Article

JOURNAL OF THE CHINESE CHEMICAL SOCIETY

Synthesis of a Furanosyl-pyranone Derivative Related to the Tri-*O*-heterocyclic Core of Herbicidins

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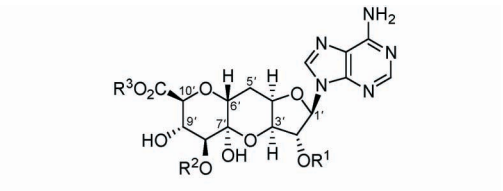
(Received: Jan. 10, 2012; Accepted: Jan. 17, 2012; Published Online: Feb. 6, 2012; DOI: 10.1002/jccs.201100744)

A new compound that is structurally related to the undecose ring structure of herbicidins has been prepared. The synthesis of this novel furanosyl-pyranone derivative was made possible through the regioselective reductive ring-opening of a 3,5-*O*-benzylidene-D-xylofuranose and the hetero-Diels–Alder reaction of an aldehyde and a Danishefsky-type diene. The highly functionalized pyranone derivative can be a useful precursor for the synthesis of herbicidins.

Keywords: Benzylidene acetal; Cycloaddition; Danishefsky-type diene; Herbicidins; Regioselectivity.

INTRODUCTION

In the 1970's, a series of undecose (C11)-based nucleoside antibiotics, collectively known as herbicidins (**1**), were isolated and characterized from the strains of *Streptomyces saganonensis* (Fig. 1).[1] These compounds were shown to exhibit valuable herbicidal and anti-fungal activity while being relatively non-toxic to animals. For example, herbicidins A (**1a**) and B (**1b**) are selectively toxic to some dicotyledons and efficiently inhibits *Xanthomonas oryzae*, the bacteria responsible for leaf blight infections in rice.



Herbicidin A (**1a**) : $R^1 = R^3 = Me$; $R^2 = CH_3CH{=}C(CH_2OH)CO$
Herbicidin B (**1b**) : $R^1 = R^3 = Me$; $R^2 = H$
Herbicidin C (**1c**) : $R^1 = Me$; $R^2 = R^3 = H$
Herbicidin E (**1d**) : $R^1 = R^3 = Me$; $R^2 = (CH_3)_2CHCO$
Herbicidin F (**1e**) : $R^1 = R^3 = Me$; $R^2 = CH_3CH{=}CH(CH_3)CO$
Herbicidin G (**1f**) : $R^1 = R^3 = H$; $R^2 = CH_3CH{=}CH(CH_3)CO$
Herbicidin H (**1g**) : $R^1 = Me$; $R^2 = CH_3CH{=}CH(CH_3)CO$; $R^3 = H$

Fig. 1. Structures of herbicidins.

Unique structural features make herbicidins a conspicuous target among synthetic chemists. The core 11-carbon structure that is β1 '-linked to adenine is an interesting furanopyranopyran ring system having an internal hemiketal bridging the C3′and C7′ positions and a *C*-glycoside linking C5′ and C6′. The rigid backbone also forces the C7′, C8′, C9′, and C10′ substituents to assume the axial position. Because the *C*-glycoside functionality separates the tri-*O*-heterocylic structure into two simple sugars, synthetic efforts primarily targeted the difficult generation of this crucial sugar link as the key step. To date, however, only Matsuda and co-workers[2] have completed the synthesis of a herbicidin congener, that is herbicidin B. Other research groups only accomplished the partial[3] or full assembly[4] of the undecose backbone. Thus, new avenues that may improve the synthesis of this important series of compounds are still much desired.

Our synthetic strategy focusing on the formation of the glycosyl core structure of herbicidins (**1**) is depicted in Scheme I. We envisioned the furanosyl-pyranone **2** as a direct precursor to the tricylic ring system and is, thus, the target material in the current work. The plan is to access

Dedicated to the memory of Professor Yung-Son Hon (1955–2011).

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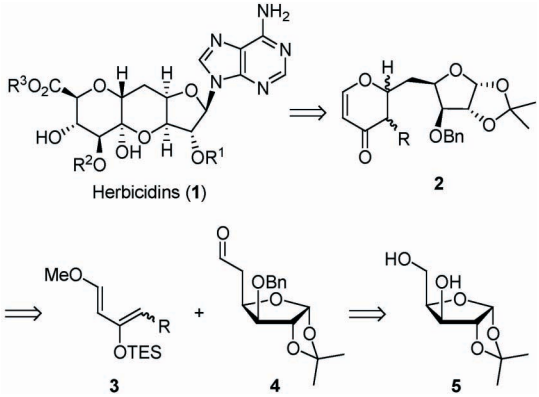
Scheme I Retrosynthetic analysis of herbicidin



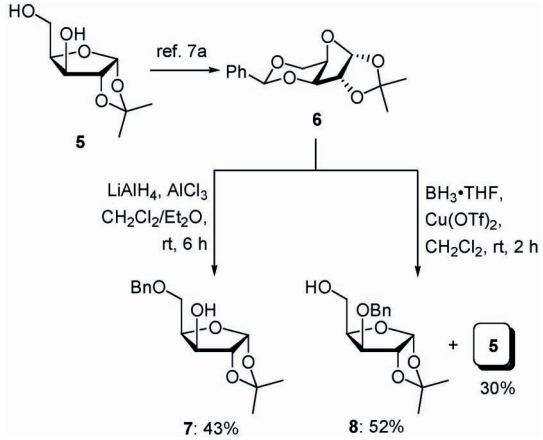
this compound through the [4 + 2]-cycloaddition of the Danishefsky-type diene **3** and the aldehyde **4**. Here, the stereoselectivity may be controlled by an appropriately selected Lewis acid catalyst.[5] Compound **4**, in turn, could be generated by transformations of the commercially abundant 1,2-*O*-isopropylidene-α-D-xylofuranose (**5**).

RESULTS AND DISCUSSION

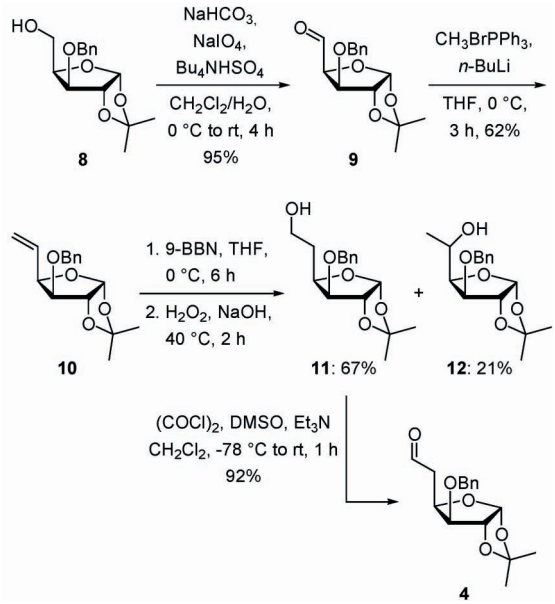
The first encountered challenge is the installation of a benzyl ether at the O3 position of the diol **5**. Presumably, this transformation may be directly achieved by regioselective reductive ring opening of an installed 3,5-*O*-benzylidene acetal. Nonetheless, although the 1,3-dioxane-type benzylidene acetals in pyranoses (e.g. 4,6-*O*-benzylidene) could be readily opened in either direction by a suitable set of reagents,[6] literature reports on the ring opening of the corresponding acetal in furanosyl sugars only resulted in the formation of the primary benzyl ether and a secondary hydroxyl group as the major isomer.[7] To test the viability of this synthetic route, compound **5** was converted to the desired acetal **6** according to a known procedure[7a] (Scheme II). Treatment of **6** with $LiAlH_4$ and $AlCl_3$ only produced the unwanted 3-OH-5-OBn regioisomer **7** in 43% yield without any trace of the target 5-alcohol **8**. Fortunately, our recently reported BH_3·THF/$Cu(OTf)_2$ combination[6a,b] delivered the primary alcohol **8** from acetal **6** together with the diol **5** in 52% and 30% yields, respectively. The corresponding 3-alcohol **7** was not isolated from the reaction mixture. To our knowledge, this is the first report of a regioselective reductive ring opening at the O5 position of a 3,5-*O*-benzylidene acetal in a furanoside.

With the 5-alcohol **8** in hand, we continued the transformations toward the required aldehyde **4** (Scheme III).

Scheme II Reductive ring opening of 3,5-*O*-benzylidene acetal



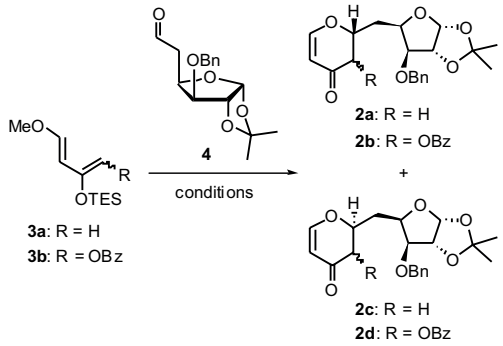
Scheme III Synthesis of the aldehyde **4**



Oxidation of compound **8** with $NaHCO_3$ and $NaIO_4$ in phase transfer conditions led to the aldehyde **9**[8] in an excellent yield. The terminal alkene **10**, generated from **9** through a typical Wittig reaction (62%), was sequentially treated with 9-borabicyclo[3.3.1]nonane (9-BBN) and H_2O_2/NaOH to form the desired primary alcohol **11** together with its isomer **12** in 67% and 21% yields, respectively. Compound **11** was, then, subjected to Swern oxidation to afford the target aldehyde **4** in 92% yield.

The formation of the furanosyl-pyranone **2** was facilitated through the hetero-Diels–Alder reaction of the Danishefsky-type diene **3** and the aldehyde dienophile **4** (Table

Table 1. Hetero-Diels–Alder cycloaddition of the Danishefsky-type diene **3** and the aldehyde **4**



Entry	Diene	Condition	Product (ratio)	Yield (%)
1	**3a**	$TiCl_4$, CH_2Cl_2, –78 °C, 1 h; TFA, rt, 1 h	**2a**/**2c** (3/1)	56
2	**3a**	$ZnCl_2$, THF, 0 °C to rt, 24 h; TFA, rt, 1 h	**2a**/**2c** (4/3)	88
3	**3b**	$ZnCl_2$, THF, 0 °C to rt, 24 h; TFA, rt, 1 h	**2b**/**2d**	77

1). The reaction requires a Lewis acid catalyst to promote the cycloaddition and subsequent treatment with trifluoroacetic acid (TFA) leads to the elimination the triethylsilyl (TES) and methoxy groups.[5a] In the present case, the *endo*-adduct is more favored, but the Lewis acid catalyst exerts an effect on the stereoselectivity. For example, $TiCl_4$ allowed for an *endo*/*exo* addition (**2a**/**2c**) ratio of 3/1 (entry 1), whereas $ZnCl_2$ gave a corresponding 4/3 ratio (entry 2). The yield of the reaction using $ZnCl_2$, however, was much higher (88%). When the benzoate **3b** (the *E*/*Z* ratio was not determined) was utilized as the diene, compounds **2b** and **2d** were furnished in a combined yield of 77% (entry 3). Collectively, pyranone **2** possesses the proper set of functional groups that may allow entry to the herbicidin tricylic core.

CONCLUSION

The reactions used in this study provided a novel approach towards herbicidins. Herein, we successfully carried out the first case of regioselective reductive ring opening of 3,5-*O*-benzylidine acetal in a furanoside that favored the primary alcohol formation. This product is a useful intermediate for the synthesis of an aldehyde dienophile that enabled access to a suitable precursor to the undecose ring system of herbicidins via hetero-Diels–Alder reaction. Future undertakings will focus on further examinations on the feasibility of this precursor in accessing the herbicidin congeners.

EXPERIMENTAL

General remarks

All solvents (CH_2Cl_2, THF, and Et_2O) were purified and dried from a safe purification system filled with anhydrous Al_2O_3. All other reagents obtained from commercial sources were used without further purification. Flash column chromatography was carried out on Silica Gel 60 (230-400 mesh, E. Merck). TLC was performed on precoated plates of Silica Gel 60 F_{254} (0.25 mm, E. Merck); detection was executed by spraying with a solution of $Ce(NH_4)_2(NO_3)_6$, $(NH_4)_6Mo_7O_{24}$, and H_2SO_4 in water and subsequent heating on a hotplate. ^1H and ^{13}C NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are in ppm from Me_4Si calibrated using the resonance of the residual proton and carbon of the deuterated solvent.

3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose (8)

BH_3·THF (1 M solution in THF, 0.36 mL, 0.36 mmol) was slowly added to the acetal **6** (20.0 mg, 0.0719 mmol) at room temperature under nitrogen atmosphere. After stirring for 10 min, freshly dried $Cu(OTf)_2$ (3.91 mg, 10.8 μmol) was added to the solution, and the mixture was kept stirring for 2 h. The reaction was quenched by sequential additions of Et_3N and methanol, and the resulting mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 1/2) to afford the 5-alcohol **8** (10.5 mg, 0.0375 mmol) and the diol **5** (4.1 mg, 0.022 mmol). $[\alpha]_D^{29}$ –33.4 (*c* 0.3, $CHCl_3$); IR (thin film) ν 3396, 1216, 1161, 1074 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 5H, ArH), 5.97 (d, *J* = 3.8 Hz, 1H, H-1), 4.70 (d, *J* = 11.9 Hz, 1H, CH_2Ph), 4.62 (d, *J* = 3.8 Hz, 1H, H-2), 4.55 (d, *J* = 11.9 Hz, 1H, CH_2Ph), 4.26 (q, *J* = 4.5 Hz, 1H, H-4), 4.00 (d, *J* = 4.5 Hz, 1H, H-3), 3.93 (dd, *J* = 12.1, 4.5 Hz, 1H, H-5_a), 3.84 (m, 1H, H-5_b), 2.13 (bs, 1H, 5-OH), 1.47 (s, 3H, CH_3), 1.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0 (C), 128.7 (CH), 128.2 (CH), 127.7 (CH), 111.8 (C), 105.1 (CH), 82.8 (CH), 82.5 (CH), 80.1 (CH), 71.9 (CH_2), 61.0 (CH_2), 26.8 (CH_3), 26.3 (CH_3); HRMS (FAB, $[M+H]^+$) calcd for $C_{15}H_{21}O_5$ 281.1389, found 281.1388.

3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-xylo-dialdose (9)

Compound **8** (0.244 g, 0.872 mmol) was dissolved in CH_2Cl_2 (1.78 mL). Water (1.33 mL) was added, followed by $NaHCO_3$ (22.0 mg, 1.74 mmol) and Bu_4NHSO_4 (29.6 mg, 0.087 mmol). The resulting mixture was cooled to 0

°C. $NaIO_4$ (0.373 g, 1.744 mmol) was added in portions for over 30 min. After another 30 min, the mixture was allowed to warm to room temperature and stirred for another 3 h. The crude target material was extracted with CH_2Cl_2, and the organic layer was concentrated and dissolved in Et_2O. The resulting solution was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 1/3) to give the aldehyde **9** (95% yield). $[\alpha]_D^{25}$ –34.5 (*c* 1.02, $CHCl_3$); IR (thin film) ν 1735, 1450, 1372 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 1.5 Hz, 1H, CHO), 7.30-7.24 (m, 5H, Ph-H), 6.11(d, *J* = 4.0 Hz, 1H, H-1), 4.64 (d, *J* = 4.0 Hz, 1H, H-2), 4.60 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.59 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.63-4.50 (m, 1H, H-4), 4.33 (d, *J* = 4.0 Hz, 1H, H-3), 1.45 (s, 3H, CH_3), 1.30 (s, 3H, CH_3).

5,6-Dideoxy-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylo-hex-5-eno-furanose (10)

The Wittig reagent was generated by dropwise addition of *n*-BuLi (2.5 M solution in hexane, 0.5 mL, 1.25 mmol) to an ice-cold solution of CH_3BrPPh_3 (0.63 g, 1.56 mmol) in THF (6 mL). After 30 min, the Wittig reagent was added dropwise to a solution of compound **9** (0.289 g, 1.04 mmol) in THF (3 mL) under nitrogen atmosphere. The reaction was stirred at 0 °C for 3 h, then, saturated $NH_4Cl_{(aq)}$ was added to the reaction mixture. The crude target material was extracted using CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (ethyl acetate/hexanes = 1/1) provided the alkene **10** (178 mg, 62%). $[\alpha]_D^{20}$ +200.4 (*c* 5.0, $CHCl_3$); IR (thin film) ν 2954, 1453, 1376, 1215, 1078, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 5H), 6.04-5.97 (m, 1H), 5.95 (d, *J* = 3.6 Hz, 1H), 5.42 (dd, *J* = 18.0, 2.8 Hz, 1H), 5.31 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.70-4.48 (m, 4H), 3.87 (d, *J* = 3.2 Hz, 1H), 1.48 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3 (C), 132.1 (CH), 128.1 (CH), 127.5 (CH), 127.2 (CH), 118.5 (CH_2), 111.1 (C), 104.5 (CH), 83.1 (CH), 82.5 (CH), 81.2 (CH), 71.7 (CH_2), 26.5 (CH_3), 25.9 (CH_3); HRMS (EI, $[M–CH_3]^+$) calcd for $C_{15}H_{17}O_4$ 261.1361, found 261.1343.

5-Deoxy-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-gluco-furanose (11)

A 1 M solution of 9-BBN in THF (30 mmol, 30 mL) was added dropwise to a solution of compound **10** (8.12 g, 29.4 mmol) in THF (80 mL) under nitrogen atmosphere. After stirring at 0 °C for 6 h, a co-solution of H_2O_2 (35%, 7.6 mL) and NaOH (5.92 g, 148 mmol) was added and allowed to stir for 2 h at 40 °C. Water was added and the crude target material was extracted using ethyl acetate, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (ethyl acetate/hexanes = 1/4) gave the 6-alcohol **11** (5.79 g, 67%). $[\alpha]_D^{20}$ –39.4 (*c* 2.0, $CHCl_3$); IR (thin film) ν 3600-3200, 1640, 1450, 1380, 1210, 1050 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 5H), 5.89 (d, *J* = 4.0 Hz, 1H), 4.66, 4.46 (ABq, *J* = 12.4 Hz, 2H), 4.59 (d, *J* = 4.0 Hz, 1H), 4.32-4.28 (m, 1H), 3.79 (d, *J* = 2.8 Hz, 1H), 3.70 (t, *J* = 6.0 Hz, 2H), 2.46 (bs, 1H, OH), 2.07-1.98 (m, 1H), 1.85-1.77 (m, 1H), 1.45 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4 (C), 128.6 (CH), 128.0 (CH), 127.7 (CH), 111.5 (C), 104.8 (CH), 82.6 (CH), 82.2 (CH), 78.5 (CH), 71.8 (CH_2), 60.3 (CH_2), 31.0 (CH_2), 26.7 (CH_3), 26.2 (CH_3); HRMS (EI, $[M]^+$) calcd for $C_{16}H_{22}O_5$ 294.1545, found 294.1549.

5-*C*-Formyl-5-deoxy-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (4)

DMSO (3.8 mL, 53.6 mmol) was added dropwise to a solution of $(COCl)_2$ (3.2 mL, 36.3 mmol) in CH_2Cl_2 (25 mL) at –78 °C. After 5 minutes, compound **11** (5.25 g, 17.9 mmol) dissolved in CH_2Cl_2 (15.0 mL) was added, and the resulting mixture was stirred at the same temperature for 12 min. Subsequently, Et_3N (12.5 mL, 89.1 mmol) was added followed by warming to room temperature for a 1-h period. Et_2O was added to the reaction mixture and any solids that formed were filtered through paper. The filtrate was concentrated to give a residue which was purified using flash column chromatography (ethyl acetate/hexanes = 1/8) to obtain the aldehyde **4** (4.81 g, 92%). $[\alpha]_D^{20}$ +56.4 (*c* 5.0, $CHCl_3$); IR (thin film) ν 2960, 2920, 1720, 1500, 1450, 1400, 1220 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.72 (d, *J* =1.6 Hz, 1H), 7.33-7.23 (m, 5H), 5.88 (d, *J* = 2.8 Hz, 1H), 4.62, 4.40 (ABq, *J* = 12.0 Hz, 2H), 4.60-4.55 (m, 2H), 3.96 (d, *J* = 3.6 Hz, 1H), 2.84-2.73 (m, 2H), 1.46 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8 (CH), 137.0 (C), 128.3 (CH), 127.7 (CH), 127.6 (CH), 111.5 (C), 104.5 (CH), 82.1 (CH), 82.0 (CH), 75.3 (CH), 71.8 (CH_2), 42.4 (CH_2), 26.6 (CH_3), 26.0 (CH_3); HRMS (EI, $[M]^+$) calcd for $C_{16}H_{20}O_5$ 292.1311, found 292.1287.

[2-(3-*O*-Benzyl-1,2-*O*-isopropylidene-5-deoxy-α-D-xylo-1,4-furanosyl)-2,3-dihydro-4H-pyran-4-one] (2a and 2c)

The Danishefsky-type diene **3a** (1.49 g, 8.66 mmol) was added to the solution of the aldehyde **4** (1.15 g, 3.94 mmol) in THF (10 mL) at room temperature under nitrogen

atmosphere. The mixture was cooled to 0 °C, and a suspension of $ZnCl_2$ (0.59 g, 4.34 mmol) in THF (15 mL) was added. After stirring for 24 h at room temperature, TFA (0.3 mL, 3.93 mmol) was added to the reaction flask and was stirred for another hour. Saturated $NaHCO_{3(aq)}$ was added to neutralize the excess acid. The crude target material was extracted with ethyl acetate, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue using flash column chromatography (ethyl acetate/hexanes = 1/8) yielded the pyranones **2a** and **2c** (1.25 g, 88%). IR (thin film) ν 2942, 1732, 1677, 1595, 1269, 1075 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 6H), 5.88 (d, J = 3.6 Hz, 1H), 5.36 (d, J = 6.0 Hz, 1H), 4.69 (dd, J = 12.0, 5.2 Hz, 1H), 4.63-4.18 (m, 5H), 3.80 (d, J = 3.2 Hz, 1H), 2.52-2.21 (m, 2H), 2.05-1.80 (m, 2H), 1.46 (s, 3H), 1.23 (s, 3H); HRMS (EI, $[M]^+$) calcd for $C_{20}H_{24}O_6$ 360.1338, found 360.1329.

[2-(3-*O*-Benzyl-1,2-*O*-isopropylidene-5-deoxy-α-D-xylo-1,4-furanosyl)-2,3-dihydro-3-(benzoyloxy)-4H-pyran-4-one] (2b and 2d)

The reaction of the diene **3b** (3.62 g, 10.8 mmol) and the aldehyde **4** (1.56 g, 5.34 mmol) following the procedure for **2a**/**2c** furnished the products **2b** and **2d** (1.97 g, 77% yield). IR (thin film) ν 2956, 1730, 1700, 1595, 1452, 1247, 1088 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04-7.99 (m, 2H), 7.61-7.50 (m, 1H), 7.46-7.14 (m, 8H), 5.89 (d, J = 3.6 Hz, 1H), 5.62-5.47 (m, 2H), 4.78-4.31 (m, 5H), 3.77 (d, J = 3.6 Hz, 1H), 2.38-1.95 (m, 2H), 1.46 (s, 3H), 1.29 (s, 3H); HRMS (EI, $[M]^+$) calcd for $C_{27}H_{28}O_8$ 480.1784, found 480.1747.

ACKNOWLEDGEMENTS

This work was supported by the National Science Council (NSC 97-2113-M-001-033-MY3, NSC 98-2119-M-001-008-MY2, NSC 98-3112-B-007-005, NSC 98-2627-B-007-008) and Academia Sinica.

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