solution (1 mL) was added to a solution of **2** (150 mg, 0.36 mmol) in methanol (10 mL), and the mixture was stirred for 1 h at room temperature, then neutralized with dry Dowex-50 (H^+) resin (1 g). The resin was filtered off and washed with methanol. The combined filtrate and washings were concentrated. The residue was purified on a column of silica gel with chloroform–methanol (10 : 1) to give **5** (128 mg, 95%): $[\alpha]_D^{25}$ -48.2° (*c* 0.93, MeOH); IR ν_{max} 1740, 3450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34, 1.36, 1.42, 1.48 (4s, 12H, $2CMe_2$), 1.79 (dd, 1H, $J_{3ax,4}$ = 11.5 Hz, $J_{3ax,3eq}$ = 13.0 Hz, H-3_{ax}), 2.37 (d, 1H, $J_{4,4OH}$ = 2.5 Hz, OH-4), 2.66 (dd, 1H, $J_{3eq,4}$ = 5.0 Hz, H-3_{eq}), 3.37 (s, 3H, OMe), 3.44 (dd, 1H, $J_{4,5}$ = 8.5 Hz, $J_{5,6}$ = 9.5 Hz, H-5), 3.52 (dd, 1H, $J_{6,7}$ = 7.5 Hz, H-6), 3.63 (m, 1H, H-4), 3.64–3.79 (m, 3H, H-8, H_2-9), 3.69 (m, 1H, H-7), 3.85 (s, 3H, COOMe); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.9, 24.6, 24.9, 29.0 ($2C\underline{Me}_2$), 38.0 (C-3), 51.6 (OMe), 52.5 (COO<u>Me</u>), 62.4 (C-8), 62.7 (C-9), 67.9 (C-4), 72.4 (C-5), 75.8 (C-7), 76.1 (C-6), 98.6, 98.8 ($2\underline{C}Me_2$), 101.9 (C-2), 168.8 (C-1); FAB-MS *m/z* 377 (M^+ + 1).

Anal. Calcd for $C_{17}H_{28}O_9$: C, 54.25; H, 7.50. Found: C, 53.96; H, 7.36.

Methyl 2,6-Anhydro-2,3-dideoxy-5,7 : 8,9-di-*O*-isopropylidene-4-oxo-D-*glycero*-D-*galacto*-non-2-enonate (6). Ruthenium (IV) oxide hydrate (0.2 g, 1.50 mmol) was suspended in carbon tetrachloride (25 mL). A solution of sodium periodate (1.6 g, 7.48 mmol) in water (25 mL) was added, and the mixture was stirred for 1 h at 0 °C. The carbon tetrachloride layer was separated, and sodium periodate (0.5 g, 2.34 mmol) in water (25 mL) was added to the solution.[9] The mixture was shaken, then the carbon tetrachloride layer was separated. This solution was added to a solution of **5** (40 mg, 0.11 mmol) in carbon tetrachloride (5 mL), and the mixture was stirred for 48 h at room temperature, then 2-propanol (2 mL) was added to the solution. The mixture was concentrated, and the residue was purified on a column of silica gel with chloroform to give **6** (26 mg, 71%): $[\alpha]_D^{26}$ -167.8° (*c* 1.00, MeOH); IR ν_{max} 1610, 1690, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38, 1.44, 1.46, 1.56 (4s, 12H, $2CMe_2$), 3.72–3.83 (m, 3H, H-8, H_2-9), 3.87 (s, 3H, COOMe), 4.03 (ddd, 1H, $J_{6,7}$ = 7.0 Hz, H-7), 4.23 (dd, 1H, $J_{5,6}$ = 13.0 Hz, H-6), 4.33 (d, 1H, H-5), 6.24 (s, 1H, H-3); FAB-MS *m/z* 343 (M^+ + 1).

Anal. Calcd for $C_{16}H_{22}O_8$: C, 56.14; H, 6.48. Found: C, 55.88; H, 6.56.

Methyl (Methyl 3-Deoxy-8,9-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (7). 2,2-Dimethoxypropane (152 mg, 1.46 mmol) and *p*-toluenesulfonic acid monohydrate (1 mg) were added to a solution of **1** (360 mg, 1.22 mmol) in acetone (20 mL). The mixture was stirred for 16 h at room temperature, and then treated with dry Dowex-1 (OH^-) anion-exchange resin (1 g) to remove the acid. The resin was filtered off and washed with acetone. The combined filtrate and washings were concentrated. The residue was purified on a column of silica gel with chloroform–methanol (10 : 1) to give **7** (370 mg, 91%): $[\alpha]_D^{26}$ -17.5° (*c* 0.95, MeOH); IR ν_{max} 1740, 3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37, 1.42 (2s, 6H, CMe_2), 1.76 (t, 1H, $J_{3ax,4}$ = 12.5 Hz, $J_{3ax,3eq}$ = 12.5 Hz, H-3_{ax}), 2.64 (dd, 1H, $J_{3eq,4}$ = 5.0 Hz, H-3_{eq}), 3.31 (s, 3H, OMe), 3.52–3.58 (m, 3H, H-4~6), 3.81 (s, 3H, COOMe), 3.99 (m, 1H, H-7), 4.06 (dd, 1H, $J_{8,9}$ = 6.0 Hz, $J_{9,9'}$ = 9.0 Hz, H-9), 4.12 (dd, 1H, $J_{8,9'}$ = 6.0, 9.0 Hz, H-9'), 4.21 (q, 1H, $J_{7,8}$ = 6.0 Hz, H-8); (C_5D_5N) δ 1.49, 1.55 (2s, 6H, CMe_2), 2.29 (t, 1H, $J_{3ax,4}$ = 12.5 Hz, $J_{3ax,3eq}$ = 12.5 Hz, H-3_{ax}), 3.19 (dd, 1H, $J_{3eq,4}$ = 5.0 Hz, H-3_{eq}), 3.40 (s, 3H, OMe), 3.69 (s, 3H, COOMe), 4.23 (dd, 1H, $J_{6,7}$ = 1.5, $J_{5,6}$ = 9.5 Hz, H-6), 4.26 (ddd, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 4.45 (t, 1H, H-5), 4.51 (dd, 1H, $J_{8,9}$ = 6.0 Hz, $J_{9,9'}$ = 9.0 Hz, H-9), 4.61 (dd, 1H, $J_{8,9'}$ = 6.0 Hz, H-9'), 4.81 (q, 1H, $J_{7,8}$ = 6.0 Hz, H-8), 4.91 (dd, 1H, H-7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6, 26.6 (2C<u>Me</u>$_2$), 39.0 (C-3), 52.0 (OMe), 52.7 (COO<u>Me</u>), 65.9 (C-9), 69.1 (C-7), 70.0 (C-4), 70.7 (C-6), 75.3 (C-5), 76.6 (C-8), 99.6 (<u>C</u>Me_2), 108.8 (C-2), 168.5 (C-1); FAB-MS *m/z* 337 (M^+ + 1).

Anal. Calcd for $C_{14}H_{24}O_9$: C, 50.00; H, 7.19. Found: C, 49.74; H, 7.24.

Methyl (Methyl 4,5-Di-*O*-benzoyl-3-deoxy-8,9-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (8). A solution of **7** (80 mg, 0.24 mmol) in pyridine (10 mL) containing benzoic anhydride (538 mg, 3.4 mmol) and 4-dimethylaminopyridine was stirred for 16 h at room temperature. The mixture was poured into saturated sodium hydrogen carbonate solution and extracted with chloroform (30 mL × 3). The extract was washed with brine, dried over sodium sulfate, and concentrated to dryness. The residue was chromatographed on a column of silica gel with *n*-hexane–ethyl acetate (2 : 1) to give **8** (68 mg, 55%) and a mixture of methyl (methyl 4,7-di-*O*-benzoyl-3-deoxy-8,9-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (**9**) and methyl (methyl 4,5,7-tri-*O*-benzoyl-3-deoxy-8,9-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (**10**). The mixture of **9** and **10** was separated by silica gel TLC with 1 : 1 *n*-hexane–ethyl acetate to give **9** (15 mg, 10%) and **10** (7 mg, 6%).

8: $[\alpha]_D^{30}$ +26.3° (*c* 1, MeOH); IR ν_{max} 1580, 1600, 1730, 3450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35, 1.36 (2s, 6H, CMe_2), 2.10 (dd, 1H, $J_{3ax,4}$ = 11.5 Hz, $J_{3ax,3eq}$ = 13.0 Hz, H-3_{ax}), 2.94 (dd, 1H, $J_{3eq,4}$ = 5.0 Hz, H-3_{eq}), 3.42 (s, 3H, OMe), 3.69 (dd, 1H, $J_{6,7}$ = 1.5 Hz, $J_{7,8}$ = 6.0 Hz, H-7), 3.93 (s, 3H, COOMe), 4.05 (dd, 1H, $J_{5,6}$ = 9.0 Hz, H-6), 4.10

(d, 1H, $J_{8,9}$ = 6.0 Hz, $J_{9,9'}$ = 9.0 Hz, H-9), 4.14 (d, 1H, $J_{8,9'}$ = 6.0 Hz, H-9'), 4.30 (q, 1H, H-8), 5.47 (ddd, 1H, $J_{4,5}$ = 9.0 Hz, H-4), 5.54 (t, 1H, H-5), 7.34 – 7.96 (10H, phenyl groups); HRMS *m/z* Calcd for $C_{28}H_{32}O_{11}Na$: (M^++Na) 567.1842. Found : (M^++Na) 567.1857.

9 : $[\alpha]_D^{30}$ +5.6° (*c* 0.14, MeOH); IR ν_{max} 1580, 1600, 1720, 1740, 3450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29, 1.37 (2s, 6H, CMe_2), 1.89 (dd, 1H, $J_{3ax,4}$ = 11.5 Hz, $J_{3ax,3eq}$ = 13.0 Hz, H-3_{ax}), 2.82 (dd, 1H, $J_{3eq,4}$ = 5.0 Hz, H-3_{eq}), 3.38 (s, 3H, OMe), 3.54 (t, 1H, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 9.0 Hz, H-5), 3.89 (s, 3H, COOMe), 3.90 (dd, 1H, $J_{6,7}$ = 1.5 Hz, H-6), 4.27 (d, 1H, $J_{8,9}$ = 6.0 Hz, $J_{9,9'}$ = 9.0 Hz, H-9), 4.34 (d, 1H, $J_{8,9'}$ = 6.0 Hz, H-9'), 4.60 (dt, 1H, $J_{7,8}$ = 3.0 Hz, H-8), 5.16 (ddd, 1H, H-4), 5.68 (dd, 1H, H-7), 7.38–8.17 (10H, phenyl groups); HRMS *m/z* Calcd for $C_{28}H_{32}O_{11}Na$: (M^++Na) 567.1842. Found : (M^++Na) 567.1870.

10 : $[\alpha]_D^{30}$ -13.7° (*c* 0.88, MeOH); IR ν_{max} 1580, 1600, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19, 1.34 (2s, 6H, CMe_2), 2.09 (dd, 1H, $J_{3ax,4}$ = 11.5 Hz, $J_{3ax,3eq}$ = 12.5 Hz, H-3_{ax}), 2.96 (dd, 1H, $J_{3eq,4}$ = 5.0 Hz, H-3_{eq}), 3.46 (s, 3H, OMe), 3.96 (s, 3H, COOMe), 4.21 (d, 2H, $J_{8,9}$ = 6.5 Hz, H_2-9), 4.35 (dd, 1H, $J_{6,7}$ = 2.0 Hz, $J_{5,6}$ = 10.0 Hz, H-6), 5.28 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 5.41 (t, 1H, H-5), 5.48 (dt, 1H, $J_{7,8}$ = 4.0 Hz, H-8), 5.75 (dd, 1H, H-7), 7.60–8.20 (15H, phenyl groups); HRMS *m/z* Calcd for $C_{35}H_{36}O_{12}Na$: (M^++Na) 671.2104. Found : (M^++Na) 671.2119.

Methyl (Methyl 2,6-Anhydro-4-*O*-benzoyl-3,5-dideoxy-8,9-*O*-isopropylidene-7-oxo-α-D-*glycero*-D-*galacto*-non-5-enepyranosid)onate (11). A ruthenium (VIII) oxide solution in carbon tetrachloride was prepared as described for **6**. This solution was added to a solution of **8** (20 mg, 0.037 mmol) in carbon tetrachloride (3 mL), and the mixture was stirred for 48 h at room temperature, then 2-propanol (5 mL) was added to the solution. The mixture was concentrated, and the residue was purified on a column of silica gel with *n*-hexane–ethyl acetate (2 : 1) to give **11** (8 mg, 52%): $[\alpha]_D^{25}$ -39.0° (*c* 1.15, MeOH); IR ν_{max} 1580, 1600, 1640, 1720, 1740, 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45, 1.49 (2s, 6H, CMe_2), 2.44 (dd, 1H, $J_{3ax,4}$ = 6.5 Hz, $J_{3ax,3eq}$ = 15.0 Hz, H-3_{ax}), 2.57 (ddd, 1H, $J_{3eq,5}$ = 1.0 Hz, $J_{3eq,4}$ = 4.5 Hz, H-3_{eq}), 3.40 (s, 3H, OMe), 3.88 (s, 3H, COOMe), 4.08 (dd, 1H, $J_{8,9}$ = 6.0 Hz, $J_{9,9'}$ = 8.5 Hz, H-9), 4.42 (dd, 1H, $J_{8,9'}$ = 8.0 Hz, H-9'), 5.15 (dd, 1H, H-8), 5.64 (dt, 1H, $J_{4,5}$ = 4.5 Hz, H-4), 6.33 (dd, 1H, H-5), 7.42–8.10 (5H, phenyl group); HRMS *m/z* Calcd for $C_{21}H_{24}O_9Na$: (M^++Na) 443.1318. Found : (M^++Na) 443.1314.

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