GLUCOSIDES OF 2,5-DIHYDROXYBENZYL ALCOHOL FROM *HOMALIUM LONGIFOLIUM*

KHOZIRAH SHAARI and PETER G. WATERMAN*

Chemistry Division, Forest Research Institute Malaysia, 52109, Kuala Lumpur, Malaysia; * Phytochemistry Research Laboratories, Department of Pharmaceutical Sciences, University of Strathclyde, Glasgow G1 1XW, U.K.

Abstract—The stems and leaves of *Homalium longifolium* have yielded eight novel glucosides based on a 2-(β-glucopyranosyloxy)-5-hydroxybenzyl alcohol skeleton. These have been characterized as 2-(β-glucopyranosyloxy)-7-{2-[(2-oxo-2-phenyl)ethyl]benzoyl}-5-hydroxybenzyl alcohol, 2-(6-benzoyl-β-glucopyranosyloxy)-7-[{2-(2-oxo-2-phenyl)ethyl]benzoyl}-5-hydroxybenzyl alcohol, 2-(2-*p*-coumaroyl-6-benzoyl-β-glucopyranosyloxy)-5-hydroxybenzyl alcohol, 2-(4,6-dibenzoyl-β-glucopyranosyloxy)-5-hydroxybenzyl alcohol, (*rel*)-2-(6-benzoyl-β-glucopyranosyloxy)-7-(1α, 2α, 6α-trihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol, (*rel*)-2-(6-benzoyl-β-glucopyranosyloxy)-7-(6α-benzoyloxy-1α, 2α-dihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol, (*rel*)-2-(4,6-dibenzoyl-β-glucopyranosyloxy)-7-(1α, 2α, 6α-trihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol and (*rel*)-2-(4,6-dibenzoyl-β-glucopyranosyloxy)-7-(6α-benzoyloxy-1α, 2α-dihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol. All compounds were characterized primarily by extensive use of 2D homonuclear and heteronuclear NMR experiments.

INTRODUCTION

Previously we have reported the isolation and structures of novel glucosides of 2,5-dihydroxybenzyl alcohol from the Malaysian flacourtiaceous species, *Scolopia spinosa* [1]. In a continuing investigation of the chemistry of the Malaysian Flacourtiaceae [1–3], we have examined the stems and leaves of *Homalium longifolium* Benth., a rain forest tree common in the southern part of the Malay Peninsula [4]. In this paper we wish to report the isolation of the known 2,5-trihydroxybenzyl alcohol glucoside poliothrysoside [5] together with eight other novel glucosides. These have been characterized on the basis of extensive NMR studies using COSY-45, COSY-LR, NOESY, TOCSY, HC-COBI and HMBC experiments. The glucose and benzyl alcohol carried a number of esterifying groups including benzoic acid, *p*-coumaric acid, 1,2,6-trihydroxy-5-oxocyclohex-3-enoic acid, and the unusual 2-{(2-oxo-2-phenyl) ethyl}benzoic acid.

RESULTS AND DISCUSSION

The glucosides were found to be concentrated in separate EtOAc extracts of the stems and leaves of *H. lon-*

gifolium. The EtOAc extract of the stems was subjected to VLC over silica gel 60 H, eluting with CHCl$_3$ and then CHCl$_3$ containing increasing amounts of MeOH. Concentration of the 10–15% MeOH fraction gave **1**, and column chromatography of the mother liquor yielded **2** and **3**.

The major compound **1**, obtained as an amorphous powder, analysed for C$_{28}$H$_{28}$O$_{10}$ by means of FAB-mass spectrometry. The ^{1}H NMR spectrum (Table 1) revealed signals attributable to a β-glucopyranosyl unit and three aromatic systems, one of which was the 2,5-dioxygenated benzyl alcohol unit, which was demonstrated by an HMBC experiment [6] to be linked to the glucose anomeric carbon through the C-2 oxygen. The benzylic methylene protons were observed to be deshielded and exhibited a ^3J correlation to an ester carbonyl carbon (δ_c 167.6) indicating esterification at this position. Analysis of the ^{1}H and ^{13}C NMR, COSY-45 and TOCSY spectra revealed that the esterifying group comprised of benzoyl and 2-methylbenzoyl spin systems, of which the latter was esterified to the benzyl alcohol. The HMBC experiment established the linkage between the two benzoyl moieties to be via the methylene (δ_c 45.8), the protons of which showed ^2J coupling to the carbonyl at δ_c 197.8 (C-7$'''$), requiring the part structure
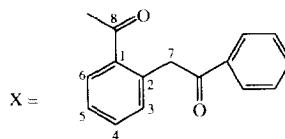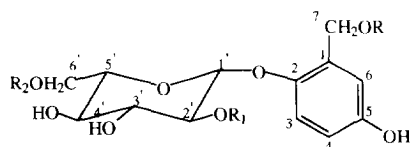
1 R = X; R₁ = H; R₂ = H

2 R = X; R₁ = H; R₂ = benzoyl

3 R = H; R₁ = para coumaroyl; R₂ = benzoyl
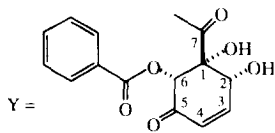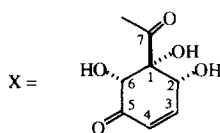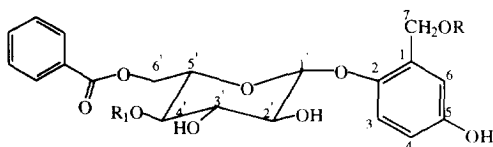
4 R = H; R₁ = benzoyl

5 R = X; R₁ = H

6 R = Y; R₁ = H

7 R = X; R₁ = benzoyl

8 R = Y; R₁ = benzoyl

to be 2-{(2-oxo-2-phenyl) ethyl}benzoic acid. Thus **1** was assigned as 2-(β-glucopyranosyloxy)-7-{2-(2-oxo-2-phenyl) ethyl}benzoyl-5-hydroxybenzyl alcohol. Full and unambiguous ^{1}H and ^{13}C NMR assignments are given in Tables 1 and 2, and C–H long-range correlations visible in the HMBC spectrum in Table 3.

The second compound (**2**) gave an [M + Na]$^+$ peak at 651 in the FAB-mass spectrum which suggested an empirical formula of $C_{35}H_{32}O_{11}$ (**1** + C_7H_4O). Both ^{1}H and ^{13}C NMR spectra revealed a structure comparable to that of **1** (see Tables 1 and 2) with additional resonances attributable to a benzoate ester. The H_2-6 protons of the glucose were deshielded in comparison to **1** and a ^3J correlation to the carbonyl of the benzoate ester in the HMBC spectrum confirmed the presence of a 6-benzoylated glucoside. Thus, **2** was identified as 2-(6-benzoyl-β-glucopyranosyloxy)-7-{2-(2-oxo-2-phenyl) ethyl}benzoyl-5-hydroxybenzyl alcohol.

The FAB-mass spectrum of **3** indicated an empirical formula $C_{29}H_{28}O_{11}$. The ^{1}H NMR spectrum (Table 1), when compared to those of **1** and **2**, suggested the presence of 6-benzoyl-β-glucopyranosyloxy and 2,5-oxygenated benzyl alcohol systems. The latter was again shown by an HMBC experiment to be linked to the anomeric position via the C-2 oxygen. There were no signals for an esterifying group on C-7 of the benzyl alcohol but analysis of the ^{1}H and ^{13}C NMR (Table 2), COSY-45 and TOCSY spectra revealed that a new esterifying group, comprising a carbonyl (δ_c 167.5), trans-olefins (J 15.9 Hz) at δ_H 8.03 (δ_c 146.4) and 6.67 (115.3), and four aromatic methines centred at δ_H 7.51 (2H, d, J 8.6 Hz) and 7.15 (2H, d, J 8.6 Hz) with a spin-coupling system indicating a 1,4 disubstituted benzene ring. The presence of an additional oxygenated quaternary carbon at δ_c 162.1 in the ^{13}C NMR spectrum suggested a hydroxyl group as the substituent, thus identifying the new esterifying group as p-coumaric acid. The deshielded chemical shift value of the glucose H-2 and a ^3J correlation from it to the carbonyl at δ_c 167.5 confirmed **3** to be 2-(2-p-coumaroyl-6-benzoyl-δ-glucopyranosyloxy)-5-hydroxybenzyl alcohol.

The EtOAc extract of the leaves was subjected to VLC, eluting with hexane, and then hexane containing increasing amounts of EtOAc. A combination of column chromatography (Sephadex LH-20, followed by silica gel) and PTLC of the VLC fractions yielded **4–8** and poliothrysoside. Poliothrysoside [2-(6-benzoyl-β-glucopyranosyloxy)-5-hydroxybenzyl alcohol] has previously been isolated from *Poliothrysis sinensis* [5] and *Scolopia spinosa* [1].

The simplest of the leaf compounds, **4**, was solved for $C_{27}H_{26}O_{10}$ by FAB-mass spectrometry. The NMR spectra showed resonances associated with 2,5-oxygenated benzyl alcohol and 6-benzoyl-β-glucopyranose, plus an additional benzoyl ester which was placed at C-4 of the glucose by a ^3J coupling between H-4 and the ester carbonyl resonating at δ_c 166.8. This substitution was further confirmed by the strongly deshielded chemical shift value of H-4. Thus, **4** must be 2-(4,6-dibenzoyl-β-glucopyranosyloxy)-5-hydroxybenzyl alcohol. ^{1}H and ^{13}C NMR data are recorded in Tables 1 and 2, respectively.

Compound **5** displayed an [M + Na]$^+$ ion at m/z 599 in the FAB-mass spectrum suggesting an empirical formula of $C_{27}H_{28}O_{14}$. The NMR spectra (Tables 1 and 2) again revealed resonances for benzyl alcohol and 6-benzoyl-β-

Table 1. ¹H NMR chemical shift and coupling constant data for compounds 1-8

	H	1	2	3	4	5	6	7	8
Glucose	1	5.43 d (7.6)	5.37 d (7.5)	5.54 d (8.1)	5.46 d (8.0)	5.35 d (7.1)	5.24 d (7.6)	5.44 d (7.7)	5.35 d (7.9)
	2	4.25 m	4.30 m	6.06 dd (9.3,8.1)	4.44 m	4.32 m	4.22 m	4.40 m	4.34 m
	3	4.32 m	4.30 m	4.51 d (8.9)	4.56 t (8.8)	4.32 m	4.29 m	4.60 t (9.0)	4.53 t (9.1)
	4	4.32 m	4.18 m	4.29 t (8.2)	5.96 t (9.6)	3.88 m	4.15 m	5.94 t (9.6)	5.90 t (9.4)
	5	4.04 m	4.23 m	4.36 m	4.44 m	3.88 m	4.15 m	4.40 m	4.35 m
	6	4.54 d (13.2)	5.27 dd (11.6, 1.8)	5.30 d (15.7)	4.94 dd (12.0, 2.4)	5.28 d (11.5)	5.26 m	4.91 d (12.1)	4.90 dd (12.0, 2.8)
		4.39 dd (13.2, 5.2)	4.93 dd (11.6, 4.7)	4.94 dd (15.7, 6.9)	4.84 dd (12.0, 6.4)	4.93 dd (11.5, 6.4)	4.91 dd (11.5, 6.6)	4.81 dd (12.1, 6.5)	4.80 dd (12.0, 6.5)
Benzyl alcohol	3	7.59 d (8.8)	7.59 d (8.7)	7.57 d (8.7)	7.65 d (8.5)	7.59 d (8.6)	7.53 d (8.8)	7.59 d (8.4)	7.55 d (8.8)
	4	7.07 dd (8.8, 2.9)	7.03 dd (8.8, 3.0)	7.04 dd (8.7, 3.2)	7.05 dd (8.7, 3.0)	7.04 dd (8.7, 2.4)	6.96 dd (8.7, 3.0)	7.04 dd (8.7, 2.8)	6.97 dd (8.8, 3.0)
	6	7.38 d (2.0)	7.33–7.37 m	7.84 d (3.2)	7.67 d (2.3)	7.50 d (2.7)	7.40 m	7.52 d (2.8)	7.42 m
	7	5.75 d (13.2)	5.73 br s	5.34 d (12.6)	5.45 d (12.6)	5.80 d (12.9)	5.73 d (12.9)	5.90 d (12.9)	5.76 d (12.6)
		5.72 d (13.2)	5.15 d (13.6)	5.37 d (12.6)	5.26 d (12.6)	5.68 d (12.6)	5.75 d (12.6)	5.68 d (12.6)	5.78 d (12.5)
Methylbenzoyl	3	7.38 m	7.38–7.51m						
	4	7.47m	7.40–7.47 m						
	5	7.26 m	7.23 m						
	6	8.18 d (7.8)	8.15 dd (7.9, 1.1)						
	CH₂	4.92 s	4.89 s						
Benzoyl	2/6	8.22 d (7.6)	8.18–8.21 m						
	3/5	7.47 m	7.40–7.47m						
	4	7.55 m	7.38–7.51 m						
6'-Benzoyl	2/6			8.21 d (8.5)	8.20 d (7.8)	8.22 d (7.1)	8.22 dd (8.3, 1.2)	8.24 d (7.7)[a]	8.18 d (8.3, 1.2)
	3/5			7.37 m	7.37 m	7.38 t (7.2)	7.40 m	7.36 t (7.0)	7.37 m
	4			7.47 tt (8.7, 1.3)	7.53 t (7.4)	7.45 t (7.2)	7.46 t (7.2)	7.44 t (7.8)[b]	7.50 m
4'-Benzoyl	2/6				8.26 d (8.0)			8.19 d (7.9)[a]	8.25 dd (8.3, 1.2)
	3/5				7.37 m			7.36 t (7.0)	7.37 m
	4				7.46 t (7.3)			7.44 t (7.8)[b]	7.50 m
p-Coumaroyl	8			6.67 d (15.9)					
	7			8.03 d (15.9)					
	2/6			7.51 d (8.6)					
	3/5			7.15 d (8.6)					
7-Cyclohexenoyl	2					5.49 br s	5.63 br t	5.51 br s	5.66 t (2.2)
	3					6.99 dd (10.3, 1.7)	7.06 dd (10.4, 2.0)	7.00 d (11.5)	7.09 dd (10.4, 2.0)
	4					6.25 dd (10.3, 2.5)	6.29 dd (10.3, 2.1)	6.26 dd (10.3, 2.1)	6.31 dd (10.3, 2.6)
	6					5.07 s	6.59 s	5.09 s	6.61 s
Benzoyl	2/6						8.09 dd (8.3, 11.2)		8.09 dd (8.3, 1.2)
	3/5						7.20 t (7.7)		7.20 m
	4						7.40 m		7.50 m

Coupling constants (J/H_z) in parentheses.
[a,b] Interchangeable signals.

Table 2. ^{13}C NMR chemical shift data for compounds **1–8**

	C	1	2	3	4	5	6	7	8
Glucose	1	104.9	105.2	102.4	105.6	104.9	105.2	105.0	105.3
	2	75.4	75.3	75.3	75.7	75.4	75.3	75.5	75.4
	3	79.1	79.0	76.7	76.2	78.9	78.9	76.0	76.0
	4	71.8	72.1	72.4	73.6	72.2	72.2	73.6	73.5
	5	79.3	75.9	76.0	73.4	76.0	75.9	73.3	73.3
	6	63.0	65.8	65.6	64.7	65.8	65.8	64.7	64.1
Benzyl alcohol	1	128.4	128.8	135.6	135.9	128.6	128.1	128.8	128.4
	2	149.8	149.7	148.6	149.9	149.7	149.8	149.5	149.7
	3	119.2	119.9	118.4	120.2	120.0	120.5	120.3	120.7
	4	116.9	116.6	114.8	115.5	117.0	117.2	117.0	117.3
	5	154.8	155.1	155.4	155.5	155.1	155.2	155.4	155.4
	6	116.6	116.8	115.3	116.5	117.3	117.4	117.3	117.5
	7	63.0	62.9	59.9	61.0	64.0	64.2	63.9	64.7
Methylbenzoyl	C =O	167.6	167.5						
	1	131.0	130.9						
	2	138.7	138.7						
	3	133.7	133.7ᵃ						
	4	133.1	133.0						
	5	127.9	127.8						
	6	131.8	131.8						
	CH$_2$	45.8	45.7						
Benzoyl	C =O	197.8	197.7						
	1	138.3	138.3						
	2/6	129.1	129.1						
	3/5	129.5	129.4						
	4	133.7	133.6ᵃ						
6'-Benzoyl	C =O		167.0	167.0	166.8	167.1	167.0	166.7	166.8
	1		131.3	131.0	131.4	131.3	131.4	131.1ᵃ	131.1ᵃ
	2/6		130.5	130.5	130.7	130.5	130.5	130.6	130.7ᵇ
	3/5		129.2	129.3	129.3	129.3	129.3	129.3	129.3
	4		133.6	134.1	133.8	133.8	133.9	133.8ᵇ	134.0
4'-Benzoyl	C =O				166.8			166.7	166.8
	1				131.1			131.0ᵃ	131.0ᵃ
	2/6				130.6			130.6	130.6ᵇ
	3/5				129.4			129.3	129.3
	4				133.9			134.0ᵇ	134.0
p-Coumaroyl	C =O			167.5					
	1			126.6					
	2/6			131.3					
	3/5			117.3					
	4			162.1					
	7			146.4					
	8			115.3					
7-Cyclohexenoyl	C =O					173.0	172.0	173.0	173.0
	1					87.3	85.4	87.3	85.4
	2					72.6	72.8	72.6	72.8
	3					151.4	152.0	151.4	152.0
	4					127.3	127.2	127.3	127.2
	5					198.8	192.3	198.7	192.2
	6					78.5	79.5	78.5	79.5
Benzoyl	C =O						166.2		166.2
	1						130.4		130.4
	2/6						130.8		130.8
	3/5						129.2		129.2
	4						134.0		134.0

ᵃ,ᵇInterchangeable signals.

Table 3. Long-range C–H correlations from an HMBC experiment on compound **1**

H	^2J	^3J
H-1'	—	149.8 (C-2)
H-2'	79.1 (C-3'), 104.9 (C-1')	—
H-3'	71.8 (C-4')	75.4 (2')
H-4'	79.1 (C-3')	—
H-6'	79.3 (C-5')	71.8 (C-4')
H-3	149.8 (C-2)	128.4 (C-1), 154.8 (C-5)
H-4	154.8 (C-5)	116.6 (C-6), 149.8 (C-2)
H-6	154.8 (C-5)	63.0 (C-7), 116.9 (C-4), 149.8 (C-2)
H-7	128.4 (C-1)	116.6 (C-6), 14.8 (C-2), 167.6 (C-8")
H-3"	—	45.8 (C-7"), 127.9 (C-5"), 131.0 (C-1")
H-4"	127.9 (C-5")	131.8 (C-6"), 138.7 (C-2")
H-5"	—	131.0 (C-1"), 133.7 (C-3")
H-6"	—	133.1 (C-4"), 138.7 (C-2"), 167.6 (C-8")
H-7"	138.7 (C-2"), 197.8 (C-7''')	131.0 (C-1"), 133.7 (C-3")
H-2'''/6'''	138.3 (C-1''')	129.1 (C-6'''/2'''), 133.7 (C-4'''), 197.8 (C-7''')
H-3'''/5'''	—	129.5 (C-5'''/3'''), 138.3 (C-1''')
H-4'''	—	129.1 (C-2'''/6''')

glucopyranose. The deshielded chemical shift value of the benzyl alcohol oxymethylene protons with respect to those of **3** suggested placement of the additional esterifying group at this position. Confirmation of this was provided by a ^3J coupling between the oxymethylene protons of the benzyl alcohol with an ester carbonyl at δ_c 173.0. Signals for the new esterifying group comprised a ketone (δ_c 198.8), a *cis*-olefin, an oxygen-bearing aliphatic quaternary carbon (δ_c 87.3) and two oxymethines. Inspection of the HMBC spectrum revealed that the olefinic proton at δ_H 6.99 had ^3J correlations with the oxygen-bearing aliphatic quaternary carbon (δ_c 87.3) and the ketone (δ_c 198.8), whilst the other olefinic proton at δ_H 6.25 showed ^3J correlations to the two oxymethines (δ_c 72.6 and 78.5). A combination of COSY-45 and COSY-LR indicated the spin system R-CH(OH)–CR(OH)–CH(OH)–CH = CH–R. These data were in agreement with the 1,2,6-trihydroxy-5-oxocyclohex-3-ene carboxylic acid moiety which has recently been determined, by X-ray crystallography, as part of a similar benzyl alcohol glucoside (xylosmin) isolated from *Xylosma flexuosa* [7]. Both **5** and xylosmin showed a small negative optical rotation and similar coupling constant for the protons of the cyclohexenone ring, suggesting that in **5** the three hydroxyl substituents were equatorial/axial/equatorial, as in xylosmin. Thus, **5** was assigned as (*rel*)-2-(6-benzoyl-β-glucopyranosyloxy)-7-(1α, 2α, 6α-trihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol.

Compound **6** analysed for $C_{34}H_{32}O_{15}$ (**5** + C_7H_5O) by means of FAB-mass spectrometry. The ^1H and ^{13}C NMR spectra (Tables 1 and 2) revealed a structure identical to that of **5** plus signals attributable to an additional benzoyl group. Inspection of the HMBC spectrum showed that the additional ester carbonyl was correlated to the H-6 oxymethine proton of the cyclohexenoic acid ester function. A 1.5 ppm deshielding observed for this oxymethine proton with respect to that of **5** confirmed the conclusion and, thus,

6 was established as (*rel*)-2-(6-benzoyl-β-glucopyranosyloxy)-7-(6α-benzoyloxy-1α, 2α- dihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol.

Compound **7**, the major leaf glucoside, showed an FAB-mass spectrum that suggested an empirical formula identical to **6** ($C_{34}H_{32}O_{15}$). The NMR spectra of **7** also showed resonances attributable to the partial structure **5** and an additional benzoyl group. However, in this case the benzoate ester was linked to the glucose C-4 rather than to the C-6 position of the cyclohexenoyl moiety, as indicated by the deshielded chemical shift value of H-4' and a ^3J coupling from H-4' to an ester carbonyl at δ_c 166.7. Thus, **7** was assigned as (*rel*)-2-(4,6-dibenzoyl-β-glucopyranosyloxy)-7-(1α, 2α, 6α-trihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol. An anomalous positive optical rotation can probably be attributed to the presence of small amounts of a contaminant, the material being only 95% pure by NMR.

The final compound **8** gave an $[M + Na]^+$ at 807 in the FAB-mass spectrum suggesting an empirical formula of $C_{41}H_{36}O_{16}$ (**7** + C_7H_4O) . Examination of both the ^{13}C and the very congested ^1H NMR spectra revealed a partial structure identical to **7** plus, once again, an additional benzoyl group. Placement of the additional benzoate ester was once again traced from a ^3J-coupling, this time between H-6 of the cyclohexenoic acid ester function and the relevant ester carbonyl. Like **6**, H-6 was deshielded by about 1.5 ppm with respect to **7**. Thus, **8** was identified as (*rel*)-2-(4,6-dibenzoyl-β-glucopyranosyloxy)-7-(6α-benzoyloxy-1α, 2α-dihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol.

Similar glucosides of benzyl alcohol have also been isolated from another species of *Homalium*, *Homalium ceylanicum* [8,9], and from *Scolopia spinosa* [1], *Poliothrysis sinensis* [5], *Xylosma velutina* [10] and *X. flexuosa* [7]. *Homalium longifolium* is unusual in esterification of

EXPERIMENTAL

Mps uncorr. UV: MeOH. IR: KBr. NMR spectra were run using standard Bruker microprogrammes (HMBC with d_6 set of $J = 7$ Hz, NOESY with d_8 set for 0.8 msec) and in pyridine-d_5 unless otherwise stated. FAB-MS were recorded with NOBA matrix. Petrol refers to petroleum (bp 40–60°).

Plant material. Stems and leaves of *H. longifolium* were collected from permanent plots in the Pasoh Forest Reserve, Negeri Sembilan, Peninsular Malaysia in February 1992 and were identified by comparison with material in the Herbarium, Forest Research Institute Malaysia (FRIM).

Extraction and isolation of compounds. Powdered stems (4.5 kg) and leaves (1.0 kg) were separately extracted (Soxhlet) with petrol and then EtOAc. The EtOAc extract of the stems was subjected to VLC over silica gel 60 H, eluting with $CHCl_3$ and then $CHCl_3$ containing increasing amounts of MeOH. Concn of the 10–15% MeOH fr. afforded a large amount of **1** (3.8 g, R_f 0.60, $CHCl_3$–MeOH 4:1) which was purified further by recrystallization from MeOH. CC (silica gel, 230–400 mesh, $CHCl_3$–MeOH 19:1) of the mother liquor yielded **2** (2.1 g, R_f 0.58, $CHCl_3$–MeOH 4:1) and **3** (103 mg, R_f 0.47, $CHCl_3$–MeOH 4:1).

The EtOAc extract of the leaves was similarly treated, using VLC with hexane–EtOAc eluates followed by EtOAc and EtOAc–MeOH eluates. The 90–100% EtOAc fr. was decolorized by running through a column of Sephadex LH-20. The clear frs were recombined and subjected to CC (silica gel, 230–400 mesh, $CHCl_3$–MeOH gradients of increasing polarity) to yield **4** (354 mg, R_f 0.23, $CHCl_3$–MeOH 9:1), **7** (1.2 g, R_f 0.09, $CHCl_3$–MeOH 9:1) and **8** (201 mg, R_f 0.22, $CHCl_3$ MeOH 9:1). The fr. eluted with 10% MeOH was also decolorized using a column of Sephadex LH-20. The early frs yielded poliothrysoside (354 mg) and PTLC ($CHCl_3$–EtOAc–MeOH, 4:5:1) of the remaining frs yielded **5** (68 mg, R_f 0.06, EtOAc–MeOH 9:1) and **6** (83 mg, R_f 0.26, EtOAc–MeOH 9:1).

Poliothrysoside. Amorphous solid, mp 211–214° (lit. [1] 204–205°), IR, ^{1}H and ^{13}C NMR spectra identical to an authentic sample.

2-(β-Glucopyranosyloxy)-7-{2-[(2-oxo-2-phenyl) ethyl] benzoyl}-5-hydroxybenzyl alcohol (**1**). Needles from EtOAc, mp 123–125°. $[\alpha]_D$ − 20° (MeOH; *c* 0.3). UV λ_{max} nm (log ε): 229 (4.72), 283 (4.02). IR ν_{max} cm^{-1}: 3450, 3010, 1698, 1662, 1596, 1491, 1258, 1078. ^{1}H and ^{13}C NMR; see Tables 1 and 2. FAB-MS, *m/z*: 547 $[C_{28}H_{28}O_{10} + Na]^+$, 525 $[C_{28}H_{28}O_{10} + H]^+$.

2-(6-Benzoyl-β-glucopyranosyloxy)-7-{2-[(2-oxo-2-phenyl) ethyl] benzoyl}-5-hydroxybenzyl alcohol (**2**). Amorphous solid from EtOAc, mp 87–88°. $[\alpha]_D$ − 17° (MeOH; *c* 0.3). UV λ_{max} nm (log ε) : 223 (4.61),

290 (4.12). IR ν_{max} cm^{-1}: 3525, 1711, 1598, 1495, 1448, 1275, 1214, 1068. ^{1}H and ^{13}C NMR: see Tables 1 and 2. FAB-MS *m/z*: 651 $[C_{35}H_{32}O_{11} + Na]^+$, 629 $[C_{35}H_{32}O_{11} + H]^+$.

2-{2-p-Coumaroyl-6-benzoyl-β-glucopyranosyloxy}-5-hydroxybenzyl alcohol (**3**). Brown amorphous solid from EtOAc, mp 206–207°. $[\alpha]_D$ − 14° (MeOH; *c* 0.150). UV λ_{max} nm (log ε) : 217 (4.82), 298 (4.41). IR ν_{max} cm^{-1}: 3430, 2945, 1726, 1601, 1506, 1447, 1081. ^{1}H and ^{13}C NMR: see Tables 1 and 2. FAB-MS *m/z*: 575 $[C_{29}H_{28}O_{11} + Na]^+$, 553 $[C_{29}H_{28}O_{11} + H]^+$.

2-(4,6-Dibenzoyl-β-glucopyranosyloxy)-5-hydroxybenzyl alcohol (**4**). Amorphous solid from EtOAc, mp 183–186°. $[\alpha]_D$ − 26° (MeOH; *c* 0.3). UV λ_{max} nm (log ε) : 280 (3.81). IR ν_{max} cm^{-1}: 3510–3285, 2945, 1721, 1599, 1503, 1449, 1274, 1120, 1070, 1029, 710. ^{1}H and ^{13}C NMR: see Tables 1 and 2. FAB-MS *m/z*: 533 $[C_{27}H_{26}O_{10} + Na]^+$, 511 $[C_{27}H_{26}O_{10} + H]^+$, 510 $[C_{27}H_{26}O_{10}]^+$.

(rel)-2-(6-Benzoyl-β-glucopyranosyloxy)-7-(1α, 2α, 6α-trihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol (**5**). Gum. $[\alpha]_D$ − 7° (MeOH; *c* 0.3). IR ν_{max} cm^{-1}: 3420, 2955, 1720, 1600, 1490, 1050. ^{1}H and ^{13}C NMR: see Tables 1 and 2. FAB-MS *m/z*: 599 $[C_{27}H_{28}O_{14} + Na]^+$.

(rel)-2-(6-benzoyl-β-glucopyranosyloxy)-7-(6α-benzoyloxy-1α, 2α-dihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol (**6**). Gum. IR ν_{max} cm^{-1}: 3410, 2910, 1725, 1610, 1560, 1060. ^{1}H and ^{13}C NMR: see Tables 1 and 2. FAB-MS *m/z*: 703 $[C_{34}H_{32}O_{15} + Na]^+$.

(rel)-2-(4,6-Dibenzoyl-β-glucopyranosyloxy)-7-(1α,2α, 6α-trihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol (**7**). Needles from EtOAc, mp 188–190°. $[\alpha]_D$ + 34° (MeOH; *c* 0.3). UV λ_{max} nm (log ε) : 220 (4.95), 275 (4.22). IR ν_{max} cm^{-1}; 3380, 2925, 1709, 1598, 1491, 1448, 1276, 1069, 715. ^{1}H and ^{13}C NMR; see Tables 1 and 2. FAB-MS *m/z*; 703 $[C_{34}H_{32}O_{15} + Na]^+$, 681 $[C_{34}H_{32}O_{15} + H]^+$.

(rel)-2-(4,6-Dibenzoyl-β-D-glucopyranosyloxy)-7-(6α-benzoyloxy-1α, 2α-dihydroxy-5-oxocyclohex-3-enoyl)-5-hydroxybenzyl alcohol (**8**). Amorphous solid from EtOAc, mp 133–135°. $[\alpha]_D$ − 13° (MeOH; *c* 0.2). UV λ_{max} nm (log ε): 223 (4.76), 275 (3.82). IR ν_{max} cm^{-1}; 3450, 1723, 1598, 1497, 1449, 1268, 1067, 709. ^{1}H and ^{13}C NMR; see Tables 1 and 2. FAB-MS *m/z*: 807 $[C_{41}H_{36}O_{16} + Na]^+$, 785 $[C_{41}H_{36}O_{16} + H]^+$.

REFERENCES

1. Shaari, K. and Waterman, P. G. (1994) *Phytochemistry* **36**, 1021.

the 4-position of the sugar, further esterification of the cyclohexenoic acid group, and the first occurrence of the 2-{(2-oxo-2-phenyl) ethyl}benzoic acid esterifying group.

2. Shaari, K., Gray, A. I., Hockless, D. C. R., Waterman, P. G. and White, A. H. (1993) *Aust. J. Chem.* **46**, 739.

3. Shaari, K. and Waterman, P. G. (1994) *J. Nat. Prod.* **57**, 720.

4. Whitmore, T. C. (1973) *Tree Flora of Malaya*, Vol. 2, p. 137. Longmans, London.

5. Gibbons, S., Gray, A. I. and Waterman, P. G. (1993) *Nat. Prod. Letters* **3**, 59.

6. Bax, Ad. and Summers, M. F. (1986) *J. Am. Chem. Soc.* **108**, 2093.

7. Gibbons, S., Gray, A. I., Waterman, P. G., Hockless, D. C. R. and White, A. H. (1994) *J. Nat. Prod.* (still in press).

8. Ekabo, O. A., Farnsworth, N. R., Santisuk, T. and Reutrakul, V. (1993) *Phytochemistry* **32**, 747.

9. Ekabo, O. A., Farnsworth, N. R., Santisuk, T. and Reutrakul, V. (1993) *J. Nat. Prod.* **56**, 699.

10. Cordell, G. A., Chang, P. T. O., Fong, H. H. S. and Farnsworth, N. R. (1977) *Lloydia* **40**, 340.