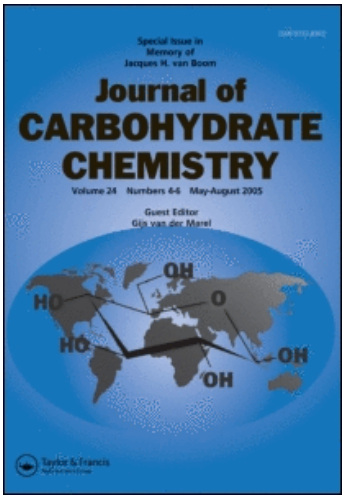

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Syntheses of 2,6-Anhydro-3-Deoxy-D-*Glycero*-D-*Galacto*-Non-2-Enonic Acid (Kdn2En) and Its Hydrogenation Products

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SYNTHESES OF 2,6-ANHYDRO-3-DEOXY-D-*GLYCERO*-D-*GALACTO*-NON-2-ENONIC ACID (KDN2en) AND ITS HYDROGENATION PRODUCTS[1]

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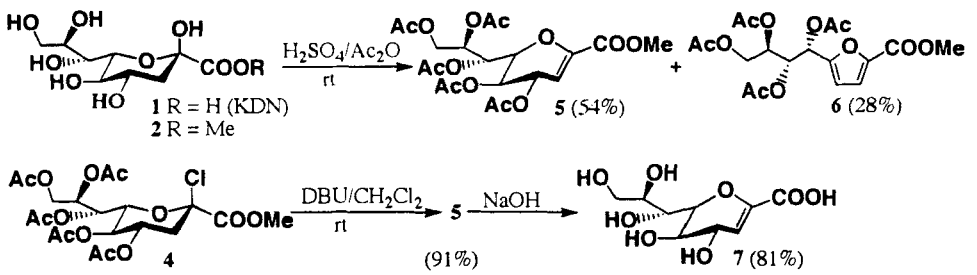
ABSTRACT

Methyl 4,5,7,8,9-penta-*O*-acetyl-2,6-anhydro-3-deoxy-D-*glycero*-D-*galacto*-non-2-enonate (**5**) was synthesized from KDN methyl ester **2** with a catalytic amount of concentrated sulfuric acid in acetic anhydride, or from 2-chloro-KDN methyl ester **4** with DBU in good yield. Hydrogenation of **4** and **5** with 10% Pd-C gave 2-deoxy-2-H_{ax}-KDN **8** and 2-deoxy-2-H_{eq}-KDN derivative **11** in high yield, respectively. The structures of these compounds were elucidated from the MS, elemental analysis, ^{1}H NMR and ^{13}C NMR data.

INTRODUCTION

2,3-Dehydro-2-deoxysialic acids are widely distributed in nature,[2] and known as inhibitors of neuraminidase from of old.[3] Recently, 5-*N*-acetyl-2,6-anhydro-3,5-dideoxy-4-guanidino-D-*glycero*-D-*galacto*-non-2-enonic acid was developed as a potent and selective inhibitor of influenza virus sialidase.[4] On the other hand, 2-deoxy-2-H_{eq}-KDO had been found to be a strong inhibitor of the CMP-KDO-synthetase.[5] Therefore, 2,3-dehydro-2-deoxysialic acids and their analogues are receiving much attention from both chemists and biologists. We had established a chemical method of preparation of KDN (**1**) on large scale, and obtained 2,3-dehydro-2-deoxy-KDN, which is not isolated from nature yet, as a by-product from the glycosylation of KDN.[6,7] As a part of our interest in the synthesis and biological activity of structurally modified sialic acids, herein, we would like



Scheme 1

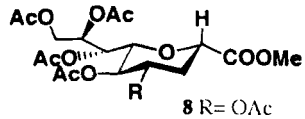
to report the straightforward syntheses of 2,3-dehydro-2-deoxy-KDN **7** and its hydrogenation products, namely, 2-deoxy-2-H_{ax}-KDN derivative **8** and 2-deoxy-2-H_{eq}-KDN derivative **11**.

RESULTS AND DISCUSSION

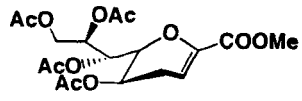
Crystalline KDN (**1**) was prepared in high purity and high yield by the aldol condensation of D-mannose with oxalacetic acid without formation of 4-*epi*-KDN.[7] KDN methyl ester **2** was prepared from KDN by the reported method.[8] The expected compound, methyl 4,5,7,8,9-penta-*O*-acetyl-2,6-anhydro-2,3-dideoxy-D-*glycero*-D-*galacto*-non-2-enonate (**5**) was obtained by treatment of **2** with a catalytic amount of concentrated sulfuric acid in acetic anhydride at room temperature. However, (1'*S*,2'*R*,3'*R*)-methyl 5-(1',2',3',4'-tetra-*O*-acetylbutyl)furoate (**6**) was also obtained as a by-product in this reaction, and the two peracetylated dehydroxy products were hard to resolve by either TLC or LC (silica gel). In particular, the formation of **6** reduced the yield of **5**, so it was an unsuitable method. Therefore, we selected 2-chloro-KDN methyl ester **4**[7] as starting material and treated it with DBU in dichloromethane to obtain **5** (92% yield) according to a literature method.[9] Deacetylation of **5** with 1N NaOH in methanol afforded the expected compound, 2,6-anhydro-3-deoxy-D-*glycero*-D-*galacto*-non-2-enonic acid (KDN2en, **7**).

The structures of these compounds were elucidated from the MS, elemental analysis, and NMR data. The ^{1}H NMR spectrum of **7** showed a doublet at 5.92 ppm ($J_{3,4}$ = 2.7 Hz) owing to H-3 and a double doublet at 4.39 ppm ($J_{3,4}$ = 2.7 Hz, $J_{4,5}$ = 7.8 Hz) owing to H-4 (β-orientation). A comparison of the ^{1}H NMR spectral data with that from the corresponding *N*-acetylneuraminic acid derivative (Neu5Ac2en)[10] indicated that the pyranoid ring of **7** was in the same half chair-half boat conformation as Neu5Ac2en.

We next turned our attention to the syntheses of 2-deoxy-2-H_{ax}-KDN derivative **8** and 2-deoxy-2-H_{eq}-KDN derivative **11**. Thus **5** was subjected to hydrogenation with catalytic 10% Pd-C in methanol to afford the expected product **8** and minor product 2,4-dideoxy-2-H_{ax}-KDN derivative **9** in 79% yield (30:1). Whereas, **9** was formed exclusively by changing the solvent to MeOH-AcOH (10:1) in 87% yield. On the other hand, catalytic hydrogenation of **5** over PtO_2 in methanol afforded 2,4-dideoxy-KDN derivative **10** and **9** in 97% yield (5:4). Another expected compound **11** was prepared from 2-chloro-KDN methyl ester **4** by catalytic reduction with 10% Pd-C/H_2 in toluene-pyridine (79%) as described in the literature,[11] but without formation of its 2-epimer **8**.



8 R= OAc
9 R= H



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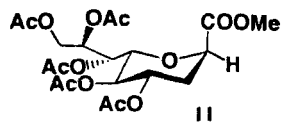

11

These compounds were identified from the MS, elemental analysis, and NMR data. The ^1H NMR spectrum (300 MHz, $CDCl_3$) of **11** showed a double doublet at 4.56 ppm ($J_{2,3ax}$ = 6.9 Hz, $J_{2,3eq}$ = 1.2 Hz) owing to H-2, a double double doublet at 2.50 ppm ($J_{3eq,3ax}$ = 13.5 Hz, $J_{2,3eq}$ = 1.2 Hz, $J_{3eq,4}$ = 5.1 Hz) owing to H-3_{eq}, and a double double doublet at 2.07 ppm ($J_{3eq,3ax}$ = 13.5 Hz, $J_{2,3ax}$ = 6.9 Hz, $J_{3ax,4}$ = 12.0 Hz) owing to H-3_{ax} indicating that H-2 was in an equatorial position. The coupling constants between H-2 and H-3 ($J_{2,3ax}$ = 12.0 Hz, $J_{2,3eq}$ = 2.4 Hz) of **8** indicated that H-2 was axial.[11] For compound **9**, with one acetyl group less than **8**, both chemical shifts of H-3_{ax} and of H-3_{eq} were shifted upfield. In addition, two protons H-4_{eq} and H-4_{ax} appeared upfield (2.77 ppm, 1.54 ppm), and H-2 was also axial as supported by the coupling constants between H-2 and H-3 ($J_{2,3ax}$ = 12.0 Hz, $J_{2,3eq}$ = 2.3 Hz). The ^1H NMR spectrum of **10** showed a double doublet at 6.04 ppm (J= 4.8, 3.3 Hz) owing to an olefinic proton H-3 and one acetyl group less than **8**, as well as two protons H-4_{eq} and H-4_{ax} which were upfield (2.67 ppm, 2.20 ppm).

In conclusion, we have developed a straightforward synthetic method for the preparation of 2,3-dehydro-2-deoxy-KDN **7** and synthesized 2-deoxy-2-H_{ax}-KDN **8** and 2-deoxy-2-H_{eq}-KDN derivative **11** in high yield.

EXPERIMENTAL

General methods. Melting points were measured on a Yamato melting point apparatus without correction. Fast atom bombardment mass spectra (FAB MS) were taken on a JEOL JMS-DX 300. Optical rotations were measured with a JASCOJIP-4 digital polarimeter (at 25 °C). The ^1H NMR spectra were determined with Varian VXR-300

spectrometer, in the solution state, with tetramethylsilane (TMS) as an internal reference. Thin-layer chromatography (TLC) was performed on Kieselgel 60 F_{254} (Merck) plates, and spots were detected under ultraviolet (UV) irradiation or by spraying 5% sulfuric acid solution. Column chromatography was conducted on silica gel 60 (70-230 mesh, Merck).

Methyl 4,5,7,8,9-Penta-*O*-acetyl-2,6-anhydro-2,3-dideoxy-D-*glycero*-D-*galacto*-non-2-enonate (5).

Procedure A. A solution of 0.06 g concentrated sulfuric acid in acetic anhydride (2 mL) was added to a solution of **2** (855 mg, 3.0 mmol) in acetic anhydride (10 mL). The mixture was stirred for 12 h at room temperature and then the reaction mixture was poured into ice-water, extracted with EtOAc (30 mL × 3). The extract was washed with sodium hydrogen carbonate solution, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified with silica gel column chromatography (*n*-hexane-acetone 4:1) to yield **5** (770 mg, 54%) and (1'*S*,2'*R*,3'*R*)-methyl 5-(1',2',3',4'-tetra-*O*-acetylbutyl)furoate (**6**) (347 mg, 28%) respectively.

5: colorless syrup; $[\alpha]_D$ -12.6° (*c* 0.54, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94 (d, 1H, $J_{3,4}$ = 3.0 Hz, H-3), 5.55 (dd, 1H, $J_{4,5}$ = 8.2 Hz, H-4), 5.20 (dd, 1H, $J_{5,6}$ = 9.6, 8.2 Hz, H-5), 4.32 (dd, 1H, $J_{6,7}$ = 3.3 Hz, H-6), 5.46 (dd, 1H, $J_{7,8}$ = 6.6 Hz, H-7), 5.35 (ddd, 1H, $J_{8,9}$ = 2.7 Hz, $J_{8,9'}$ = 6.6 Hz, H-8), 4.16 (dd, 1H, $J_{9,9'}$ = 12.6 Hz, 9-H), 4.55 (dd, 1H, H-9'), 3.80 (s, 3H, $COOCH_3$), 2.01, 2.03, 2.04, 2.05, 2.07 (each s, 3H, OAc ×5); FAB MS *m/z*: 475 (M^++1) (*m* -NBA as matrix).

Anal. Calcd for $C_{20}H_{26}O_{13}$: C, 50.63; H, 5.52. Found: C, 50.70; H, 5.48.

6: colorless needles; mp 89-91 ℃; $[\alpha]_D$ -29° (*c* 0.61, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d 1H, $J_{3,4}$ = 3.9 Hz, H-3), 6.42 (d, 1H, H-4), 6.12 (d, 1H, $J_{6,7}$ = 3.3 Hz, H-6), 5.58 (dd, 1H, $J_{7,8}$ = 9.3 Hz, H-7), 5.22 (ddd, 1H, $J_{8,9}$ = 3.0 Hz, $J_{8,9'}$ = 5.1 Hz, H-8), 4.24 (dd, 1H, $J_{9,9'}$ = 12.6 Hz, H-9), 4.13 (dd, 1H, H-9'), 3.86 (s, 3H, $COOCH_3$), 2.03, 2.06, 2.08, 2.09 (each s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.35, 20.57, 20.72 ($CO\underline{C}H_3$), 51.92 ($COO\underline{C}H_3$), 61.56 (C-9), 65.77 (C-6), 68.19 (C-8), 69.37 (C-7), 111.15 (C-4), 118.29 (C-3), 144.73 (C-2), 152.92 (C-5), 158.62 (C-1), 169.30, 169.54, 169.66, 170.49 ($\underline{C}OCH_3$ ×4); FAB MS *m/z*: 415 (M^++1) (*m* -NBA as matrix).

Anal. Calcd for $C_{18}H_{12}O_{11}$: C, 52.18; H, 5.35. Found: C, 52.21; H, 5.30.

Procedure B. To a solution of **4** (122 mg, 0.239 mmol) in dry dichloromethane (15 mL) was added DBU (0.25 mL, 7 eq) dropwise, The reaction was completed after 1 h with magnetic stirring (TLC: ether:*n*-hexane 3:1). The solution was then acidified with 33% HCl, extracted with EtOAc (30 mL×3). The extract was washed with sodium hydrogen carbonate solution, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was then purified by silica gel column chromatography (*n*-hexane: acetone 4:1) to yield **5** (107 mg, 95%).

2,6-Anhydro-3-deoxy-D-*glycero*-D-*galacto*-non-2-enonic acid (7). To a solution of **5** (107 mg, 0.227 mmol) in dry MeOH (10 mL) was added sodium methoxide (25 mg, 0.45 mmol, 2 eq). The reaction mixture was stirred for 30 min at room temperature (TLC: $CHCl_3$:MeOH 6:1), then neutralized to pH 7 with Dowex 50W-1(H^+) cation-exchange resin. The resin was filtered off and washed twice with MeOH. The filtrate was concentrated to dryness, and the residue was dissolved in aq 0.1 M NaOH (10 mL). After 20 min with magnetic stirring at room temperature, the solution was gradually acidified with Dowex 50W-1(H^+) cation-exchange resin to pH 7-7.5 and freeze-dried to yield **7** (50 mg, 81%).

7: amorphous powder; $[\alpha]_D$ -134° (*c* 0.78, D_2O); ^1H NMR (300 MHz, D_2O) δ 5.92 (d, 1H, $J_{3,4}$ = 2.7 Hz, H-3), 4.39 (dd, 1H, $J_{4,5}$ = 7.8 Hz, H-4), 4.14 (dd, 1H, $J_{5,6}$ = 10.8 Hz, $J_{6,7}$ = 1.2 Hz, H-6), 3.84 (m, 3H, H-7, 8, 9), 3.75 (dd, 1H, H-5), 3.64 (dd, 1H, $J_{9,9'}$ = 11.4 Hz, $J_{8,9'}$ = 6.0 Hz, H-9'); ^{13}C NMR (75 MHz, D_2O) δ 69.73 (C-9), 70.05 (C-5), 70.17 (C-7), 71.83 (C-4), 72.72 (C-8), 79.59 (C-6), 114.79 (C-3), 146.09 (C-2), 168.29 (C-1); FAB MS *m/z*: 273 (M^++1) (*m* -NBA as matrix).

Methyl (2*S*) 4,5,7,8,9-Penta-*O*-acetyl-2,6-anhydro-2,3-dideoxy-D-*glycero*-D-*galacto*-nonulosonate (8).

Procedure A. A solution of **5** (200 mg, 0.4 mmol) in methanol (20 mL) was hydrogenated with 10% Pd-C (200 mg) at room temperature. After 12 h the reaction mixture was filtered to remove Pd-C, and the filtrate was concentrated to dryness under reduced pressure, the residue was purified by silica gel chromatography (*n*-hexane-EtOAc 4:1) to yield **8** (150 mg, 75%) and methyl (2*S*) 5,7,8,9-tetra-*O*-acetyl-2,6-anhydro-2,3,4-trideoxy-D-*manno*-nonulosonate (**9**) (13 mg, 4%).

8: colorless syrup; $[\alpha]_D$ +11° (*c* 0.56, MeOH); ^1H NMR (300 MHz, $CDCl_3$) δ 4.04 (dd, 1H, $J_{2,3ax}$ = 12.0 Hz, $J_{2,3eq}$ = 2.4 Hz, H-2), 1.83 (ddd, 1H, $J_{3ax,3eq}$ = 12.9 Hz, $J_{3ax,4}$ = 11.7 Hz, H-3_{ax}), 2.47 (ddd, 1H, $J_{3eq,4}$ = 5.1 Hz, H-3_{eq}), 5.01 (ddd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 4.90 (t, 1H, $J_{5,6}$ = 9.6 Hz, H-5), 3.69 (dd, 1H, $J_{6,7}$ = 2.1 Hz, H-6), 5.35 (dd, 1H, $J_{7,8}$ = 6.0 Hz, H-7), 5.30 (ddd, 1H, $J_{8,9}$ = 2.3 Hz, $J_{8,9'}$ = 6.3 Hz, H-8), 4.55 (dd, 1H, $J_{9,9'}$ = 12.6 Hz, H-9), 4.14 (dd, 1H, 9'-H), 3.76 (s, 3H, $COOCH_3$), 1.99, 2.01, 2.03, 2.06, 2.09 (each s, 3H, OAc × 5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.59 (C-1), 74.42 (C-2), 33.05 (C-3), 71.73 (C-4), 67.52 (C-5), 76.50 (C-6), 67.26 (C-7), 70.50 (C-8), 62.20 (C-9), 52.43 ($COO\underline{C}H_3$), 170.46, 170.16, 169.93, 169.80, 169.68 ($\underline{C}OCH_3$ × 5), 20.79, 20.73, 20.67, 20.60, 20.55 ($CO\underline{C}H_3$ × 5); FAB MS *m/z*: 477 (M^++1) (*m*-NBA as matrix).

Anal. Calcd for $C_{20}H_{28}O_{13}$: C, 50.04; H, 5.88. Found: C, 50.14; H, 5.92.

9: colorless syrup; $[\alpha]_D$ -1° (*c* 0.40, MeOH); ^1H NMR (300 MHz, $CDCl_3$) δ 3.96 (dd, 1H, $J_{2,3ax}$ = 12.0 Hz, $J_{2,3eq}$ = 2.3 Hz, H-2), 1.77 (m, 1H, H-3_{ax}), 1.99 (m, 1H, H-3_{eq}), 1.54 (m, 1H, H-4_{ax}), 2.27 (m, 1H, H-4_{eq}), 4.60 (ddd, 1H, $J_{5,6}$ = 10.5 Hz, $J_{4ax,5}$ =

10.2 Hz, $J_{4eq,5,9}$ = 5.4 Hz, H-5), 3.94 (dd, 1H, $J_{6,7}$ = 2.4 Hz, H-6), 5.42 (dd, 1H, $J_{7,8}$ = 5.7 Hz, H-7), 5.34 (ddd, 1H, $J_{8,9}$ = 2.7 Hz, $J_{8,9'}$ = 6.9 Hz, H-8), 4.62 (dd, 1H, $J_{9,9'}$ = 12.6 Hz, H-9), 4.38 (dd, 1H, H-9'), 3.75 (s, 3H, $COOCH_3$), 2.02, 2.04, 2.07, 2.09 (each s, 3H, OAc×4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.96 (C-1), 76.63 (C-2), 27.33 (C-3), 28.90 (C-4), 68.82 (C-5), 78.08 (C-6), 68.04 (C-7), 70.81 (C-8), 62.47 (C-9), 52.23 ($COO\underline{C}H_3$), 170.14, 170.13, 169.92, 169.74 ($\underline{C}OCH_3$×4), 20.90, 20.77, 20.54 ($CO\underline{C}H_3$ ×4); FAB MS *m/z*: 441 (M^++Na) (*m*-NBA as matrix).

Anal. Calcd for $C_{18}H_{26}O_{11}$: C, 51.67; H, 6.22. Found: C, 51.60; H, 6.34.

Procedure B. A solution of **5** (100 mg, 0.2 mmol) in methanol and acetic acid (3:1, 20 mL) was hydrogenated with 10% Pd-C (200 mg) at room temperature. After 12 h the mixture was processed as described for **8** to yield **9** (83 mg, 87%).

Procedure C. A solution of **5** (50 mg, 0.1 mmol) in methanol (20 mL) was hydrogenated with PtO_2 (50 mg) at room temperature. After 2 h the mixture was processed as described for **8** to yield **9** (26 mg, 51%) and methyl 5,7,8,9-tetra-*O*-acetyl-2,6-anhydro-3,4-dideoxy-D-*manno*-non-2-enonate (**10**) (20 mg, 46%).

10: colorless syrup; $[\alpha]_D$ -23° (*c* 0.41, MeOH); ^1H NMR (300 MHz, $CDCl_3$) δ 6.04 (dd, 1H, $J_{3,4eq}$ = 4.8 Hz, $J_{3,4ax}$ = 3.3 Hz, H-3), 2.20 (ddd, 1H, $J_{4eq,4ax}$ = 18.6 Hz, $J_{4ax,5}$ = 7.8 Hz, H-4_{ax}), 2.67 (ddd, 1H, $J_{4eq,5}$ = 6.3 Hz, H-4_{eq}), 4.93 (ddd, 1H, $J_{5,6}$ = 8.4 Hz, H-5), 4.09 (dd, 1H, $J_{6,7}$ = 3.0 Hz, H-6), 5.50 (dd, 1H, $J_{7,8}$ = 5.7 Hz, H-7), 5.33 (ddd, 1H, $J_{8,9}$ = 3.0 Hz, $J_{8,9'}$ = 6.6 Hz, H-8), 4.61 (dd, 1H, $J_{9,9'}$ = 12.6 Hz, H-9), 4.21 (dd, 1H, H-9'), 3.76 (s, 3H, $COOCH_3$), 2.04, 2.05, 2.06, 2.07 (each s, 3H, OAc×4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.04 (C-1), 143.29 (C-2), 108.68 (C-3), 27.16 (C-4), 63.62 (C-5), 75.11 (C-6), 67.51 (C-7), 70.38 (C-8), 61.94 (C-9), 52.17 ($COO\underline{C}H_3$), 170.54, 169.92, 169.88, 169.82 ($\underline{C}OCH_3$×4), 20.83, 20.83, 20.70, 20.48 ($CO\underline{C}H_3$×4); FAB MS *m/z*: 417 (M^++1) (*m*-NBA as matrix).

Anal. Calcd for $C_{18}H_{24}O_{11}$: C, 51.92; H, 5.77. Found: C, 51.75; H, 6.02.

Methyl (2R) 4,5,7,8,9-Penta-*O*-acetyl-2,6-anhydro-2,3-dideoxy-D-*glycero*-D-*galacto*-nonulosonate (11). A solution of **4** (300 mg, 0.6 mmol) in toluene-pyridine (1:1, 10 mL) was hydrogenated with 10% Pd-C (300 mg) at room temperature. After 12 h the reaction mixture was processed as described for **8** to yield **11** (60 mg, 71%).

11: colorless prism; mp 125-127 °C; $[\alpha]_D$ -45° (*c* 0.66, MeOH); ^1H NMR (300 MHz, $CDCl_3$) δ 4.56 (dd, 1H, $J_{2,3ax}$ = 6.9 Hz, $J_{2,3eq}$ = 1.2 Hz, H-2), 2.07 (ddd, 1H, $J_{3ax,3eq}$ = 13.5 Hz, $J_{3ax,4}$ = 12.0 Hz, H-3_{ax}), 2.50 (ddd, 1H, $J_{3eq,4}$ = 5.1 Hz, H-3_{eq}), 4.94 (ddd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 4.81 (t, 1H, $J_{5,6}$ = 9.6 Hz, 5-H), 4.29 (dd, 1H, $J_{6,7}$ = 1.7 Hz, H-6), 5.36 (dd, 1H, $J_{7,8}$ = 3.3 Hz, H-7), 5.37 (ddd, 1H, $J_{8,9}$ = 1.8 Hz, $J_{8,9'}$ = 4.2 Hz, H-8), 4.30 (dd, 1H, $J_{9,9'}$ = 12.6 Hz, H-9), 4.15 (dd, 1H, H-9'), 3.75 (s, 3H, $COOCH_3$), 2.00, 2.01,

2.03, 2.09, 2.15 (each s, 3H, OAc × 5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.67 (C-1), 71.37 (C-2), 31.58 (C-3), 69.87 (C-4), 68.21 (C-5), 71.755 (C-6), 66.80 (C-7), 68.40 (C-8), 62.05 (C-9), 52.35 ($COO\underline{C}H_3$), 170.32, 170.16, 170.03, 169.87, 169.75 ($\underline{C}OCH_3$ ×5), 21.06, 20.89, 20.74, 20.69, 20.59 ($CO\underline{C}H_3$ ×5); FAB MS *m/z*: 477 (M^++1) (*m*-NBA as matrix).

Anal. Calcd for $C_{20}H_{28}O_{13}$: C, 50.04; H, 5.88. Found: C, 50.24; H, 5.72.

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