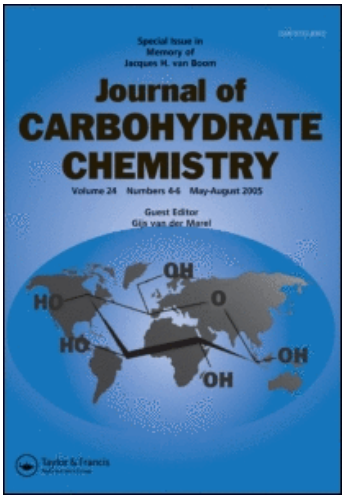

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SYNTHESIS AND ^{13}C NMR SPECTRA OF 1,8-DIHYDROXY-10-GLYCOPYRANOSYL-9(10*H*)-ANTHRACENONES

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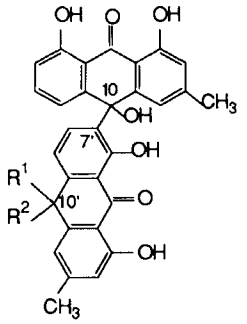
ABSTRACT

C-glycosides 10-β-D-glucopyranosyl-, 10-β-D-xylopyranosyl-, 10-α-L-arabinopyranosyl-, 10-(6'-deoxy-β-D-glucopyranosyl)-, 10-β-L-fucopyranosyl-, 10-(6'-deoxy-β-L-gulopyranosyl)-, and 10-α-L-rhamnopyranosyl-1,8-dihydroxy-9(10*H*)-anthracenone have been synthetized as model compounds for natural *C*-glycosides by reaction of the corresponding acylated glycosyl bromides with 1,8-dihydroxy-9(10*H*)-anthracenone. Full assignment of their carbohydrate ^{1}H and ^{13}C NMR signals is reported.

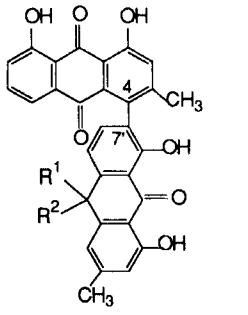
INTRODUCTION

Recently we isolated from *Asphodelus ramosus* bulbs a series of *C*-glycosides that constitute two new classes of natural products.[1-3] Compounds **1-4** form the group of 7'-10-bianthrone 10'-*C*-glycosides and compounds **5-10** form the group of anthrone-4,7'-anthraquinone 10'-*C*-glycosides. The latter were also found to show interesting LC_{50} values to the *Artemia salina* bioassay.[3]

The structure of the aglycone moiety of these compounds has been determined mainly on the basis of their ^1H NMR, ^{13}C NMR and FAB-MS spectra, while the elucidation of the sugar moiety was determined from ^1H NMR spectral data and from identification of the monosaccharides obtained by cleavage of the *C*-glycosidic bond. ^{13}C NMR signals of the carbohydrate carbons have been assigned only for glycoside **1** and, partly, for **3** and **4**. Complete assignment of the ^{13}C NMR signals for the glycones of **3** and **4** and of the remaining compounds was hampered by both the lack of sufficiently available material and the fact that only relevant literature data for the glucopyranosyl moiety of *C*-glucosides aloins A and B have been published.[4]



1 R^1 = OH R^2 = β-D-Glc*p*
2 R^1 = OH R^2 = β-D-Xyl*p*
3 R^1 = OH R^2 = β-D-Glc*p*-(1→4)-β-D-Glc*p*
4 R^1 = H R^2 = β-D-Glc*p*



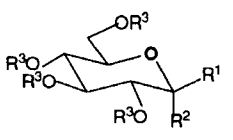
5 R^1 = H R^2 = α-Rha*p*
6 R^1 = H R^2 = β-D-Xyl*p*
7 R^1 = H R^2 = 6-deoxy-β-Gul*p*
8 R^1 = H R^2 = α-Ara*p*
9 R^1 = β-D-Xyl*p* R^2 = H
10 R^1 = H R^2 = 6-deoxy-β-Glc*p*

In order to meet the lack of ^{13}C NMR data and to support further NMR studies of the isolated glycosides, we prepared a series of model compounds, **11a-17a**, where β-D-glucopyranose, β-D-xylopyranose, α-L-arabinopyranose, 6-deoxy-β-D-glucopyranose (β-D-quinovose), 6-deoxy-β-L-galactopyranose (β-L-fucose), 6-deoxy-β-L-gulopyranose (β-L-antiarose) and 6-deoxy-α-L-mannopyranose (α-L-rhamnose) are linked through a *C*-glycosidic bond to carbon-10 of 1,8-dihydroxy-9(10*H*)-anthracenone **18**.

RESULTS AND DISCUSION

Glycosyl residues have been linked to carbon-10 of **18** through the Mühlemann procedure[5,6] by reaction of the corresponding suitably protected bromides with 1,8-dihydroxy-9(10*H*)-anthracenone and aq NaOH in acetone, under a helium atmosphere.

Fully acetylated α-D-glucopyranosyl (**11c**), α-D-xylopyranosyl (**12c**), β-L-arabinopyranosyl (**13c**), 6-deoxy-α-D-glucopyranosyl (**14c**), α-L-fucopyranosyl (**15c**), and α-L-rhamnopyranosyl (**19**) bromides were prepared by well established procedures.[7,8] 2,3,4-Tri-*O*-acetyl-6-deoxy-α-L-gulopyranosyl bromide **16c** was obtained from 1,2,3,4-tetra-*O*-acetyl-6-deoxy-β-L-gulopyranose (**16**, R^1 = OAc, R^2 = H, R^3 = Ac) by treatment with HBr/AcOH. The α-configuration of **16c** was inferred from the 4.4 Hz values for all NMR ^3J coupling constants of the ring proton signals, indicating the absence of any diaxial relationship between the vicinal protons of the ring, the latter, moreover, possessing a $^1C_4$ (L) conformation.



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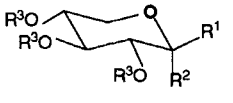

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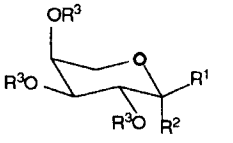

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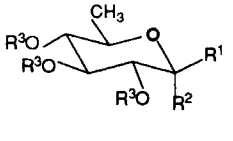

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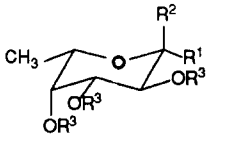

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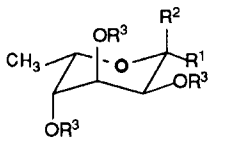

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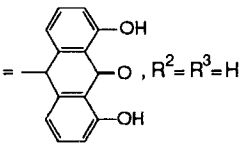
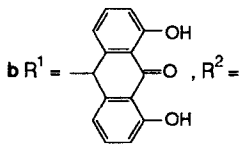
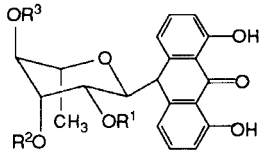
a R^1 =  , $R^2 = R^3 = H$

b R^1 =  , $R^2 = H$, $R^3 = Ac$

c $R^1 = H$, $R^2 = Br$, $R^3 = Ac$

Reaction of the bromides **11c-16c** with **18** gave the expected acetylated *C*-glycosides **11b-16b** in yields of 20-55%. The α-configuration of **13b** and the β-configuration of **11b**,**12b**, and **14b-16b** was confirmed from the $^3J_{H\text{-}1',H\text{-}2'}$ values, being >9 Hz in all cases. Unlike **11c-16c**, acetylated α-L-rhamnopyranosyl bromide **19** failed to give the *C*-glycosylation product. 2,3,4-Tri-*O*-acetyl-L-rhamnose was the only product identified in the complex reaction mixture obtained. This failure might be related to the *trans* relationship between the C_1-Br bond and the participating C_2-$OCOCH_3$ group[9-11] and to the bulky nucleophile. However, when 4-*O*-acetyl-2,3-*O*-carbonyl-α-L-rhamnopyranosyl bromide **20**[12] was used, *C*-glycoside **17b** was obtained in a yield of 27%. Owing to the deformation of the pyranose ring of **17b** due to the *cis*-fusion with the five-member ring,[13] the value of 8.9 Hz for $^3J_{H\text{-}1',H\text{-}2'}$ merely

suggests the *trans* relationship of the 1'- and the 2'-proton. That this is the case was indicated by the comparable value (9.0 Hz) of this coupling constant for the underivatized *C*-glycoside **17a**, obtained by MeONa/MeOH deacylation of **17b**. The value for $^{3}J_{H\text{-}1',H\text{-}2'}$ can only be due to a *trans*-diaxial arrangement of the two protons in a $^{4}C_{1}$ (L) conformation (as depicted in **17**). On the other hand, natural *C*-α-rhamnopyranoside **5** has been also shown to possess that conformation because of the steric requirements of the aglycone moiety.[3] It must be noted that the formation of the *trans C*-glycoside **17b** by reaction of **20** and **18** is quite surprising, since **20** is the starting material of choice for the synthesis of *cis O*-β-L-rhamnopyranosides.[12]



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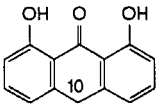

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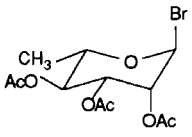

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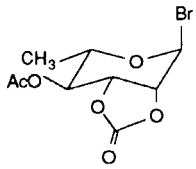

20

a $R^1=R^2=R^3=H$

b $R^1,R^2= >C=O$, $R^3=Ac$

Deacylation of *C*-glycosides **11b-16b** was easily achieved with satisfactory yields by treatment with M BCl_3/CH_2Cl_2,[14] which was found ineffective for removal of the carbonate group of **17b**.

The ^{13}C NMR data for the sugar carbons of *C*-glycosides **11a-17a** are reported in the Table. Assignments are based on analysis of ^{1}H NMR spectra, 2D ^{1}H-^{1}H COSY and 2D ^{1}H-^{13}C HETCOR experiments. 1'-Carbon chemical shifts for **11a-17a** appear to be at higher field than the correspondig methyl *O*-glycosides,[15] but at lower field than in the case of alkyl *C*-glycosides.[16,17] 1'-Carbon of **16a** and **17a** resonates at comparably higher field (81.0 and 77.7 ppm, respectively) than for **11a-15a**. This may be due to steric γ-effects exerted by the axial substituents at the 3'-position of **16a** and at the 3'- and 5'-positions of **17a**.

EXPERIMENTAL

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a 400-AM FT spectrometer (Bruker). 2D COSY and ^{1}H-^{13}C correlated experiments were

Table. ^1H and ^{13}C NMR selected data (δ) of compounds **11a-17a** in DMSO-d_6 (*apparent coupling constants in Hz*).[a]

	11a		**12a**		**13a**	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1'	3.32 *dd (1.4, 9.4)*	85.0	3.26 *dd (1.2, 9.0)*	86.4	3.20 *m*	86.8
2'	2.84 *t (9.4)*	70.2	2.94 *t (9.0)*	70.1		67.2[b]
					3.33 *m*, 2H	
3'	3.15 *t (9.4)*	78.1	3.13 *t (9.0)*	78.2		74.1[b]
4'	2.72 *t (9.4)*	70.2	2.91 *m*	69.6	3.52 *s*	68.6
5'	2.78 *m*	80.8	2.65 *t (11.0)*	70.3	3.03 *d (11.9)*	70.8
			3.48 *dd (5.5, 11.0)*		3.44 *d (11.9)*	
6'	3.18 *dd (5.5, 12.5)*	61.3				
	3.41 *dd (2.0, 12.5)*					
10	4.65 *d (1.4)*	44.1	4.64 *d (1.2)*	43.5	4.67 *s*	43.4

	14a		**15a**[c]		**16a**	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1'	3.28 *dd (1.9, 8.7)*	84.7	3.77 *d (9.5)*	86.9	3.66 *dd (1.0, 8.7)*	81.0
2'	2.93 *t (8.7)*	70.3	4.12 *t (9.5)*	68.6	3.31 *dd (3.4, 8.7)*	64.8
3'	3.15 *t (8.7)*	77.8	3.95 *dd (3.1, 9.5)*	77.0	3.68 *t (3.4)*	71.4
4'	2.47 *t (8.7)*	75.3	3.79 *d (3.1)*	75.6	3.19 *dd (1.1, 3.4)*	71.6
5'	2.80 *m*	75.7	3.37 *q (6.9)*	72.7	3.36 *dq (1.1, 6.8)*	70.4
6'	0.85 *d (6.1)*	17.9	1.12 *d (6.9)*	17.0	0.76 *d (6.8)*	16.1
10	4.65 *d (1.9)*	43.9	5.08 *s*	45.3	4.60 *d (1.0)*	43.8

	17a	
	^1H	^{13}C
1'	3.81 *dd (3.1, 9.0)*	77.7
2'	3.53 *dd (3.1, 9.0)*	65.2
3'	3.68 *t (3.1)*	72.5
4'	3.24 *t (3.1)*	73.7
5'	3.02 *m*	72.9
6'	0.83 *d (6.9)*	16.5
10	4.64 *d (3.1)*	43.7

a. Chemical shifts are relative to TMS. Multiplicity and coupling constants of protons were measured on samples treated with D_2O.
b. Interchangeable signals.
c. Measured in pyridine-d_5, proton signals in DMSO-d_6 being overlapped. Carbohydrate carbon signals in DMSO-d_6 : 16.6, 66.6, 71.1, 74.1, 74.9, 85.4.

performed as reported.[1] Specific rotations were determined with a Perkin-Elmer model 141 polarimeter.

2,3,4-Tri-*O*-acetyl-6-deoxy-α-L-gulopyranosyl bromide (16c). 6-Deoxy-L-gulopyranose[18] (288 mg) was dissolved in pyridine (5 mL) and treated overnight with Ac_2O (1.5 mL) at room temperature. After usual work up and column chromatography on silica gel (chloroform), 1,2,3,4-tetra-*O*-acetyl-6-deoxy-β-L-gulopyranose (519 mg, 89%) was obtained as an oil: $[\alpha]_D^{20}$ = -9.8° (*c* 0.7, chloroform); ^1H NMR ($CDCl_3$) δ 1.20 (d, 3H, $J_{5',6'}$ = 6.5 Hz, 6'-H_3), 2.00 (s, 3H, $OCOCH_3$), 2.12 (s, 3H, $OCOCH_3$), 2.15 (s, 3H, $OCOCH_3$), 2.18 (s, 3H, $OCOCH_3$), 4.28

(dq, 1H, $J_{4',5'}$ = 1.3 Hz, $J_{5',6'}$ = 6.5 Hz, 5'-H), 4.88 (dd, 1H, $J_{4',5'}$ = 1.3 Hz, $J_{3',4'}$ = 3.4 Hz, 4'-H), 5.11 (dd, 1H, $J_{1',2'}$ = 8.0 Hz, $J_{2',3'}$ = 3.4 Hz, 2'-H), 5.41 (1H, t, $J_{2',3'}$ = $J_{3',4'}$ = 3.4 Hz, 3'-H), 5.91 (d, 1H, $J_{1',2'}$ = 8.0 Hz, 1'-H).

Anal. Calcd for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.31; H, 6.02.

The tetraacetate (500 mg) was dissolved in chloroform (20 mL) and treated with HBr/AcOH (33% w/v, 5 mL). After stirring at room temperature for 1 h, the mixture was diluted with cold ethyl acetate (100 mL), washed with ice water (2x100 mL), saturated aq $NaHCO_3$ (3x20 mL) and ice water (2x50 mL), dried (Na_2SO_4) and concentrated to give **16c** (460 mg, 87%) as a syrup: $[\alpha]_D^{20}$ = -146.9° (*c* 0.8, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.21 (d, 3H, $J_{5',6'}$ = 6.5 Hz, 6'-H_3), 2.05 (s, 3H, $OCOCH_3$), 2.11 (s, 6H, 2 $OCOCH_3$), 4.55 (q, 1H, $J_{5',6'}$ = 6.5 Hz, 5'-H), 4.97 (d, 1H, $J_{3',4'}$ = 4.4 Hz, 4'-H), 5.15 (t, 1H, $J_{1',2'}$ = $J_{2',3'}$ = 4.4 Hz, 2'-H), 5.32 (t, 1H, $J_{2',3'}$ = $J_{3',4'}$ = 4.4 Hz, 3'-H), 6.50 (d, 1H, $J_{1',2'}$ = 4.4 Hz, 1'-H).

Anal. Calcd for $C_{12}H_{17}O_7Br$: C, 40.81; H, 4.85. Found: C, 40.67; H, 4.80.

Reaction of Glycopyranosyl Bromides 11c-16c, 19 and 20 with 18. 1,8-Dihydroxy-9(10*H*)-anthracenone **18** (678 mg, 3 mmol) was dissolved in acetone (25 mL) while helium was bubbled gently through the solvent. M NaOH (3.3 mL, prepared under helium) and then 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide **11c** (1.356 g, 3.3 mmol) dissolved under helium in acetone (7 mL) was added while the mixture was being stirred magnetically. The mixture was stirred at room temperature in the dark for 3 h and monitored by TLC (9:1 chloroform-ethyl acetate). The mixture was then concentrated under reduced pressure (max 30 °C) and the residue was extracted with chloroform. The extracts were washed with water, dried (Na_2SO_4) and concentrated. Column chromatography of the residue (1.45 g) on silica gel (45 g, chloroform) gave **11b** (645 mg, 35%) as a yellow crystalline mass: mp 187-188 °C (from chloroform-ethanol) (lit.[5] mp 188-188.5 °C); $[\alpha]_D^{20}$ = -16.7° (*c* 0.9, chloroform); ^{1}H NMR data ($CDCl_3$) δ 3.75 (dd, 1H, $J_{1',10}$ = 1.3 Hz, $J_{1',2'}$ = 9.2 Hz, 1'-H), 4.39 (d, 1H, $J_{1',10}$ = 1.3 Hz, 10-H).

Anal. Calcd for $C_{28}H_{28}O_{12}$: C, 60.43; H, 5.07. Found: C, 60.47; H, 5.01.

Reaction of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide **12c**[7] (680 mg), 2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl bromide **13c**[7] (610 mg), 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-glucopyranosyl bromide **14c**[7] (324 mg), 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide **15c**[8] (580 mg), and 2,3,4-tri-*O*-acetyl-6-deoxy-α-L-gulopyranosyl bromide **16c** (357 mg) under the same conditions gave, after column chromatography, **12b** [205 mg, 21%: syrup; $[\alpha]_D^{20}$ = -20.9° (*c* 0.6, chloroform); ^{1}H NMR data ($CDCl_3$) δ 3.75 (dd, 1H, $J_{1',10}$ = 1.2 Hz, $J_{1',2'}$ = 9.8 Hz, 1'-H), 4.33 (d, 1H,

$J_{1',10}$ = 1.2 Hz, 10-H)], **13b** [222 mg, 25%: syrup; $[\alpha]_D^{20}$ = -11.7° (*c* 1, chloroform); ^{1}H NMR data ($CDCl_3$) δ 3.75 (dd, 1H, $J_{1',10}$ = 1.3 Hz, $J_{1',2'}$ = 9.5 Hz, 1'-H), 4.32 (d, 1H, $J_{1',10}$ = 1.3 Hz, 10-H)], **14b** [255 mg, 56%: syrup; $[\alpha]_D^{20}$ = -44.6° (*c* 0.6, chloroform); ^{1}H NMR data ($CDCl_3$) δ 3.74 (dd, 1H, $J_{1',10}$ = 1.9 Hz, $J_{1',2'}$ = 9.6 Hz, 1'-H), 4.24 (d, 1H, $J_{1',10}$ = 1.9 Hz, 10-H)], **15b** [190 mg, 23%: syrup; $[\alpha]_D^{20}$ = +35.5° (*c* 0.4, chloroform); ^{1}H NMR data ($CDCl_3$) δ 3.81 (dd, 1H, $J_{1',10}$ = 1.6 Hz, $J_{1',2'}$ = 9.2 Hz, 1'-H), 4.33 (d, 1H, $J_{1',10}$ = 1.6 Hz, 10-H)], and **16b** [112 mg, 22%: syrup; $[\alpha]_D^{20}$ = -9.1° (*c* 0.4, chloroform); ^{1}H NMR data ($CDCl_3$) δ 3.93 (dd, 1H, $J_{1',10}$ = 1.6 Hz, $J_{1',2'}$ = 10.0 Hz, 1'-H), 4.31 (d, 1H, $J_{1',10}$ = 1.6 Hz, 10-H)], respectively.

Anal. Calcd for $C_{25}H_{24}O_{10}$: C, 61.98; H, 4.99. Found for **12b**: C, 61.90; H, 4.92. Found for **13b**: C, 61.87; H, 4.92.

Anal. Calcd for $C_{26}H_{26}O_{10}$: C, 62.65; H, 5.26. Found for **14b**: C, 62.57; H, 5.20. Found for **15b**: C, 62.60; H, 5.25. Found for **16b**: C, 62.70; H, 5.22.

Reaction of 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide **19**[7] under the above conditions gave a complex mixture. Column chromatography on silica gel led to the isolation of 2,3,4-tri-*O*-acetyl-L-rhamnose[7] as the only identified product.

Reaction of 4-*O*-acetyl-2,3-*O*-carbonyl-α-L-rhamnopyranosyl bromide **20**[12] (504 mg) yielded, after column chromatography, **17b** (204 mg, 27%) as a syrup: $[\alpha]_D^{20}$ = -70.1° (*c* 0.2, chloroform); ^{1}H NMR data ($CDCl_3$) δ 0.81 (d, 3H, $J_{5',6'}$ = 7 Hz, 6'-H_3), 3.60 (m, 1H, 5'-H), 3.88 (dd, 1H, $J_{1',2'}$ = 8.9 Hz, $J_{1',10}$ = 2.5 Hz, 1'-H), 4.36 (d, 1H, $J_{1',10}$ = 2.5 Hz, 10-H), 4.58 (dd, 1H, $J_{3',4'}$ = 7.6 Hz, $J_{2',3'}$ = 8.9 Hz, 3'-H), 4.64 (t, 1H, $J_{2',3'} = J_{1',2'}$ = 8.9 Hz, 2'-H), 5.06 (t, 1H, $J_{3',4'} = J_{4',5'}$ = 7.6 Hz, 4'-H).

Anal. Calcd for $C_{23}H_{20}O_9$: C, 62.73; H, 4.58. Found: C, 62.65; H, 4.51.

1,8-Dihydroxy-10-α-L-rhamnopyranosyl-9(10*H*)-anthracenone (17a). *C*-glycoside **17b** (C86 mg) was dissolved in dry methanol (10 mL) and treated with 0.1M MeONa/MeOH (3 mL) in the dark under helium. The mixture was stirred at room temperature for 1 h, neutralized by addition of Amberlite IR-120 (H^+) ion-exchange resin, filtered and concentrated. TLC of the residue (silica gel 0.5 mm; 9:1 chloroform-methanol, 1 run) gave **17a** (21 mg, 29%) as a syrup: $[\alpha]_D^{20}$ = -51.2° (*c* 0.3, DMSO); ^{1}H and ^{13}C NMR data: see the Table.

Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.47; H, 5.48.

C-Glycosides 11a-16a. A sample (0.2 mmol) of each acylated *C*-glycoside **11b-16b** was dissolved in dry CH_2Cl_2 (4 mL). To the cooled (-78 °C) solution M BCl_3/CH_2Cl_2 (1 mL) was added in the dark under stirring. The mixture was kept at -78

°C for 30 min, then allowed to warm to room temperature and stirred for 60 h. After this period, the solvent and BCl_3 were removed by a nitrogen stream. Methanol (2 mL) was added three times and each time removed by the gas stream. TLC (silica gel 0.5 mm; 9:1 chloroform-methanol, 1 run) of the residue gave deacylated *C*-glycoside.

1,8-Dihydroxy-10-β-D-glucopyranosyl-9(10*H*)-anthracenone **11a**: 47 mg, 60%; yellow solid; mp 120-122 °C (from 2-propanol; lit.[19] mp 123 °C); $[\alpha]_D^{20}$ = -21.6° (*c* 0.9, DMSO).

Anal. Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19. Found: C, 61.62; H, 5.12.

1,8-Dihydroxy-10-β-D-xylopyranosyl-9(10*H*)-anthracenone **12a**: 37 mg, 52%; amorphous mass; $[\alpha]_D^{20}$ = -56.9° (*c* 0.6, DMSO).

Anal. Calcd for $C_{19}H_{18}O_7$: C, 63.68; H, 5.06. Found: C, 63.60; H, 4.99.

1,8-Dihydroxy-10-α-L-arabinopyranosyl-9(10*H*)-anthracenone **13a**: 38 mg, 53%; amorphous mass; $[\alpha]_D^{20}$ = -33.8° (*c* 0.6, DMSO).

Anal. Calcd for $C_{19}H_{18}O_7$: C, 63.68; H, 5.06. Found: C, 63.66; H, 5.03.

1,8-Dihydroxy-10-(6'-deoxy-β-D-glucopyranosyl)-9(10*H*)-anthracenone **14a**: 43 mg, 58%; amorphous mass; $[\alpha]_D^{20}$ = -42.8° (*c* 0.5, DMSO).

Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.37; H, 5.43.

1,8-Dihydroxy-10-β-L-fucopyranosyl-9(10*H*)-anthracenone **15a**: 39 mg, 53%; amorphous mass; $[\alpha]_D^{20}$ = +4.3° (*c* 0.7, DMSO).

Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.60; H, 5.36.

1,8-Dihydroxy-10-(6'-deoxy-β-L-gulopyranosyl)-9(10*H*)-anthracenone **16a**: 38 mg, 51%; amorphous mass; $[\alpha]_D^{20}$ = +14.0° (*c* 0.8, DMSO).

Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.46; H, 5.30.

^1H and ^{13}C NMR data of **11a-16a**: see the Table.

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