

BENZOYLATED DERIVATIVES OF 2- β -GLUCOPYRANOSYLOXY-2,5-DIHYDROXYBENZYL ALCOHOL FROM *XYLOSMA FLEXUOSUM*:
STRUCTURE AND RELATIVE CONFIGURATION OF XYLOSMINSIMON GIBBONS,¹ ALEXANDER I. GRAY, PETER G. WATERMAN,*Phytochemistry Research Laboratories, Department of Pharmaceutical Sciences,
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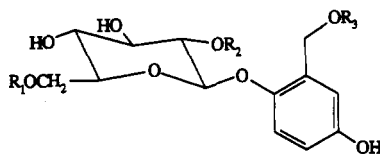
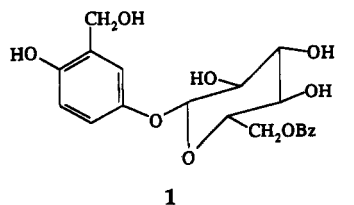
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ABSTRACT.—Comprehensive 2D nmr, ms, and X-ray diffraction studies have led to the characterization of a novel derivative of 2-(β -glucopyranosyloxy)-2,5-dihydroxybenzyl alcohol from the aerial parts of *Xylosma flexuosum*. This compound, which has been given the trivial name xylosmin, was identified as (*rel*)-2-([2,6-dibenzoyle]- β -glucopyranosyloxy)-5-hydroxy-benzyl-1*R*,2*R*,6*R*-trihydroxy-3-oxocyclohex-4-enoate. Three related compounds were identified as salireposide, poliothryside and 2'-benzoylpoliothryside, the last of which is also new.

In a recent paper (1) we reported the isolation of two novel derivatives of the 2-*O*-glucoside of 2,5-dihydroxybenzyl alcohol from *Poliothrysis sinensi* Hook. f. (Flacourtiaceae), both of which were characterized by the presence of the ester of 1 ξ -hydroxy-2-oxo-5-cyclohexene carboxylic acid. Similar phenolic glucosides were reported, at about the same time, from *Homalium ceylanicum* (2,3), another species of the Flacourtiaceae. Xylosmacin [1], a glucoside isomeric with poliothryside [2], had earlier been obtained (4) from *Xylosma velutina* (also Flacourtiaceae), and this observation has led us to investigate *Xylosma flexuosum* Hemsl. from Costa Rica, in the hope of finding more examples of this interesting group of metabolites.

By vlc and subsequent recrystallization a novel glycoside was obtained from the CHCl₃ extract of *X. flexuosum*. On the basis of fabms data, the empirical formula C₃₄H₃₂O₁₅ was established and the ¹H-nmr and ¹³C-nmr spectra showed resonances that were readily attributed to β -glucose, two benzoate esters, and a 2,5-



	R ₁	R ₂	R ₃
2	Bz	H	H
4	Bz	Bz	H
5	H	H	Bz

dihydroxybenzyl alcohol (Table 1). The placement of the benzoate esters at C-2 and C-6 of the glucose and the linkage of the glucose through an ether from C-1 of the sugar to C-2 of the benzyl alcohol was established unambiguously by analysis of the ²J and ³J heteronuclear couplings visualized through an HMBC experiment (Table 2) (5).

The benzylic oxymethylene signals were deshielded in the proton domain, indicating the presence of an esterifying group. From an analysis of nmr data

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TABLE 1. ^1H - and ^{13}C -Nmr Shift Values for Compounds 3-5.^a

Position	^1H			^{13}C		
	3	4	5	3	4	5
1	—	—	—	127.6	134.4	128.4
2	—	—	—	148.5	148.4	150.0
3	7.12 d (8.9)	7.04 d (8.7)	7.05 d (8.8)	118.6	117.9	119.9
4	6.62 dd (8.9, 2.9)	6.49 dd (8.7, 3.1)	6.52 dd (8.8, 3.0)	116.1	114.3	116.9
5	—	—	—	153.8	153.9	154.2
6	6.88 d (2.9)	6.88 d (3.1)	6.78 d (3.0)	116.0	114.9	117.3
7	5.18 d (13.3)	4.49 d (14.4)	5.35 d (12.5)	63.1	59.7	64.6
	5.10 d (13.3)	4.30 d (14.4)	5.25 d (12.5)			
1'	5.28 d (8.0)	5.20 d (8.1)	4.79 m	101.3	101.5	104.2
2'	5.39 dd (8.1, 8.0)	5.32 dd (9.5, 8.1)	3.52 m	75.2	75.3	75.1
3'	4.03 m	4.00 dd (9.5, 7.1)	3.52 m	75.7	75.3	78.0
4'	3.80 t (9.2)	3.74 dd (8.9, 7.1)	3.45 dd (10.0, 8.8)	71.9	72.0	72.2
5'	4.01 m	3.98 m	3.72 m	75.2	75.8	75.6
6'	4.83 dd (11.8, 2.0)	4.83 dd (11.8, 2.2)	4.71 dd (9.7, 2.0)	64.9	65.0	65.3
	4.54 dd (11.8, 7.2)	4.50 dd (11.8, 7.1)	4.42 dd (9.7, 5.2)			
1''	—	—	—	130.0	131.4	
2''/6''	8.08 dd (7.0, 1.4)	8.10 dd (6.2, 1.3)	—	130.3	130.5	
3''/5''	7.54 dt (7.3, 1.3)	7.57 dt (7.8, 1.5)	—	129.4	129.5	
4''	7.67 dt (7.3, 1.4)	7.68 dt (7.4, 1.3)	—	134.0	134.1	
7''	—	—	—	166.7	166.7	
1'''	—	—	—	130.0	131.3	
2'''/6'''	8.10 dd (7.0, 1.4)	8.09 dd (6.2, 1.3)	—	130.6	130.4	
3'''/5'''	7.49 dt (7.3, 1.3)	7.51 dt (7.8, 1.5)	—	129.4	129.5	
4'''	7.60 dt (7.3, 1.4)	7.63 dt (7.3, 1.3)	—	134.0	134.1	
7'''	—	—	—	166.3	166.2	
1''''	—	—	—	85.4		131.4
2''''	4.49 s	—	8.00 dd (6.9, 1.5)	76.9		130.8
3''''	—	—	7.49 t (7.9)	197.2		129.8
4''''	6.03 dd (10.4, 2.6)	—	7.62 dt (7.4, 1.2)	126.6		134.5
5''''	6.76 dd (10.4, 1.9)	—	7.49 t (7.9)	150.8		129.8
6''''	4.95 s	—	8.00 dd (6.9, 1.5)	71.4		130.8
7''''	—	—	—	171.4		173.0

^aSpectra of 3 were run in $\text{Me}_2\text{CO}-d_6$, and those of 4 and 5 in $\text{MeOH}-d_4$.

(Table 1) this ester contained two carbonyls (one an ester), two secondary and one tertiary oxygen-bearing carbons, and two cis-substituted olefinic protons. The ir spectrum suggested the presence of an α,β unsaturated ketone while a COSY-45 nmr spectrum revealed the spin system $-\text{CH}(\text{O})-\text{CH}=\text{CH}-\text{CO}-\text{CH}(\text{O})-$. An

analysis of the HMBC spectrum (Table 2) allowed this system to be encompassed in a six-membered ring, the sixth carbon being the oxygen-bearing quaternary. On this basis, the compound must be assigned structure 3, to which we have given the trivial name xylosmin.

An X-ray diffraction study of 3 (Fig-

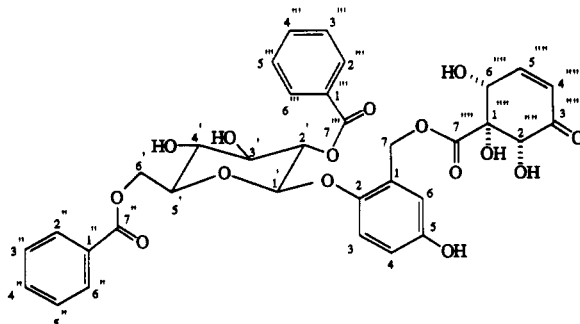


TABLE 2. Long-range C-H Connectivities in Compound **3**, Established by HMBC.^a

C/H	δ_H	2J	3J
3	7.12	116.1 (C-4), 148.5 (C-2)	127.6 (C-1), 153.8 (C-5)
4	6.62	118.6 (C-3), 153.8 (C-5)	148.5 (C-2)
6	6.88	153.8 (C-5)	63.1 (C-7), 116.1 (C-4), 148.5 (C-2)
7	5.18/5.10	127.6 (C-1)	116.0 (C-6), 148.5 (C-2), 171.4 (C-7''')
1'	5.28	75.2 (C-2')	148.5 (C-2)
2'	5.39	75.7 (C-3'), 101.3 (C-1')	166.3 (C-7''')
6'	4.83/4.54	75.2 (C-5')	71.9 (C-4'), 166.7 (C-7'')
2''/6''	8.08	129.4 (C-3''/5''), 130.0 (C-1'')	130.3 (C-2''/6''), 134.0 (C-4''), 166.7 (C-7'')
3''/5''	7.54	130.3 (C-2''/6''), 134.0 (C-4'')	129.4 (C-3''/5''), 130.0 (C-1'')
4''	7.67	129.4 (C-3''/5'')	130.3 (C-2''/6'')
2'''/6'''	8.10	129.4 (C-3'''/5'''), 130.0 (C-1''')	130.6 (C-2'''/6'''), 134.0 (C-4'''), 166.3 (C-7''')
3'''/5'''	7.49	130.6 (C-2'''/6'''), 134.0 (C-4''')	129.4 (C-3'''/5'''), 130.0 (C-1''')
4'''	7.60	129.4 (C-3'''/5''')	130.6 (C-2'''/6''')
2''''	4.49	85.4 (C-1''')	71.4 (C-6'''), 171.4 (C-7''')
4''''	6.03		71.4 (C-6'''), 76.9 (C-2''')
5''''	6.76		85.4 (C-1'''), 197.2 (C-3''')

^aSpectra were run in Me₂CO-*d*₆.

ure 1, Tables 3 and 4) was carried out in order to determine the relative stereochemistry of the substituents on the cyclohexenoic acid ester. The quaternary (C-1''') hydroxyl was found to be axial (assigned α relative), with the C-2''' and C-6''' hydroxyls both equatorial and α . In the crystal the cyclohexene ring adopts a "normal" half-boat conformation (Figure 1).

The three other glycosides isolated all showed the presence of the 2-

glucosyloxy-5-hydroxybenzyl alcohol. Two were identified as the known compounds poliothryside [2] and salireposide [5], the former by direct comparison with an authentic sample (1) and the latter by comparison with literature data (6). The third was identical to poliothryside except for the presence of an additional benzoyl esterifying group. This was placed at C-2' of the glucose on the basis of nmr

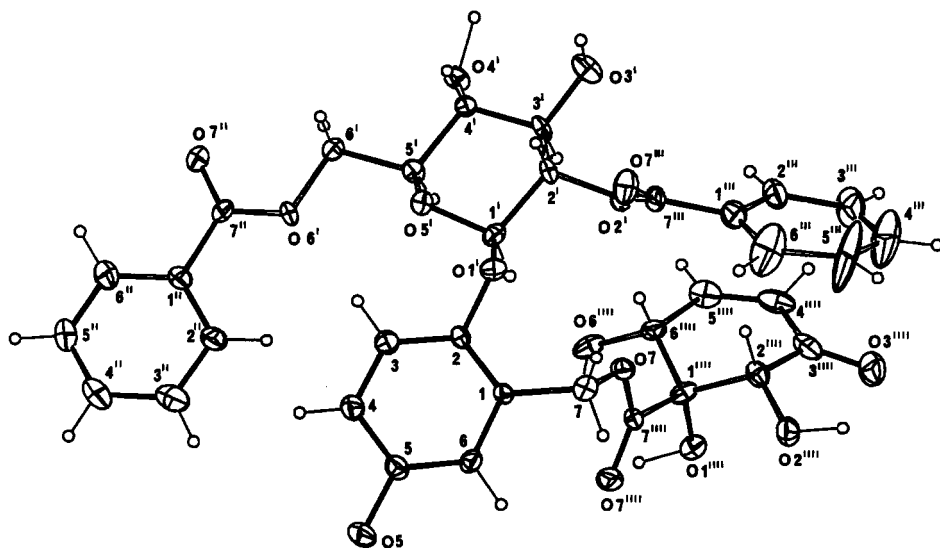


FIGURE 1. Molecular projection of **3**; 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

TABLE 3. Non-Hydrogen Positional and Isotropic Displacement Parameters for Compound 3.

Atom	x	y	z	U(eq) Å ²
C-1	0.1115 (8)	0.5000 (0)	0.5662 (7)	0.032 (4)
C-2	0.0868 (8)	0.379 (1)	0.5723 (7)	0.037 (4)
C-3	0.064 (1)	0.326 (1)	0.6573 (8)	0.055 (5)
C-4	0.065 (1)	0.398 (1)	0.7410 (8)	0.058 (5)
C-5	0.0922 (8)	0.519 (1)	0.7357 (8)	0.048 (4)
O-5	0.0953 (8)	0.588 (1)	0.8206 (6)	0.076 (4)
C-6	0.1185 (8)	0.570 (1)	0.6500 (8)	0.044 (4)
C-7	0.1345 (8)	0.560 (1)	0.4727 (8)	0.045 (4)
O-7	0.2352 (6)	0.523 (1)	0.4356 (5)	0.047 (3)
O-1'	0.0791 (5)	0.308 (1)	0.4869 (5)	0.044 (3)
C-1'	0.1632 (9)	0.223 (1)	0.4790 (7)	0.043 (3)
C-2'	0.1638 (9)	0.179 (1)	0.3747 (6)	0.037 (4)
O-2'	0.1966 (5)	0.275 (1)	0.3152 (5)	0.043 (3)
C-3'	0.2434 (8)	0.074 (1)	0.3686 (7)	0.041 (4)
O-3'	0.2363 (6)	0.027 (1)	0.2749 (5)	0.066 (3)
C-4'	0.2284 (8)	-0.027 (1)	0.4384 (7)	0.041 (4)
O-4'	0.3112 (6)	-0.112 (1)	0.4457 (5)	0.049 (3)
C-5'	0.2168 (8)	0.029 (1)	0.5414 (7)	0.041 (4)
O-5'	0.1328 (5)	0.118 (1)	0.5365 (5)	0.040 (3)
C-6'	0.1850 (9)	-0.068 (1)	0.6129 (8)	0.048 (4)
O-6'	0.1807 (6)	-0.010 (1)	0.7050 (5)	0.049 (3)
C-1''	0.170 (1)	-0.013 (1)	0.8723 (8)	0.054 (5)
C-2''	0.170 (1)	0.114 (2)	0.8736 (9)	0.066 (6)
C-3''	0.152 (1)	0.176 (2)	0.959 (1)	0.095 (7)
C-4''	0.133 (2)	0.105 (2)	1.041 (1)	0.102 (8)
C-5''	0.136 (2)	-0.019 (2)	1.037 (1)	0.109 (9)
C-6''	0.149 (1)	-0.080 (2)	0.952 (1)	0.094 (7)
C-7''	0.1926 (9)	-0.083 (1)	0.7825 (8)	0.043 (4)
O-7''	0.2088 (7)	-0.191 (1)	0.7806 (5)	0.057 (3)
C-1'''	0.166 (1)	0.420 (2)	0.1896 (8)	0.065 (5)
C-2'''	0.263 (1)	0.388 (2)	0.1474 (8)	0.063 (5)
C-3'''	0.297 (1)	0.466 (2)	0.076 (1)	0.106 (9)
C-4'''	0.243 (2)	0.569 (2)	0.047 (2)	0.16 (1)
C-5'''	0.161 (2)	0.592 (2)	0.087 (2)	0.20 (2)
C-6'''	0.112 (1)	0.527 (2)	0.164 (1)	0.129 (2)
C-7'''	0.122 (1)	0.339 (1)	0.2621 (8)	0.044 (4)
O-7'''	0.0274 (7)	0.332 (1)	0.2711 (6)	0.066 (4)
C-1''''	0.4208 (8)	0.544 (1)	0.4158 (9)	0.046 (4)
O-1''''	0.5153 (6)	0.598 (1)	0.4584 (5)	0.052 (3)
C-2''''	0.3984 (8)	0.593 (2)	0.3135 (8)	0.049 (5)
O-2''''	0.3756 (6)	0.721 (1)	0.3136 (5)	0.058 (3)
C-3''''	0.491 (1)	0.559 (2)	0.2550 (9)	0.065 (6)
O-3''''	0.5261 (9)	0.641 (1)	0.2031 (7)	0.098 (5)
C-4''''	0.535 (1)	0.440 (2)	0.268 (1)	0.068 (6)
C-5''''	0.5145 (9)	0.370 (2)	0.340 (1)	0.062 (5)
C-6''''	0.439 (1)	0.407 (1)	0.4108 (8)	0.048 (4)
O-6''''	0.4709 (6)	0.359 (1)	0.5032 (7)	0.064 (3)
C-7''''	0.3259 (9)	0.574 (1)	0.4740 (7)	0.038 (4)
O-7''''	0.3306 (6)	0.642 (1)	0.5424 (6)	0.059 (3)
C-01	0.472 (1)	0.486 (2)	0.808 (2)	0.21 (2)
O-01	0.476 (2)	0.557 (3)	0.891 (2)	0.49 (3)
C-02	0.561 (1)	0.450 (2)	0.774 (1)	0.13 (1)
C-03	0.363 (2)	0.437 (4)	0.760 (2)	0.26 (2)

TABLE 4. Non-Hydrogen Bond Lengths (Å) for Compound 3.

Atom	Distance	Atom	Distance
C-1—C-2	1.35 (1)	C-1 ^{'''} —C-2 ^{'''}	1.42 (2)
C-1—C-6	1.39 (1)	C-1 ^{'''} —C-6 ^{'''}	1.38 (3)
C-1—C-7	1.49 (1)	C-1 ^{'''} —C-7 ^{'''}	1.47 (2)
C-2—C-3	1.36 (2)	C-2 ^{'''} —C-3 ^{'''}	1.39 (3)
C-2—O-1'	1.41 (1)	C-3 ^{'''} —C-4 ^{'''}	1.36 (4)
C-3—C-4	1.40 (2)	C-4 ^{'''} —C-5 ^{'''}	1.23 (4)
C-4—C-5	1.37 (2)	C-5 ^{'''} —C-6 ^{'''}	1.45 (4)
C-5—O-5	1.39 (2)	C-7 ^{'''} —O-7 ^{'''}	1.19 (2)
C-5—C-6	1.37 (2)	C-1 ^{'''} —O-1 ^{'''}	1.41 (1)
C-7—O-7	1.45 (1)	C-1 ^{'''} —C-2 ^{'''}	1.52 (2)
O-7—C-7 ^{'''}	1.34 (1)	C-1 ^{'''} —C-6 ^{'''}	1.51 (2)
O-1'—C-1'	1.41 (2)	C-1 ^{'''} —C-7 ^{'''}	1.52 (2)
C-1'—C-2'	1.52 (1)	C-2 ^{'''} —O-2 ^{'''}	1.41 (2)
C-1'—O-5'	1.45 (2)	C-2 ^{'''} —C-3 ^{'''}	1.51 (2)
C-2'—O-2'	1.41 (2)	C-3 ^{'''} —O-3 ^{'''}	1.25 (2)
C-2'—C-3'	1.52 (2)	C-3 ^{'''} —C-4 ^{'''}	1.40 (3)
O-2'—C-7 ^{'''}	1.35 (1)	C-4 ^{'''} —C-5 ^{'''}	1.30 (2)
C-3'—O-3'	1.39 (1)	C-5 ^{'''} —C-6 ^{'''}	1.46 (2)
C-3'—C-4'	1.48 (2)	C-6 ^{'''} —O-6 ^{'''}	1.42 (2)
C-4'—O-4'	1.39 (2)	C-7 ^{'''} —O-7 ^{'''}	1.20 (2)
C-4'—C-5'	1.57 (2)	C-01—O-01	1.39 (4)
C-5'—O-5'	1.43 (2)	C-01—C-02	1.29 (3)
C-5'—C-6'	1.51 (2)	C-01—C-03	1.57 (3)
C-6'—O-6'	1.42 (1)		
O-6'—C-7 ^{'''}	1.33 (2)		
C-1 ^{''} —C-2 ^{''}	1.38 (2)		
C-1 ^{''} —C-6 ^{''}	1.36 (2)		
C-1 ^{''} —C-7 ^{''}	1.50 (2)		
C-2 ^{''} —C-3 ^{''}	1.40 (2)		
C-3 ^{''} —C-4 ^{''}	1.40 (3)		
C-4 ^{''} —C-5 ^{''}	1.35 (3)		
C-5 ^{''} —C-6 ^{''}	1.37 (2)		
C-7 ^{''} —O-7 ^{''}	1.20 (2)		

studies (Table 1) allowing its identification as 2'-benzoylpoliiothrysoside [4], which is novel.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps were obtained on a Gallenkamp melting-point apparatus and are uncorrected. Uv spectra were run in EtOH and ir spectra were recorded as KBr disks. Nmr spectra were run on a Bruker AMX400 instrument using standard microprograms (HMBC with d_6 set for $J=7$ Hz) and in $(\text{CD}_3)_2\text{CO}$ unless otherwise stated. Fabms were obtained using a NOBA matrix.

PLANT MATERIAL.—The aerial parts of *Xylosma flexuosum* were collected near the entrance to Santa Rosa National Park, Costa Rica, in August 1992. A voucher specimen has been deposited at the Herbarium of the Instituto Nacional de Biodiversidad, Costa Rica.

EXTRACTION AND ISOLATION.—Ground aerial parts (1 kg) were extracted by a Soxhlet apparatus successively with petroleum ether (bp 40–60°), CHCl_3 , and MeOH. The CHCl_3 -soluble fraction was subjected to vlc over Si gel 60H eluting with petroleum ether and then petroleum ether containing increasing volumes of EtOAc. The eluate obtained with 80% EtOAc contained predominantly one compound which was recrystallized to give **3** (120 mg).

The MeOH-soluble fraction was treated in an identical manner. Elution with 90% EtOAc in petroleum ether followed by concentration of the eluate and recrystallization gave **4** (147 mg). Elution with 7% MeOH in EtOAc and subsequent circular prep. tlc [Si gel 60F₂₅₄; CHCl_3 -MeOH (17:3)] gave **2** (22 mg). Prep. tlc of the 15% EtOAc in MeOH fraction [Si gel 60F₂₅₄; CHCl_3 -MeOH (9:1, multiple elution)] yielded **5** (20 mg).

Poliiothrysoside [2].—Amorphous solid, $[\alpha]_D^{+40}$ ($c=0.1$, MeOH). Identical in all respects with a sample isolated from *Poliiothrysis sinensis* (1).

Xylosmin [3].—Cubes, mp 138°; $[\alpha]_D -4^\circ$ ($c=0.1$, MeOH); uv λ max 280 nm; ir ν max 3421, 1734, 1705 cm^{-1} ; ^1H - and ^{13}C -nmr data, see Table 1; fabms m/z 703 $[(\text{M}+\text{Na})^+, \text{C}_{34}\text{H}_{32}\text{O}_{15}\text{Na}]$.

Crystal data.— $\text{C}_{34}\text{H}_{32}\text{O}_{15} \cdot \text{C}_3\text{H}_6\text{O}$, $M=738.7$. Monoclinic, space group $P2_1$ (C_2^2 , No. 4), $a=12.474(2)$, $b=10.874(1)$, $c=13.867(2)$ Å, $\beta=93.94(1)^\circ$, $U=1876.5(5)$ Å³. D_c ($Z=2$) = 1.31 $\text{g}\cdot\text{cm}^{-3}$; $F(000)=764$. $\mu_{\text{Mo}}=1.0$ cm^{-1} ; specimen: $0.41 \times 0.38 \times 0.09$ mm.

Structure determination and analysis.—A unique diffractometer data set (2θ max 50° , $2\theta/\theta$ scan mode; monochromatic Mo K α radiation, $\lambda 0.71073$ Å) was measured at $\approx 295^\circ$ K, yielding 3278 independent reflections; 2271 with $I > 3\sigma(I)$ were considered "observed" and used in the full matrix least squares refinement without absorption correction, after solution of the structure by direct methods. Anisotropic thermal parameters were refined for C, O; difference map artifacts were modeled as an Me_2CO of solvation. Thermal motion of the latter was very high; refinement of site occupancy yielded a value not significantly different from unity and it was constrained at that value after assignment of the oxygen on the basis of geometry and of refinement behavior. Nevertheless, vibrational amplitudes on the solvent are unrealistic and probably a foil for unresolved disorder. In the glycoside, high vibrational amplitudes are also found in a number of peripheral groups. Hydroxylic hydrogen atoms were located in difference maps and, together with the ring hydrogen atoms, were included with (x , y , z , U_{150}) constrained at "improved"/estimated values (exception: the hydrogen of O-5 which was not locatable; O-5 has no particularly strong interactions with other nearby oxygen atoms and the hydrogen may be inherently "diffuse." Hydrogen-bonding interactions in general are in keeping with the high thermal motion, involving no O...O contacts less than 2.7 Å). In consequence of the above considerations, final conventional residuals R , R_w , and $|F|$ are unpleasantly high at 0.077, 0.089, although the required connectivity and stereochemistry are unambiguous. Neutral atom complex scattering factors were employed; computation used the XTAL 3.2 program system

implemented by Hall (7). Pertinent results are given in Figure 1 and Tables 3 and 4.²

2'-Benzoylpolyothryoside [4].—Amorphous solid, mp 175°; $[\alpha]_D 0^\circ$ ($c=0.1$, MeOH); uv λ max 280 nm; ir ν max 3600–3200, 2950, 1714, 1638, 1618, 1498, 1452, 1275, 1208 cm^{-1} ; ^1H - and ^{13}C -nmr data, see Table 1; fabms m/z 533 $(\text{M}+\text{Na})^+$, 511 $[(\text{M}+\text{H})^+; \text{C}_{27}\text{H}_{22}\text{O}_{10}]$, 493, 371.

Salireposide [5].—Amorphous solid, mp 205° [lit. (6) 206–207°]; $[\alpha]_D -15^\circ$ ($c=0.1$, Me_2CO); uv λ max 280 nm; ir ν max 3682, 3450, 2974, 1712, 1609, 1584, 1455, 1391, 1123, 1068 cm^{-1} ; ^1H - and ^{13}C -nmr data, see Table 1; fabms m/z 429 $[(\text{M}+\text{Na})^+; \text{C}_{20}\text{H}_{22}\text{O}_9\text{Na}]$, 415, 389, 371, 353, 321, 307.

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²Hydrogen coordinates, thermal parameters, bond distances and angles, and observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre and can be obtained upon request from Dr. Olga Kennard, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK.