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PREPARATION AND STRUCTURAL DETERMINATION OF METHYL 4,6-*O*-BENZYLIDENE-2,3-DIDEOXY-β-D-*erythro*-HEXOPYRANOSID[2,3-*d*]TRIAZOLE AND OF ITS ADDUCTS WITH 3-NITROHEX-2-ENOPYRANOSIDES

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ABSTRACT

A 3-nitrohex-2-enopyranoside whose C-1 atom was mostly deuterated was prepared from (1*S*)-1,5-anhydro-D-(1-^{2}H)glucitol and subjected to an addition reaction with methyl 4,6-*O*-benzylidene-2,3-dideoxy-β-D-*erythro*-hexopyranosid-[2,3-*d*]triazole, derived from the nitro alkene with lithium azide. The structure of the adducts was, by ^{1}H-n.m.r. spectroscopy, assigned the D-*gluco* configuration for the nitro sugar moiety.

INTRODUCTION

In our studies on nucleophilic addition reactions to nitro sugars, we reported the reaction of nitro acetate **1** or nitro alkene **8** with sodium azide to give phenyl 4,6-*O*-benzylidene-2,3-dideoxy-β-D-*erythro*-hexopyranosid[2,3-*d*]triazole (**13**) and phenyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-2-(phenyl 4,6-*O*-benzylidene-2,3-dideoxy-β-D-*erythro*-hexopyranosid[2,3-*d*]triazolyl)-β-D-glucopyranoside (**15**), besides the expected azide[1] **2**. The triazolyl derivative **15** was also prepared by treatment of triazole **13** with nitro alkene **8**. The formation of **15** is not likely to involve the 1,3-cycloaddition of azido derivative **2** to nitro alkene **8**, because the reaction of methyl 3-nitrohex-2-enopyranoside **9** with sodium azide in the presence of phenyl 2-azido derivative **2** afforded a similar triazolyl derivative (**16**) and unchanged azide **2** in 62 and 70% yield, respectively[1]. The configuration of C-2 of the nitro sugar moiety of **16** could not, however, be determined at that time. We now report the structural determination of **16**, which was accomplished by preparation of its 1-deuterio derivative **17**.

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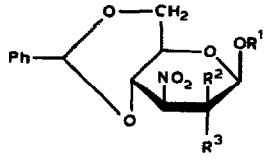
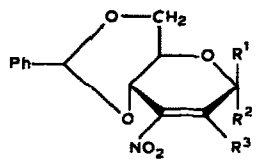
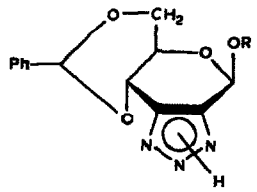


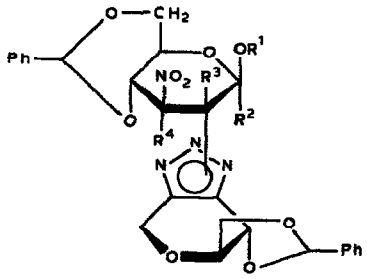
1 R^1 = Ph, R^2 = H, R^3 = OAc
2 R^1 = Ph, R^2 = H, R^3 = N_3
3 R^1 = Me, R^2 = H, R^3 = OAc
4 R^1 = Me, R^2 = H, R^3 = N_3
5 R^1 = Me, R^2 = D; R^3 = H
6 R^1 = Me, R^2 = H, R^3 = Cl
7 R^1 = Me, R^2 = H, R^3 = SePh



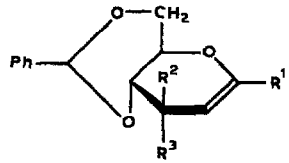
8 R^1 = OPh, R^2 = R^3 = H
9 R^1 = OMe, R^2 = R^3 = H
10 R^1 = OMe, R^2 = H, R^3 = D
11 R^1 = R^2 = R^3 = H
12 R^1 = OMe, R^2 = D, R^3 = H



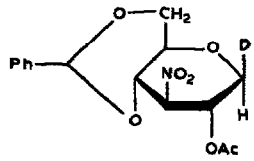
13 R = Ph
14 R = Me



15 R^1 = R^5 = Ph, R^2 = R^3 = R^4 = H
16 R^1 = R^5 = Me, R^2 = R^3 = R^4 = H
17 R^1 = R^5 = Me, R^2 = D, R^3 = R^4 = H
18 R^1 = R^5 = Me, R^2 = R^3 = H, R^4 = D
19 R^1 = R^5 = Me, R^2 = R^4 = H, R^3 = D
20 R^1 = Me, R^2 = R^3 = R^4 = H, R^5 = Ph



21 R^1 = R^3 = H, R^4 = NO_2
22 R^1 = D, R^2 = NO_2, R^3 = H
23 R^1 = D, R^2 = H, R^3 = NO_2



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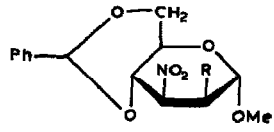

25 R = SePh

RESULTS AND DISCUSSION

Treatment of methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside (**3**) with an equimolar amount of sodium azide in 8:1 (v/v) acetonitrile–water afforded the nitro azide **4** in 91% yield. On the other hand, when this reaction was performed in *N,N*-dimethylformamide (DMF), triazolyl derivative **16** was obtained in 85% yield. The reaction of nitro alkene **9** with lithium azide in distilled DMF afforded the triazole **14** in 12% yield, together with nitro

azide **4** (10%) and triazolyl derivative **16** (56%). The *gluco* structure for nitro azide **4** was deduced from the coupling constants: $J_{1,2}$ 7.5 and $J_{2,3} = J_{3,4} = 10$ Hz. The i.r. spectrum of triazole **14** showed no absorption bands corresponding to nitro and azide groups. The elemental analysis agreed with the formula $C_{14}H_{15}N_3O_4$, which was confirmed by the appearance of a molecular-ion peak at *m/z* 289.1011. The triazole structure was also supported by the ^{1}H-n.m.r. spectrum; the sugar moiety contains only five protons. The i.r. and ^{1}H-n.m.r. spectra of **14** were very similar to those of phenyl analog[1] **13**. In the 400-MHz, ^{1}H-n.m.r. spectrum of **16**, all protons were assigned by a decoupling technique, but the configuration of C-2 could not be determined, because the H-3 signal unexpectedly appeared as a septet. To elucidate the possibility that such complexity occurs by long-range coupling between H-1 and H-3, we prepared the 2-deuterio triazolyl derivative **19** from triazole **14** and 2-deuterio-nitro alkene **10**; the latter compound was synthesized by (phenylselenenyl)ation of methyl (2*S*)-(2-^{2}H)-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*arabino*-hexopyranoside[2] (**5**), followed by oxidative elimination of the seleno group[3,4]. The H-3 signal appears as a doublet ($J_{3,4}$ 9.7 Hz) in the case of **19**, indicating that virtual coupling[5] makes the H-3 signal of **16** complicated. Although the triazolyl derivative **18**, partially deuterated at C-3, was obtained by the use of deuterium oxide instead of water in the preparation of **16**, complete deuteration failed.

Therefore, the 1-deuterio triazolyl derivative **17** was necessary for determination of the configuration of C-2. Incidentally, we found that the double bond of 1,5-anhydro-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-D-*erythro*-hex-2-enitol (**11**) readily migrates, to give the 1,5-anhydro-1-enitol derivative[6] **21**. Assuming that the axial anomeric proton is more acidic than the equatorial one (due to stereoelectronic control[7]), we synthesized (1*S*)-(1-^{2}H)-2-*O*-acetyl-1,5-anhydro-4,6-*O*-benzylidene-3-deoxy-3-nitro-D-glucitol (**24**) from (1*S*)-(1-^{2}H)-1,5-anhydro-D-glucitol[8]. Treatment of **24** with triethylamine gave the 1-enitol derivatives having the *arabino* (**22**) and *ribo* configuration (**23**) in 64 and 20% yield, respectively, in which most of the deuterium atoms were retained. Then, the conversion of **22** into methyl (1-^{2}H)-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside (**12**) was investigated. Chlorination of the undeuterated model compound **21** in methanol gave a mixture from which methyl 2-chloro-2-deoxy-β-D-glucopyranoside (**6**) crystallized in 40% yield. More-satisfactory results were obtained by (phenylselenenyl)ation of **21** in methanol, to afford methyl 2-deoxy-2-(phenylselenenyl)-β-D-glucopyranoside (**7**) and -α-D-mannopyranoside (**25**) in 50 and 26% yield, respectively. Oxidative elimination of the phenylseleno group from the 1-deuterio derivative of **7** afforded, almost quantitatively, the nitro alkene **12** possessing the deuterio atom on C-1. The addition reaction of **12** with triazole **14** gave the triazolyl derivative **17**, the ^{1}H-n.m.r. spectrum of which showed H-2 and H-3 signals that, respectively, appeared as a doublet and a double doublet ($J_{2,3}$ 10.5 and $J_{3,4}$ 9.7 Hz), revealing that the nitro sugar moiety of **17** has the β-D-*gluco* configuration.

Similar treatment of triazole **13** with methyl 3-nitrohex-2-enopyranoside **9** gave adduct **20**, having the β-D-*gluco* configuration.

Fragmentation in the e.i. mass spectra of triazole **14** and triazolyl derivative **16** was significantly different from that[1] of the corresponding phenyl analogs **13** and **15**, respectively. Comparison of the mass spectra of these compounds, as well as of the partially 3-*C*-deuterated derivative of **16**, revealed the following bias: (*1*) although the mass spectra of **13** and **15** showed strong peaks arising from $M^+ - C_6H_5O^\cdot$ and subsequent fragmentation[1], the corresponding peaks of methyl derivatives **14** and **16** were weak, (*2*) the mass spectrum of triazole derivative **14** was complicated, but the strong peaks at *m/z* 149.0632 and 140.0490 are attributed to the simultaneous cleavage of the pyranose and benzylidene rings[9]. Corresponding strong peaks were observed at *m/z* 149 and 433 for **16**, but they were weak at *m/z* 149 and 202 for **13**, and *m/z* 149 and 557 for **15**.

EXPERIMENTAL

General methods. — All melting points are uncorrected. Optical rotations were determined with a Carl Zeiss photoelectric polarimeter. I.r. spectra were recorded for potassium bromide pellets. Solutions were evaporated under diminished pressure. Column chromatography was conducted on silica gel (Wakogel C-300). ^{1}H-N.m.r. spectra were recorded at 100 MHz with a JEOL spectrometer (JNM-4H-100), with tetramethylsilane as the internal standard, unless otherwise stated.

Methyl 4,6-O-benzylidene-2,3-dideoxy-2-(methyl 4,6-O-benzylidene-2,3-dideoxy-β-D-erythro-hexopyranosid[2,3-d]triazolyl)-3-nitro-β-D-glucopyranoside (**16**). — (*a*) *From the nitroacetate* **3**. A mixture of **3** (ref. 10; 708 mg, 2 mmol), sodium azide (143 mg, 2.2 mmol), DMF (12 mL), and water (1.5 mL) was stirred for 7 h at room temperature. A precipitate generated on addition of water (100 mL) was filtered off and recrystallized from acetonitrile, to give 495 mg (85%) of **16**. Its i.r. and ^{1}H-n.m.r. spectra were identical with those of an authentic sample[1] of **16**: ^{1}H-n.m.r. (400 MHz): δ 5.15 (q, 2 H, *J* 2.0 and 4.8 Hz, H-1,2), 5.39 (hept, 1 H, $J_{3,4}$ 9.7 Hz, H-3), 4.30 (t, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 3.74 (sex, 1 H, $J_{5,6a}$ 10.2, $J_{5,6e}$ 4.4 Hz, H-5), 3.91 (t, 1 H, $J_{6a,6e}$ 10.4 Hz, H-6*a*), 4.46 (q, 1 H, H-6*e*), 5.90 (s, 1 H, H-1′), 4.94 (d, 1 H, $J_{4',5'}$ 8.6 Hz, H-4′), 3.86 (sex, 1 H, $J_{5',6'a}$ 10.4, $J_{5',6'e}$ 4.4 Hz, H-5′), 4.05 (t, 1 H, $J_{6'a,6'e}$ 10.4 Hz, H-6′*a*), 4.45 (q, 1 H, H-6′*e*), 3.60 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), 5.58 (s, 1 H, PhCH), and 5.77 (s, 1 H, PhCH).

Similar treatment, except using deuterium oxide instead of water, gave the partially deuterated derivative (at C-3) of **16**.

(*b*) *From the nitro azide* **4**. The triazole **16** was prepared from **4** in 72% yield under the conditions just described.

(*c*) *From the triazole* **14** *and nitro alkene* **9**. Compound **14** (9.6 mg) and **9** (ref. 10; 9.8 mg) were dissolved in dimethyl sulfoxide-d_6 (0.2 mL) in a n.m.r. sample tube, and the reaction was monitored by n.m.r. spectroscopy. After 1 h, most of the starting materials had disappeared, and compound **16** was formed. After 12 h, the mixture was poured into water (10 mL), and the precipitate was filtered off, and dried (17.3 mg, 89%). It was pure **16**, as judged from its ^{1}H-n.m.r. spectrum.

Similar treatment of 2-deuterio nitro alkene **10** (14.7 mg), prepared from[2] **5** according to a procedure in the literature[3,4], and of 1-deuterio nitro alkene **12** (14.7 mg), described later in this section, with triazole **14** (14.5 mg) in dimethyl sulfoxide-d_6 gave the triazolyl derivatives **19** and **17**, respectively, in 90% yields.

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-β-*D*-*erythro*-hexopyranosid[2,3-d]triazole* (**14**). — To a solution of the nitro alkene **9** (ref. 10; 440 mg, 1.5 mmol) in distilled DMF (7 mL) was added lithium azide (73 mg, 1.5 mmol). The mixture was stirred for 10 h at room temperature, poured into water (80 mL), and extracted with chloroform. The extracts were washed with water and evaporated, to give a residue, to which addition of water caused a precipitate. After filtration, the precipitate was chromatographed with benzene as the eluant. The first fraction was the nitro azide **4** (10%), the second was the triazolyl derivative **16** (56%), and the third was the triazole derivative **14** (20%), which was recrystallized from ethanol to give 52 mg (12%) of **14**, m.p. 182–183°, $[\alpha]_D^{20}$ −102° (*c* 1, chloroform); ^{1}H-n.m.r.: δ 5.89 (s, 1 H, H-1 or PhCH), 4.91 (d, 1 H, $J_{4,5}$ 8.1 Hz, H-4), 3.77 (sex, 1 H, $J_{5,6a}$ 10, $J_{5,6e}$ 3.8 Hz, H-5), 4.01 (t, 1 H, $J_{6a,6e}$ 10 Hz, H-6*a*), 4.38 (q, 1 H, H-6*e*), 3.56 (s, 3 H, OMe), and 5.73 (s, 1 H, PhCH or H-1).

Anal. Calc. for $C_{14}H_{15}N_3O_4$: C, 58.12; H, 5.23; N, 14.53. Found: C, 58.22; H, 5.28; N, 14.86.

*Methyl 2-azido-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-*D*-glucopyranoside* (**4**). — To a solution of acetate **3** (ref. 10; 708 mg, 2 mmol) in acetonitrile (24 mL) and water (3 mL) was added sodium azide (143 mg, 2.2 mmol). The mixture was stirred for 7 h at room temperature and then evaporated. The residue was washed with water, and crystallized from ethanol, to give 614 mg (91.3%) of **4**; m.p. 159.5–160.5°, $[\alpha]_D^{20}$ −95.0° (*c* 1, chloroform); ν_{max} 2190 (N_3) and 1560 cm^{-1} (NO_2); ^{1}H-n.m.r.: δ 4.40 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.97 (q, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.52 (t, 1 H, $J_{3,4}$ 10 Hz, H-3), 4.07 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 3.45 (sex, 1 H, $J_{5,6a}$ 10, $J_{5,6e}$ 4.9 Hz, H-5), 3.82 (t, 1 H, $J_{6a,6e}$ 10 Hz, H-6*a*), 4.38 (q, 1 H, H-6*e*), 3.61 (s, 3 H, OMe), and 5.50 (s, 1 H, PhCH).

Anal. Calc. for $C_{14}H_{16}N_4O_6$: C, 50.00; H, 4.80; N, 16.66. Found: C, 49.81; H, 4.89; N, 16.40.

*(1-^{2}H)-1,5-Anhydro-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-*D*-arabino-* (**22**) *and* -D-ribo-*hex-1-enitol* (**23**). — To a solution of 1-deuterio acetate **24** (162 mg, 0.5 mmol), prepared from (1*S*)-(1-^{2}H)-1,5-anhydro-D-glucitol (264 mg, 1.6 mmol) according to the literature[6], in dichloromethane (5 mL) was added triethylamine (278 mg, 2.5 mmol), and the mixture was stirred for 70 min. After addition of chloroform, the mixture was successively washed with dilute hydrochloric acid and water, dried, and evaporated. The residue was chromatographed with 1:1 (v/v) carbon tetrachloride–benzene as the eluant, to give, successively, 99 mg (76%) of *arabino* isomer **22** and 29 mg (22%) of *ribo* isomer **23**, identical with respective authentic samples[4] by m.p. and i.r. spectrum. Their ^{1}H-n.m.r. spectra showed (integration) that the signals due to H-1 at δ 6.48 and 6.71, respectively, are about one fourth of those of the benzylidene methine proton.

Methyl 4,6-O-benzylidene-2-chloro-2,3-dideoxy-3-nitro-β-D-glucopyranoside (**6**). — To a solution of **21** (refs. 6 and 11; 132 mg, 0.5 mmol) in methanol (3 mL) in the presence of lithium carbonate (600 mg) was added carbon tetrachloride containing an excess of chlorine. After being stirred for 3 h, the mixture was evaporated to a residue, the ^{1}H-n.m.r. spectrum of which showed the presence of at least three compounds. Attempts at separation by column chromatography failed, presumably due to generation of hydrogen chloride during chromatographic separation. Crystallization from isopropyl alcohol gave 66 mg (40%) of **6**; m.p. 172–173°, $[\alpha]_D^{20}$ −43° (*c* 0.5, tetrahydrofuran); ν_{max} 1560 cm^{-1} (NO_2); ^{1}H-n.m.r.: δ 4.47 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.19 (q, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 4.81 (t, 1 H, $J_{3,4}$ 9.7 Hz, H-3), 4.07 (t, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 3.53 (sex, 1 H, $J_{5,6a}$ 9.7, $J_{5,6e}$ 4.9 Hz, H-5), 3.81 (t, 1 H, $J_{6a,6e}$ 9.7 Hz, H-6*a*), 4.39 (q, 1 H, H-6*e*), 3.58 (s, 3 H, OMe), and 5.50 (s, 1 H, PhCH).

Anal. Calc. for $C_{14}H_{16}ClNO_6$: C, 51.00; H, 4.89; N, 4.25. Found: C, 51.13; H, 4.78; N, 4.44.

Methyl 4,6-O-benzylidene-2,3-dideoxy-3-nitro-2-(phenylselenenyl)-β-D-gluco- (**7**) *and -α-D-mannopyranoside* (**25**). — Addition of phenylselenenyl chloride (200 mg, 1 mmol) to a stirred methanolic solution (5 mL) of **21** (Refs. 6 and 11; 263 mg, 1 mmol) immediately afforded crystalline material, which was filtered off after 8 min, to give 193 mg of **7**. The filtrate was evaporated, the residue partitioned between dichloromethane and water, and the organic layer washed with water, dried, and evaporated. The syrupy residue was chromatographed, with benzene as the eluant, to give successively 117 mg (20%) of *α-D-manno* **25** and 32 mg (total 50%) of *β-D-gluco* isomer **7**. Both products were recrystallized from ethanol.

Compound **7** had m.p. 174–175°, $[\alpha]_D^{20}$ +47.1° (*c* 0.5, dichloromethane); ν_{max} 1550 cm^{-1} (NO_2); ^{1}H-n.m.r.: δ 4.29 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 3.44 (q, 1 H, $J_{2,3}$ 12.1 Hz, H-2), 4.68 (t, 1 H, $J_{3,4}$ 9.8 Hz, H-3), 4.08 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 3.31 (sex, 1 H, $J_{5,6a}$ 10.2, $J_{5,6a}$ 4.9 Hz, H-5), 3.78 (t, 1 H, $J_{6a,6e}$ 10.2 Hz, H-6*a*), 4.31 (q, 1 H, H-6*e*), 3.56 (s, 3 H, OMe), and 5.49 (s, 1 H, PhCH).

Anal. Calc. for $C_{20}H_{21}NO_6Se$: C, 53.34; H, 4.70; N, 3.11. Found: C, 53.32; H, 4.67; N, 3.45.

Compound **25** had m.p. 126–127°, $[\alpha]_D^{20}$ +34.2° (*c* 0.1, acetone); ν_{max} 1553 cm^{-1} (NO_2); ^{1}H-n.m.r.: δ 5.14 (d, 1 H, $J_{1,2}$ 0.7 Hz, H-1), 3.85 (q, 1 H, $J_{2,3}$ 4.5 Hz, H-2), 5.15 (t, 1 H, $J_{3,4}$ 10.5 Hz, H-3), 4.4–3.7 (m, 4 H, H-4,5,6*a*,6*e*), 3.37 (s, 3 H, OMe), and 5.69 (s, 1 H, PhCH).

Anal. Calc. for $C_{20}H_{21}NO_6Se$: C, 53.34; H, 4.70; N, 3.11. Found: C, 53.60; H, 4.75; N, 2.96.

*Methyl (1-^{2}H)-4,6-O-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro-*hex-2-eno-pyranoside* (**12**). — To the 1-deuterio derivative of **7** (30 mg, 6 μmol), prepared from **22**, was added 35% aqueous hydrogen peroxide (0.2 mL) in tetrahydrofuran (4 mL), and the mixture was stirred for 2 h. After addition of water, the organic solvent was evaporated. The precipitate generated was filtered off, and chromatographed, with benzene as the eluant, to give 18 mg (92%) of **12**.

*Methyl 4,6-O-benzylidene-2,3-dideoxy-3-nitro-2-(phenyl 4,6-O-benzylidene-2,3-dideoxy-β-*D-erythro-*hexopyranosido*[2,3-d]*triazolyl)-β-*D-*glucopyranoside* (**20**). A solution of the nitro alkene **9** (ref. 10; 147 mg, 0.5 mmol) and triazole[1] **13** (175 mg, 0.5 mmol) in acetonitrile (12 mL) was stirred for 8 h at room temperature, and then the mixture was evaporated to afford a solid residue. Its ^{1}H-n.m.r. spectrum showed that it was almost pure **20**. Recrystallization from ethanol–acetone gave 290 mg (90%) of **20**; m.p. 275–276°, $[\alpha]_D^{20}$ −57.7° (*c* 0.1, dimethyl sulfoxide); ν_{max} 1570 cm^{-1} (NO_2): ^{1}H-n.m.r. (dimethyl sulfoxide-d_6): δ 5.32 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 5.11 (q, 1 H, $J_{2,3}$ 10 Hz, H-2), 5.71 (t, 1 H, $J_{3,4}$ 10 Hz, H-3), 6.88 (s, 1 H, H-1′), 5.14 (d, 1 H, $J_{4',5'}$ 8.6 Hz), 4.5–3.4 (m, 7 H, H-4,5,6*a*,6*e*,5′,6′*a*,6′*e*), 3.35 (s, 3H, OMe), 5.75 (s, 1 H, PhCH), and 5.93 (s, 1 H, PhCH).

Anal. Calc. for $C_{33}H_{32}N_4O_{10}$: C, 61.48; H, 5.00; N, 8.69. Found: C, 61.77; H, 4.97; N, 8.75.

ACKNOWLEDGMENT

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