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AN EASY AND EFFICIENT PREPARATION OF ARYL α-*O*-Δ^2-GLYCOSIDES

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ABSTRACT. Ferrier reaction between acetylglycals and *p*-NO_2, *m*-NO_2 and *p*-*t*-butylphenol after recrystallization gave aryl *O*-Δ^2-glycosides as the pure α anomers. Deacetylation of these compounds and benzylation of the crude diol led to the corresponding aryl α-*O*-Δ^2-4,6-di-*O*-benzyl-glycosides in large amounts.

Stereoselective synthesis of *C*-glycosides has attracted considerable attention during the last few years in connection with their importance in the synthesis of biologically active natural compounds. [1] The high degree of stereochemical control generally accompanying transition metal mediated transformations, and particularly palladium complexes, [2] has prompted several groups to employ such methodology

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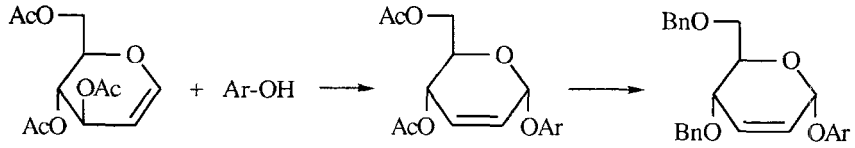
for *C*-glycosidation. [3] We have shown that the palladium(0) catalyzed alkylation of 2,3-unsaturated phenyl glycopyranosides occurred stereospecifically with retention of configuration at the anomeric center. [4] However this methodology required pure α or β aryl *O*-Δ^2-glycosides in order to control the stereoselectivity at the anomeric center, and the major drawback of our methodology was the very difficult obtaining of pure α or β anomers. We describe here an easy preparation of pure α-*O*-aryl glycosides of 2,3-unsaturated glycals in multigrams quantities.

Our approach involved a Ferrier rearrangement [5] of 3,4,6-tri-*O*-acetyl-D-glucal with phenol bearing bulky substituents such as *m*-NO_2, *p*-NO_2 and *p*-*t*-butyl, expecting that recrystallization of the crude mixture would give only a single anomer. Effectively the Ferrier rearrangement at reflux of toluene using *m*-*nitrophenol*, *p*-*nitrophenol* or *p*-*t*-*butylphenol* gave a mixture of aryl *O*-Δ^2-glycosides where the α anomer was generally predominant (Table 1). The assignment of the anomeric configuration was made on the crude mixture according to the γ-effect rule as shown previously. [6] After removal of the excess of phenol, a single recrystallization of the crude product gave the desired pure aryl α-*O*-Δ^2-glycoside **2** in quite good yields.



1 **2** **3**

a Ar = *m*-NO_2-C_6H_4 ; **b** Ar = *p*-NO_2-C_6H_4 ; **c** Ar = *p*-*t*-Bu-C_6H_4

Scheme 1

Table 1. Synthesis of α-*O*-aryl-2-hexenopyranosides **2**

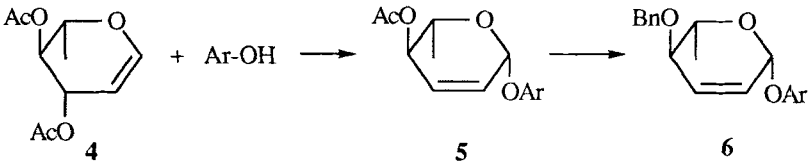
Phenol	ratio 2α/2β [a]	Yield 2α % [b]
m-NO_2-C_6H_4	80/20	31
p-NO_2-C_6H_4	70/30	40
p-*t*-Bu-C_6H_4	50/50	49

[a] Determined from NMR spectra of the crude mixture. [b] After recrystallization.

The palladium catalyzed alkylation required benzyl protecting groups at the 4- and 6-position of the unsaturated carbohydrate. The next step was the deacetylation of the pure aryl α-*O*-Δ^2-glycoside **2** and the benzylation of the crude diol. Deacetylation of nitroaryl α-*O*-Δ^2-glycosides **2a** and **2b** using the usual conditions (catalytic amount of CH_3ONa in CH_3OH) gave the desired diol contaminated however with by-products arising from the cleavage of the anomeric bond. On the other hand compound **2c** gave the expected product in a pure form. Benzylation of the crude diols using benzyl chloride in the presence of an aqueous sodium hydroxyde solution and tetrabutylammonium bromide in toluene at 60 °C for 5 hours gave the unsaturated aryl α-*O*-Δ^2-4,6-di-*O*-benzyl glycosides **3** in quite good yields.

This methodology was applied to 3,4-di-*O*-acetyl-6-deoxy-L-glucal **4** and *p*-*t*-butyl phenol giving the aryl *O*-Δ^2-glycoside **5** as a mixture α/β = 80/20, the pure α anomer being obtained after recrystallization in 56% yield (Scheme 2); this α anomer was easily transformed into the unsaturated dibenzylated compound **6** in 50% chemical yield using the previously described methodology.

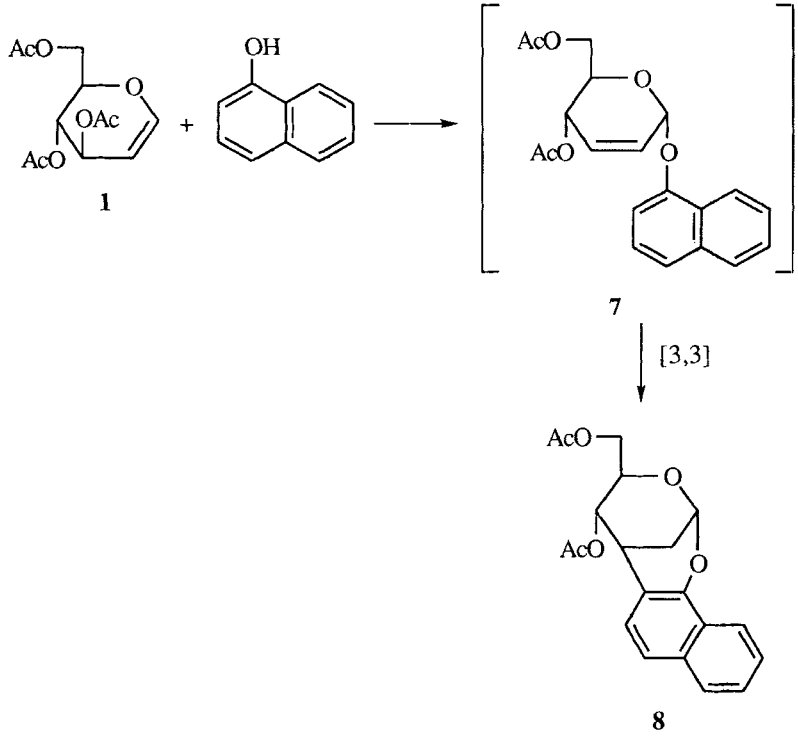
Starting from 3,4,6-tri-*O*-acetyl-D-glucal **1** and using α-naphthol as the phenol, the only observed product was the bicyclic compound **8** (Scheme 3).



4 5 6

Ar = *p*-*t*-Bu-C_6H_4

Scheme 2



1 7 8

Scheme 3

The formation of this compound could be explained by a [3,3] rearrangement of the product of *O*-arylation **7** under the reaction conditions of the Ferrier transformation.

In conclusion pure aryl α-Δ^2-4,6-di-*O*-benzyl-glycosides could be obtained in large amounts using the Ferrier reaction, followed by deacetylation and benzylation. The application of these compounds to the synthesis of natural products is now in progress in our laboratory.

EXPERIMENTAL

Melting points are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Proton and carbon NMR spectra were recorded on a Brucker AC 200 or AM 300 spectrometer with $CDCl_3$ as solvent and Me_4Si as internal standard. Thin-layer chromatography was performed on precoated silica gel plates (Merck F 254) and silica gel 60 GF 254 (230-400 mesh Merck) was used for preparative chromatography.

General procedure for the synthesis of compounds ***2*** *and* ***5***. 3,4,6-Tri-*O*-acetyl-D-glucal (**1**) (10.0 g, 36.8 mmol) or 3,4-di-*O*-acetyl-6-deoxy-L-glucal (**4**) (5.0 g, 23.3 mmol) and the corresponding phenol (110.4 mmol or 63.3 mmol in the case of compounds **1** or **4** respectively) were heated in boiling chlorobenzene (150 mL) for 15 h. The solvent and the excess phenol were removed under vacuum. After addition of CH_2Cl_2 (100 mL), the residual phenol was extracted with saturated sodium bicarbonate aqueous solution (3 x 20 mL), and the organic layer was then dried. Removal of the solvent and recrystallization in ethanol afforded the pure α anomer (31 to 56 % yield).

General procedure for the synthesis of compounds 3 and 6. A solution of glycoside **2** or **5** (65 mmol) in methanol (80 mL) was added to a solution of sodium methylate formed *in situ* from metallic sodium (catalytic amount) in methanol (20 mL), and then was stirred at 25 °C for 24 h. After evaporation of the solvent under vacuum, the crude diol was dissolved in toluene (50 mL) in the presence of 50 % aqueous sodium hydoxyde (78 mL) and *t*-butylammonium bromide (13 mmol, 4.19 g). The mixture was stirred for 15 min at 60 °C, and benzyl chloride (143 mmol, 18.1 g) in methanol (10 mL) was slowly added. The reaction was stirred at 60 °C for 5 h. The solvent was removed under vacuum and the mixture was dissolved in CH_2Cl_2 (50 mL). The organic solution was washed with 0.1N hydrochloric acid (2 x 30mL) and a saturated aqueous solution of sodium chloride (2 x 30mL). The organic layer was dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was recrystallized in ethanol (35 to 70 % yield).

m-Nitrophenyl 4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (2a). Yield 31%; mp 54-55 °C (ethanol) ; TLC R_f 0.67 (AcOEt/hexane 1/1); $[\alpha]_D^{20}$ + 104.9° (*c* 1, $CHCl_3$); ^1H NMR (300 MHz) δ 1.98 (3 H, s, CH_3), 2.12 (3 H, s, CH_3), 4.14 (1 H, dd, *J* = 11.3 and 1.7 Hz, H-6), 4.18-4.25 (1 H, m, H-5), 4.27 (1 H, dd, *J* = 11.3 and 5.4 Hz, H-6'), 5.40 (1 H, dm, *J* = 9.2 Hz, H-4), 5.77 (1 H, bs, H-1), 6.01 (1 H, ddd, *J* = 10.3, 2.3 and 2.3 Hz, H-3), 6.10 (1 H, d, *J* = 10.3, H-2), 7.41-7.50 (2 H, m, C_6H_4), 7.92-7.98 (2 H, m, C_6H_4); ^{13}C NMR (50 MHz) δ 20.6 (CH_3), 20.9 (CH_3), 62.6 (C-6), 64.6 (C-4), 68.2 (C-5), 93.2 (C-1), 112.3, 117.3, 123.4, 126.2, 149.1 and 157.5 (C_6H_4), 130.1 and 130.9 (C-2, C-3), 170.2 (CO_2), 170.7 (CO_2). Anal. Calcd for $C_{16}H_{17}NO_8$: C, 54.70; H, 4.96; N, 3.99. Found: C, 54.60; H, 4.96; N, 4.16.

p-Nitrophenyl 4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (2b). Yield 40%; mp 95 °C (ethanol) [litt.[7] 96-97 °C]; TLC R_f 0.36

(AcOEt/hexane 1/3); $[\alpha]_D^{20}$ + 174.0° (*c* 1.6, CH_2Cl_2) [litt.[7] $[\alpha]_D^{20}$ +174.0° (*c* 0.2, C_6H_6]; ^1H NMR (300 MHz) δ 1.97 (3 H, s, CH_3), 2.12 (3 H, s, CH_3), 4.11-4.19 (2 H, m, H-5, H-6), 4.27 (1 H, dd, *J* = 12.6 and 5.8 Hz, H-6'), 5.41 (1 H, dm, *J* = 9.5 Hz, H-4), 5.81 (1 H, bs, H-1), 6.01 (1 H, ddd, *J* = 10.2, 2.4 and 2.4 Hz, H-3), 6.11 (1 H, bd, *J* = 10.2, H-2), 7.19 (2 H, d, *J* = 9.3 Hz, C_6H_4), 8.22 (2 H, d, *J* = 9.3 Hz, C_6H_4); ^{13}C NMR (50 MHz) δ 20.6 (CH_3), 20.9 (CH_3), 62.4 (C-6), 64.7 (C-4), 68.4 (C-5), 92.7 (C-1), 116.7, 125.7, 142.6 and 161.9 (C_6H_4), 125.9 (C-2), 131.2 (C-3), 170.1 (CO_2), 170.5 (CO_2).

*p-t-Butylphenyl 4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2c**).* Yield 49 %; mp 116-117 °C (ethanol); TLC R_f 0.54 (AcOEt/hexane 1/3); $[\alpha]_D^{20}$ + 129.0° (*c* 1, $CHCl_3$); ^1H NMR (300 MHz) δ 1.31 (9 H, s, *t*-Bu), 1.99 (3 H, s, CH_3), 2.11 (3 H, s, CH_3), 4.14 (1 H, dd, *J* = 11.4 and 1.6 Hz, H-6), 4.23 (1 H, ddd, *J* = 9.1, 5.4 and 1.6 Hz, H-5), 4.30 (1 H, dd, *J* = 11.4 and 5.4 Hz, H-6'), 5.40 (1 H, dm, *J* = 9.1 Hz, H-4), 5.68 (1 H, bs, H-1), 5.97-6.05 (2 H, m, H-2, H-3), 7.05 (2 H, d, *J* = 8.9 Hz, C_6H_4), 7.30 (2 H, d, *J* = 8.9 Hz, C_6H_4); ^{13}C NMR (50 MHz) δ 20.6 ($COCH_3$), 20.9 ($COCH_3$), 31.4 (CMe_3), 34.1 (CMe_3), 62.6 (C-6), 65.1 (C-4), 67.7 (C-5), 93.0 (C-1), 116.6, 126.2, 145.2 and 154.8 (C_6H_4), 127.2 and 130.0 (C-2, C-3), 170.2 (CO_2), 170.6 (CO_2). Anal. Calcd for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C, 66.56; H, 7.05.

*m-Nitrophenyl 4,6-Di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3a**).* Yield 40 %; oil; TLC R_f 0.31 (AcOEt/hexane 1/4); $[\alpha]_D^{20}$ + 163.0° (*c* 1, $CHCl_3$); ^1H NMR (300 MHz) δ 3.60-3.75 (2 H, m, H-6, H-6'), 3.99-4.07 (1 H, m, H-5), 4.27 (1 H, ddd, *J* = 9.5, 4.0 and 1.5 Hz, H-4), 4.47 (1 H, d, *J* = 12.3 Hz, $CH_2C_6H_5$), 4.48 (1 H, d, *J* = 11.5 Hz, $CH_2C_6H_5$), 4.59 (1 H, d, *J* = 12.3 Hz, $CH_2C_6H_5$), 4.65 (1 H, d, *J* = 11.5 Hz, $CH_2C_6H_5$), 5.76 (1 H, bs, H-1), 5.92

(1 H, dd, J = 10.2 and 2.0 Hz, H-3), 6.26 (1 H, d, J = 10.2, H-2), 7.25-8.00 (14 H, m, arom.); ^{13}C NMR (50 MHz) δ 68.4 (C-6), 69.8 (C-4), 70.6 (C-5), 71.4 ($CH_2C_6H_5$), 73.3 ($CH_2C_6H_5$), 93.5 (C-1), 112.0- 137.9, 149.0 and 157.7 (C-2, C-3 and arom.). Anal. Calcd for $C_{26}H_{25}NO_6$: C, 69.79; H, 5.63; N, 3.13. Found: C, 70.15; H, 5.92; N, 3.08.

*p-Nitrophenyl 4,6-Di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3b**).* Yield 40 %; mp 78 °C (ethanol); TLC R_f 0.83 (AcOEt/hexane 1/1); $[\alpha]_D^{20}$ + 178.0° (*c* 1, CH_2Cl_2); ^1H NMR (300 MHz) δ 3.62 (1 H, dd, J = 10.8 and 1.8 Hz, H-6), 3.71 (1 H, dd, J = 10.8 and 3.9 Hz, H-6'), 3.98 (1 H, ddd, J = 9.4, 3.9 and 1.8 Hz, H-5), 4.25 (1 H, bd, J = 9.4 Hz, H-4), 4.45 (1 H, d, J = 11.5 Hz, $CH_2C_6H_5$), 4.49 (1 H, d, J = 12.1 Hz, $CH_2C_6H_5$), 4.59 (1 H, d, J = 12.1 Hz, $CH_2C_6H_5$), 4.64 (1 H, d, J = 11.5 Hz, $CH_2C_6H_5$), 5.75 (1 H, bs, H-1), 5.87 (1 H, ddd, J = 10.2, 2.0 and 2.0 Hz, H-3), 6.24 (1 H, d, J = 10.2, H-2), 7.12 (2H, d, J = 9.2 Hz, C_6H_4), 7.32 (10 H, m, arom.), 8.10 (2 H, d, J = 9.2 Hz, C_6H_4); ^{13}C NMR (50 MHz) δ 68.4 (C-6), 69.6 (C-4), 70.7 (C-5), 71.4 ($CH_2C_6H_5$), 73.2 ($CH_2C_6H_5$), 92.9 (C-1), 116.6-138.2, 142.2 and 162.1 (C-2, C-3 and arom.). Anal. Calcd. for $C_{26}H_{25}NO_6$: C, 69.79; H, 5.63; N, 3.13. Found: C, 69.89; H, 5.69; N, 3.07.

*p-t-Butylphenyl 4,6-Di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3c**).* Yield 60 %; mp 58-59 °C (ethanol) ; TLC R_f 0.60 (AcOEt/hexane 1/4); $[\alpha]_D^{20}$ + 163.0° (*c* 1, CH_2Cl_2); ^1H NMR (300 MHz) δ 1.30 (9 H, s, *t*-Bu), 3.70 (1 H, dd, J = 10.9 and 2.1 Hz, H-6), 3.76 (1 H, dd, J = 10.9 and 3.6 Hz, H-6'), 4.10 (1 H, ddd, J = 9.5, 3.6 and 2.1 Hz, H-5), 4.28 (1 H, bdd, J = 9.5 and 1.3 Hz, H-4), 4.48 (1 H, d, J = 11.5 Hz, $CH_2C_6H_5$), 4.49 (1 H, d, J = 12.1 Hz, $CH_2C_6H_5$), 4.63 (1 H, d, J = 11.5 Hz, $CH_2C_6H_5$), 4.64 (1 H, d, J = 12.1 Hz,

$CH_2C_6H_5$), 5.67 (1 H, bs, H-1), 5.90 (1 H, ddd, *J* = 10.2, 2.1 and 2.1 Hz, H-3), 6.20 (1 H, d, *J* = 10.2 Hz, H-2), 7.06 (2H, d, *J* = 8.8 Hz, C_6H_4), 7.26-7.36 (12 H, m, arom.); ^{13}C NMR (50 MHz) δ 31.5 (CH_3), 34.1 (CMe_3), 68.7 (C-6), 70.1 (C-4), 70.2 (C-5), 71.2 ($CH_2C_6H_5$), 73.3 ($CH_2C_6H_5$), 93.5 (C-1), 116.6 -138.2, 138.0, 138.2, 144.7 and 155.2 (C-2, C-3 and arom.). Anal. Calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47. Found: C, 78.60; H, 7.50.

p-t-Butylphenyl 4-O-Acetyl-6-deoxy-2,3-dideoxy-α-L-erythro-hex-2-enopyranoside (5). Yield 56 %; mp 93-94 °C (ethanol); TLC R_f 0.65 (AcOEt/hexane 1/4); $[\alpha]_D^{20}$ - 162.0° (*c* 1, $CHCl_3$); ^1H NMR (200 MHz) δ 1.22 (3 H, d, *J* = 6.2 Hz, CH_3), 1.31 (9 H, s, *t*-Bu), 2.11 (3 H, s, $COCH_3$), 4.10 (1 H, dq, *J* = 9.3 and 6.2 Hz, H-5), 5.12 (1 H, bd, *J* = 9.3 Hz, H-4), 5.62 (1 H, s, H-1), 5.97 (2 H, bs, H-2, H-3), 7.03 (2 H, d, *J* = 8.7 Hz, C_6H_4), 7.32 (2 H, d, *J* = 8.7 Hz, C_6H_4); ^{13}C NMR (50 MHz) δ 18.0 (CH_3), 21.0 ($COCH_3$), 31.5 (CMe_3), 34.1 (CMe_3), 65.7 (C-5), 70.6 (C-4), 93.1 (C-1), 127.2 and 130.5 (C-2, C-3), 116.6, 126.2, 144.9 and 155.2 (C_6H_4), 170.4 (CO_2). Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 70.34; H, 8.22.

p-t-Butylphenyl 4-O-Benzyl-6-deoxy-2,3-dideoxy-α-L-erythro-hex-2-enopyranoside (6). Yield 50 %; mp 75-76 °C (ethanol) ; TLC R_f 0.78 (AcOEt/hexane 1/3); $[\alpha]_D^{20}$ - 164.0° (*c* 1, $CHCl_3$); ^1H NMR (200 MHz) δ 1.28 (3 H, d, *J* = 6.1 Hz, CH_3), 1.30 (9 H, s, *t*-Bu), 3.76 (1 H, bd, *J* = 9.0 Hz, H-4), 4.05 (1 H, dq, *J* = 9.0 and 6.1 Hz, H-5), 4.58 (1 H, d, *J* = 11.6 Hz, $CH_2C_6H_5$), 4.71 (1 H, d, *J* = 11.6 Hz, $CH_2C_6H_5$), 5.59 (1 H, bs, H-1), 5.90 (1 H, ddd, *J* = 10.2, 2.3 and 2.3 Hz, H-3), 6.19 (1 H, d, *J* = 10.2 Hz, H-2), 7.02 (1 H, d, *J* = 8.8 Hz, C_6H_4), 7.26-7.35 (8 H, m, arom.); ^{13}C NMR (50 MHz) δ 19.0 (CH_3), 32.3 (CMe_3), 34.9 (CMe_3), 67.5 (C-5), 71.7 ($CH_2C_6H_5$), 76.9 (C-4), 94.1 (C-1), 117.1,

127.0, 128.6, 129.2, 132.3, 138.8, 145.4 and 156.1 (C-2, C-3 and arom.); MS (E.I.) *m/z* (%) 352 ($M^{+\cdot}$, 1), 203 ([M - OC_6H_4-*t*-Bu]$^+$, 18), 91 ($C_7H_7^+$, 100). Anal. Calcd for $C_{23}H_{28}O_3$: C, 78.38; H, 8.01. Found: C, 77.78; H, 7.97.

Synthesis of compound 8. Yield 20 %; oil; TLC R_f 0.36 (AcOEt/hexane 1/3); $[\alpha]_D^{20}$ - 67.5° (*c* 1, $CHCl_3$); ^{1}H NMR (200 MHz) δ 1.89 (3 H, s, CH_3), 1.97 (1 H, bd, *J* = 13.7 Hz, H-2), 2.17 (3 H, s, CH_3), 2.50 (1 H, ddd, *J* = 13.7, 2.5 and 2.5 Hz, h-2'), 3.23 (1 H, m, H-3), 3.76 (1 H, dd, *J* = 11.5 and 7.1 Hz, H-6), 3.86 (1 H, dd, *J* = 11.5 and 4.3 Hz, H-6'), 3.95 (1 H, ddd, *J* = 7.1, 5.1 and 4.3 Hz, H-5), 4.94 (1 H, d, *J* = 5.1 Hz, H-4), 6.10 (1 H, bs, H-1), 7.37-7.54 (4 H, m, arom.), 7.75-7.80 (1 H, m, arom.), 8.17-8.22 (1 H, m, arom.); ^{13}C NMR (50 MHz) δ 20.6 (CH3), 21.3 (CH3), 22.6 (C-2), 31.9 (C-3), 64.8 (C-6), 70.3 (C-5), 72.9 (C-4), 92.9 (C-1), 116.0, 121.2, 121.7, 124.7, 125.7, 126.7, 126.6, 127.5, 134.1, 146.7 (arom.), 170.2 (CO_2), 170.5 (CO_2); MS (E.I.) *m/z* (%) 356 ($M^{+\cdot}$, 15.7), 236 ([M - 2 AcOH]$^{+\cdot}$, 22.6), 223 (62.3), 181 (32.8), 43 (CH_3-CO^+, 100). Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 66.79; H, 5.54.

BIBLIOGRAPHY

1. a. Hanessian, S. "*Total Synthesis of Natural Products; The Chiron Approach*", Pergamon Press, Oxford, 1983.

b. Inch, T. D. *Tetrahedron* **1984**, *40*, 3161.

c. Hacksell, U. and Daves, G. D., *Jr. Prog. Med. Chem.* **1985**, *22*, 1.

d. Buchanan, J. G. *Prog. Chem. Org. Natl. Prod.* **1983**, *44*, 243.

e. Freeman, F. and Robarze, K. D. *Carbohydr. Res.* **1987**, *171*, 1 and following articles in *Carbohydr. Res.* **1987**, *171* related to *C*-glycoside formation.

2. a. Trost, B. M. and Verhoeven, T. R. "*Comprehensive Organometallic Chemistry*" Pergamon Press, New York, 1982, pp. 799-938.

b. Heck, R. F. "*Palladium Reagents in Organic Synthesis*" Academic Press, London, 1985.

c. Goldeski, S. A. "*Comprehensive Organic Synthesis*", Ed. Trost, B. M., Pergamon Press, Oxford, 1991, Vol. 4, pp. 585-661.

d. Frost, C. G.; Howarth, J. and Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089.

3. a. Daves, G. D. Jr. and Hallberg, A. *Chem. Rev.* **1989**, *89*, 1433.

b. Daves, G. D. Jr. *Acc. Chem. Res.* **1990**, *23*, 201.

c. Jaramillo, C. and Knapp, S. *Synthesis* **1994**, 1.

d. Postema, M. H. D. *Tetrahedron* **1992**, *48*, 8545.

4. a. Brakta, M. Lhoste, P. and Sinou, D. *J. Org. Chem.* **1987**, *54*, 1890.

b. Chaguir, B., Brakta, M., Bolitt, V., Lhoste, P. and Sinou, D. *J. Carbohydr. Chem.* **1992**, *11*, 609.

5. a. Ferrier, R. J. and Prasad, N. *J. Chem. Soc.* **1969**, 570.

b. Grynkiewicz, G.; Preibe, W. and Zamojski, Q. *Carbohydr. Res.* **1979**, *68*, 33.

6. Brakta, M.; Farr, R. N.; Chaguir, Br.; Massiot, G.; Lavaud, C.; Anderson, R. W.; Sinou, D. and Daves, G. D., Jr. *J. Org. Chem.* **1993**, *58*, 2992.

7. Ferrier, R. J.; Overend, W. G.; Ryan, A. E. *J. Chem. Soc.* **1962**, 3667.

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