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# PHENOLIC GLUCOSIDES FROM THE HEARTWOOD OF *PRUNUS GRA YANA*

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**Key Word Index**—*Prunus* **grayana**; Rosaceae; phenolic glucosides; salicin; populine; pruyanaside A, pruyanaside B; dehydrodicatechin A.

**Abstract-Two** new phenohc glucosides, pruyanaside A and pruyanaside B, have been isolated from the heartwood of *Prunus grayana.* Their structures have been shown by the spectral evidence to be 2′-β-D-glucopyranosyloxybenzyl 2-(6-*O*-benzoyl-β-D-glucopyranosyloxy)benzoate and 2′-(6-*O*-benzoyl-β-D-glucopyranosyloxy)benzyl 2-β-D-glucopyranosyloxy-6-hydroxybenzoate.

## INTRODUCTION

The bark of *Prunus grayana* Maxim. has been used as a crude drug for the treatment of coughs in Europe and America. Several phenylpropanoid glucosides have been isolated from the bark [1, 2]. However, no study on the chemical constituents of the heartwood has been carried out. In this paper, we report two new phenolic glucosides, pruyanaside A and B, in addition to the known compounds, (+)-taxifolin, dehydrodicatechin A, virgaureoside A, henryoside, and populine.

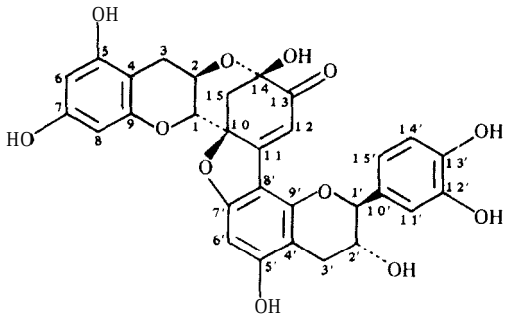
## RESULTS AND DISCUSSION

The heartwood of *P. grayana* was extracted with methanol. From the n-butanol-soluble portion of the methanol extract, compounds 1-7 were obtained by repeated silica gel and Sephadex LH-20 column chromatography.

Compounds **1** and 2 were identified as (+)-taxifolin [3], and dehydrodicatechin A [4–6], respectively. Compounds **3–5** were identified as known salicin derivatives, virgaureoside A [7], henryoside [8], and populine [9], by their spectroscopic data.

Pruyanaside A (**6**), $C_{33}H_{36}O_{15}$, gave a negative colouration with benzidine reagent. It showed IR absorption bands of hydroxy groups (3420 cm-‘), carbonyl groups of esters (1730 and 1710 $cm^{-1}$) and aromatic rings (1605 cm-i). The $^1H$ and $^{13}C$ NMR spectra showed signals due to two glucose moieties, two *ortho*-disubstituted aromatic rings, and methylene protons as in 3. In addition, the presence of a benzoyl group in the molecule was indicated by the $^1H$ NMR [δ8.18 (H-2” and H-6”), 7.52 (H-4”) 7.39 (H-3” and H-S’)], and $^{13}C$ NMR [δ166.5 (C-7”) 133.3 (C-4”) 130.8 (C-l”), 130.0 (C-2” and C-6”) 128.8 (C-3” and C-5”)] spectra. Acetylation of 6 with acetic anhydride in pyridine afforded a heptaacetate (**6b**). The electron impact mass spectrum of **6b** gave a molecular ion peak at *m/z* 966 and a fragment ion peak at m/z 331, corresponding to the tetraacetyl glucose oxonium ion. The $^1H$ NMR spectrum of **6b** exhibited the presence of seven aliphatic acetate groups and no aromatic acetate group. Alkaline hydrolysis of 6 with 3% sodium methoxide gave 3, together with salicin (**6a**) [9], and methyl 2-β-D-glucopyranosyloxybenzoate (**6a’**). From the findings presented above, 6 was a benzoyl ester of 3. The location of the benzoyl group in 6 was determined to be the C-6 hydroxy position of one of the two glucose moieties by comparison of the $^{13}C$ NMR spectrum of 6 with that of 3. The signal easily assignable to the C-6 position of either glucose moiety of 6 was shifted downfield (665.2) while the C-5 was shifted upfield (675.7) as compared with those of 3 (C-6, 662.5; C-5, δ79.1). The above conclusion was also supported by the appearance of the deshielded H-6 proton signals in the $^1H$ NMR spectrum of 6. The signals attributable to the H-6 methylene protons of either glucose moiety (65.26 and 4.92, each 1H) showed a downfield shift by *ca* 0.7 ppm as compared with those of 3 (64.6-4.1, overlapping). In addition, the assignment of the proton signals due to glucose moieties and aromatic rings of 6 were performed by means of $^1H$ NMR decoupling experiment. In the 2D-NOESY spectrum of 6, correlations were observed between the H-5 proton (64.34) of the glucose residue whose H-6 hydroxyl position was esterified with the benzoyl group and an anomeric proton (S5.55) of glucose, and between the H-5 proton (64.10) of the unesterified glucose moiety and another anomeric proton (65.61) were observed. Furthermore, correlations were observed between the anomeric proton (6 5.55) and H-3 (67.64) and between the anomeric proton (65.61) and H-3’ (67.58). Accordingly, 6 is characterized as 2′-β-D-glucopyranosyloxybenzyl 2-(6-*O*-benzoyl-β-D-glucopyranosyloxy)benzoate.

Pruyanaside B (**7**), $C_{33}H_{36}O_{16}$, and gave a positive coloration with benzidine reagent. It showed IR absorption bands of hydroxy groups (3400 $cm^{-1}$), carbonyl groups of esters (1705 and 1645 $cm^{-1}$) and aromatic rings (1605 cm-‘). The $^1H$ and $^{13}C$ NMR spectra of 7 were almost identical to those of 4 and 6 except for the aromatic region. Acetylation of 7 with acetic anhydride in pyridine afforded the octaacetate (**76**) as a colourless amorphous powder. The EIMS of **7b** gave a molecular ion peak at *m/z* 1024, and a fragment ion peak at m/z 509.



**2**

Table 1. $^{13}$C NMR data (100 MHz) for compounds 3–7.

| C | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| 1 | 122.2 | 110.7 | 122.0 | 110.8 | |
| 2 | 158.0 | 157.7 | 158.1 | 157.6 | |
| 3 | 117.7 | 106.6 | 117.6 | 106.8 | |
| 4 | 133.8 | 132.6 | 134.1 | 132.7 | |
| 5 | 122.4 | 111.9 | 122.4 | 112.2 | |
| 6 | 131.8 | 158.9 | 131.8 | 158.8 | |
| 7 | 166.4 | 168.3 | 166.7 | 168.4 | |
| 1' | 126.1 | 126.5 | 126.1 | 126.3 | 124.0 |
| 2' | 156.3 | 155.6 | 156.3 | 155.8 | 156.7 |
| 3' | 115.8 | 116.0 | 115.9 | 1 15.6 | 116.9 |
| 4 | 129.7 | 129.1 | 129.5 | 129.4 | 128.6 |
| 5' | 122.5 | 122.8 | 122.6 | 122.6 | 123.1 |
| 6' | 129.4 | 129.0 | 129.8 | 129.0 | 128.6 |
| 7' | 62.6 | 62.6 | 62.7 | 62.7 | 60.5 |
| 1'' | 130.8 | 130.8 | | | 130.9 |
| 2" | 130.0 | 130.0 | | | 130.0 |
| 3'' | 128.8 | 128.8 | | | 128.8 |
| 4" | 133.3 | 133.3 | | | 133.3 |
| 5" | 128.8 | 128.8 | | | 128.8 |
| 6" | 130.0 | 130.0 | | | 130.0 |
| 7'' | 166.5 | 166.5 | | | 166.5 |
| Glucose moiety | | | | | |
| 1 | 102.6 | 102.5 | 102.7 | 102.6 | |
| 2 | 74.8 | 74.7 | 74.8 | 74.8 | |
| 3 | 78.0 | 78.5 | 78.1 | 78.5 | |
| 4 | 7 1.4 | 71.2 | 71.3 | 71.2 | |
| 5 | 75.7 | 79.0 | 79.1 | 78.9 | |
| 6 | 65.2 | 62.4 | 62.5 | 62.4 | |
| 1' | 103.3 | 102.9 | 103.4 | 102.7 | 103.9 |
| 2' | 74.9 | 74.9 | 75.1 | 74.9 | 75.1 |
| 3' | 78.6 | 78.5 | 78.6 | 78.5 | 78.5 |
| 4' | 71.2 | 71.5 | 71.3 | 71.2 | 71.6 |
| 5' | 78.9 | 75.5 | 78.9 | 79.0 | 75.6 |
| 6' | 62.3 | 65.3 | 62.4 | 62.4 | 65.3 |

Spectra of compounds **3**–**7** were recorded in $C_5D_5N$

The $^1$H NMR spectrum of **7b** exhibited the presence of seven aliphatic acetate groups and an aromatic acetate group. Treatment of 7 with 3% sodium methoxide in methanol gave 4, together with **5**, **6a**, and methyl 2-$\beta$-D-glucopyranosyloxy-6-hydroxybenzoate **(7a)** [8], which were determined by direct comparison with authentic samples (TLC). From the findings presented above, 7 was a benzoyl ester of 4. In the $^1$H and $^{13}$C NMR spectra of 7, the signal patterns of the glucose moieties were almost similar to those of 6, indicating that the benzoyl group was attached to the C-6 position of one of the two glucose moieties. The $^1$H NMR decoupling experiment confirmed the relationships of the protons on glucose moieties and aromatic rings. In the NOESY spectrum of 7, correlations between the H-5 proton (64.34) of the glucose residue whose H-6 hydroxyl position was esterified with the benzoyl group and an anomeric proton (65.52) of the glucose, and between the H-S proton ($\delta$4.1 I) of the unesterified glucose moiety and another anomeric proton (65.69) were observed. Furthermore, cross peaks were observed between the anomeric proton (65.52) and H-3' ($\delta$7.53), and between the anomeric proton (65.69) and H-3 ($\delta$7.14). Therefore, 7 was determined to be 2'-(6-*O*-benzoyl-$\beta$-D-glucopyranosyloxy)benzyl 2-$\beta$-D-glucopyranosyloxy-6-hydroxybenzoate.

Pruyanaside A and B have not been reported as naturally occurring phenolic glucosides. Compounds 2-7 have never been isolated from this plant before. Our investigations on chemical compounds of ***Prunus*** species are still in progress.

## EXPERIMENTAL

NMR were measured at 400 MHz for $^1$H NMR and at 100 MHz for $^{13}$C NMR. Chemical shifts were given on the $\delta$(ppm) scale with TMS at int. standard.

*Isolation.* Fresh heartwood of *Prunus grayana* (1.5 kg), collected in the botanical garden of this college in April 1987, was extracted with hot MeOH under reflux. The MeOH extract was concd under red. pres. and the residue suspended in $H_2O$. The suspension was extracted with $CHCl_3$ and then with *n*-BuOH. The *n*-BuOH extract was repeatedly chromatographed on silica gel and Sephadex LH-20 to give compounds 1-7.

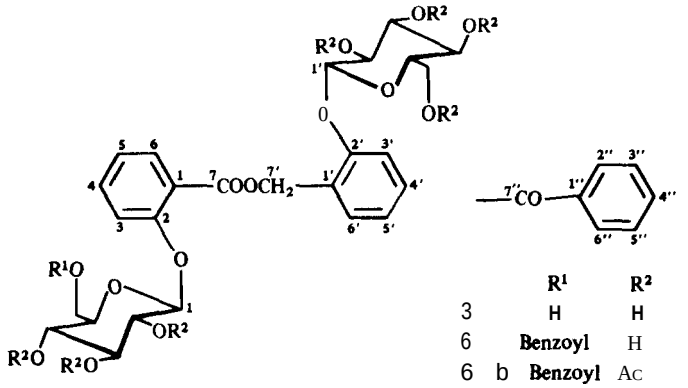
(+)-*Taxifolin* (1). Orange needles (10.4 mg), mp 210°, $[\alpha]_D^{24}$ +11.4° (EtOH; *c* 1.18). All spectral data were identical with those of the reported data.

*Dehydrodicatechin A (2).* Yellow needles (93.0 mg), mp > ***300*** dec., $[\alpha]_D^{26}$ −405.3° ($Me_2CO$; *c* 0.22); $^{13}$C NMR ($C_5D_5N$): 679.5 (C-l), 67.5 (C-2), 28.4 (C-3), 104.8 (C-4), 158.1 (C-S), 96.4 (C-6), 158.7 (C-7), 95.3 (C-8), 156.2 (C-9). 89.4 (C-lo), 165.5 (C-l 1), 113.4 (C-12), 193.4 (C-13), 100.1 (C-14), 46.0 (C-15), 83.7 (C-l'), 66.1 (C-2'), 29.3 (C-3'), 104.9 (C-4'), 161.8 (C-5'), 90.8 (C-6'), 166.9 (C-7'), 97.4 (C-8'). 154.8 (C-9'), 130.9 (C-lo'), 115.5 (C-l 1'). 147.3 (C-12'), 147.4 (C-13'). 116.4 (C-14'), 119.3 (C-15'). Other spectral data were identical with those of the reported data.

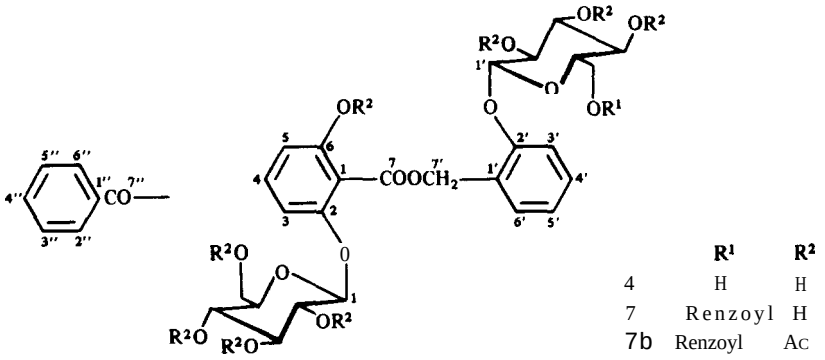
*Virgaureoside A (3).* Colourless needles (610 mg), mp 180°, $[\alpha]_D^{26}$ -- 53.0" (MeOH–$H_2O$ 1: 1; *c* 1.05). IR $\nu_{max}^{KBr}$ cm-': 3400, 1710, 1600; $^1$H NMR ($C_5D_5N$): $\delta$7.97 (IH, d-like, *J* = 7.7 Hz, H-6), 7.72 (1H, *d*-like, *J* = 7.4 Hz, H-6'), 7.65 (1H, *d*-like, *J* = 7.7 Hz. H-3), 7.59 and hidden under the peak of solvent (1 H, H-3'), 7.34 (1 H, t-like, *J* = 7.7 Hz, H-4). 7.22 and hidden under the peak of solvent (1H, H-4'), 7.07 (1H, t-like. *J* = 7.4 Hz, H-5'). 6.97 (1H, *t*-like, *J* = 7.7 Hz, H-5), 5.78 (1H, *d*, *J* = 13.2 Hz, H-7'), 5.67 (1H, *d*, *J* = 13.2 Hz, H-7'), glucose moiety: $\delta$5.61 (1H, *d*, *J* = 6.9 Hz, H-l'), 5.57 (1H, *d*, *J* = 6.9 Hz, H-l), 4.6–4.1 (12H, overlapping).

***Nenryoside*** (4). Colourless needles (86.5 mg), mp 128–130°, $[\alpha]_D^{24}$ -42.0" (MeOH; *c* 0.5). All spectral data were identical with those of reported data.

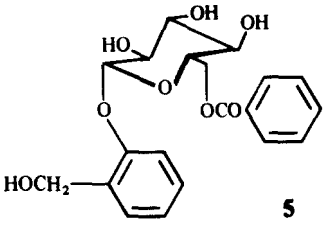
*Populine (5).* Colourless needles (6.3 mg). mp 176–177°, $[\alpha]_D^2$ -33.0" ($Me_2CO$; *c* 0.5). All spectral data were identical with those of the reported data.



| | $R^1$ | $R^2$ |
|---|---|---|
| 3 | H | H |
| 6 | Benzoyl | H |
| 6 b | Benzoyl | Ac |



| | $R^1$ | $R^2$ |
|---|---|---|
| 4 | H | H |
| 7 | Renzoyl | H |
| 7b | Renzoyl | Ac |



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***Pruyanaside A (6).*** Colourless needles (30.4 mg), mp 195°, $[\alpha]_D^{28}$ − 39.6° (MeOH; *c* 0.39); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3420, 1730, 1710, 1605; EIMS m/z (rel. int.): 595 (30), 507 (100), 386 (80), 267 (100), 138 (100); $^1H$ NMR ($C_5D_5N$): 68.18 (2H, d-like, J = 7.8 Hz, H-2" and H-6"), 7.96 (1H, *dd, J* = 7.4, 1.4 Hz, H-6), 7.70 (1H, *dd, J* = 7.5, 1.5 Hz, H-6'), 7.64 (1H, *dd, J* = 7.4, *0.8* Hz, H-3), 7.58 (1H, *dd, J* = 7.5, 0.8 Hz, H-3'), 7.52 (1H, *t*-like, *J* = 7.8 Hz, H-4"), 7.39 (2H, *t*-like, *J* = 7.8 Hz, H-3" and H-5"), 7.35 (1H, *dt, J* = 7.4, 1.4 Hz, H-4), 7.23 (1H, *dt, J* = 7.5, 1.5 Hz, H-4'), 7.05 (1H, *dt, J* = 7.5, 0.8 Hz, H-S), 7.00 (1H, *dt, J* = 7.4, 0.8 Hz, H-5), 5.76 (1H, *d, J* = 13.2 Hz, H-7'). 5.65 (1H, *d, J*= 13.2 Hz, H-7'), glucose moiety: δ5.61 (1H, *d, J* = 7.1 Hz, H-l'), 5.55 (1H, *d, J* = 7.3 Hz, H-l), 5.26 (1H, *dd, J* = 11.7, 2.0 Hz, H-6), 4.92 (1H, *dd, J* = 11.7, 7.3 Hz, H-6), 4.54 (1H, dd, *J*= 12.0, 2.3 Hz, H-6'), 4.43-4.31 (7H, overlapping, H-2-5, H-2, H-3', and H-6'), 4.21 (1H, *m*, H-4'), 4.10 (1H, *m*, H-S).

***Alkaline hydrolysis of6 with*** NaOMe. Compound 6 (6.0 mg) was dissolved in methanolic 3% NaOMe and the soln allowed to stand 1 hr at room temp. The mixt. was passed through an Amberlite IR-120($H^+$) column and the eluate concd under red. pres. The residue was subjected to silica gel CC to give 3, salicin (6a) and methyl 2-β-D-glucopyranosyloxybenzoate (6a'). 6a; IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3350, 1590; $^1H$ NMR ($C_5D_5N$): 67.76 (1H, *dd, J* = 7.5, *1.5* Hz, H-6), 7.65 (1H, dd, *J* = 7.5, 1.5 Hz, H-3), 7.25 (1H, *td, J* = 7.5, 1.5 Hz, H-4), 7.11 (1H, *td, J* = 7.5, *1.5* Hz, H-5), 6.60 (2H, s-like, H-7), glucose moiety: 65.50 (1H, *d, J* = 7.1 Hz, H-l), 5.3–4.0 (6H). 6a'; IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3400, 1710, 1600; 'HNMR ($C_5D_5N$): 67.85 (1H, d-like, *J* = 7.7 Hz, H-6), 7.67 (1H, d-like, *J* = 7.7 Hz, H-3), 7.38 (1H, t-like, *J* = 7.7 Hz, H-4), 7.02 (1H, r-like, *J* = 7.7 Hz, H-5), glucose moiety: 65.55 (1H, *d, J* = 7.1 Hz, H-l), 4.6–4.1 (6H), methoxy group: 63.74 (3H, *s*, −COOMe).

***Acetylation of 6.*** Compound 6 (6.4 mg) was dissolved in pyridine (0.5 ml) and $Ac_2O$ (2.0 ml) and left at room temp. overnight to afford the heptaacetate 6b (9.7 mg) as a colourless amorphous powder. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1760, 1750, 1740, 1735, 1720, 1605; EIMS m/z (rel. int.): 966 $[M]^+$ (1.2), 681 (1.2), 429 (25), 393 (100), 331 (100); $^1H$ NMR (CDCI,): 68.04 (2H, d-like, *J* = 7.4 Hz, H-2", H-6"), 7.74 (1H, d-like, *J* = 7.7 Hz, H-6), 7.60 (1H, t-like, J = 7.4 Hz, H-4"), 7.48-7.41 (3H, overlapping, H-6, H-3", and H-5"), 7.29 (1H, d-like, *J*= 7.7 Hz, H-3), 7.26 and hidden under the peak of solvent (1H, H-4), 7.18 (1H, d-like, *J* = 7.7 Hz, H-3'), 7.12-7.07 (3H, overlapping, H-5, H-4, and H-5'), 5.36–5.08 (2H, overlapping to glucose signals, H-7') glucose moiety: 65.36-5.08

(8H, overlapping, H-l-4 and H-1′–4′), 4.56 (1H, dd, $J = 12.1$, 2.5 Hz, H-6). 4.38 (1H, *dd*, $J = 12.1$, 6.3 Hz, H-6), 4.29 (1H, ***dd***, $J = 12.3, 5.4$ Hz, H-6'), 4.19 (1H, ***dd***, $J = 12.3, 2.4$ Hz, H-6'), 3.99 (1H, *m*, H-5), 3.87 (1H, *m*, H-S), acetoxy groups: $\delta$2.08, 2.07 × 2, 2.05 × 2. 2.03 x 2 (each 3H, s, –OAc).

***Pruyanaside B (7).*** A colourless amorphous powder (32.4 mg), $[\alpha]_D^{24} - 19.3°$ (MeOH; *c* 1.05); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3400, 1705, 1645, 1605; EIMS ***m/z*** (rel. int.): ***643*** (4), ***555*** (10), 482 (42), 402 (68), 322 (100); $^1$H NMR ($C_5D_5N$): 68.21 (2H, d-like, $J = 7.1$ Hz, H-2" and H-6"), 8.03 (1H, d-like, $J = 7.2$ Hz, H-6'). 7.53 (1H, d-like, J = 7.2 Hz, H-3'), 7.52 (1H, t-like, $J = 7.1$ Hz, H-4"), 7.39 (2H, t-like, $J = 7.1$ Hz, H-3" and H-S'), 7.21 and hidden under the peak of solvent, (1H, H-4), 7.15 (1H, t-like, $J = 7.2$ Hz, H-4'), 7.14 (1H, *d*-like, $J = 8.0$ Hz, H-3), 7.10 (1H, r-like, $J = 7.2$ Hz, H-5'), 6.79 (1H, *d*-like, $J = 8.0$ Hz, H-5), 5.97 (1H, *d*, $J = 14.0$ Hz, H-7'), 5.79 (1H, *d*, $J = 14.0$ Hz, H-7'), glucose moiety: 65.69 (1H, ***d***, $J = 7.0$ Hz, H-l), 5.52 (1H, *d*, $J = 7.5$ Hz, H-1′), 5.29 (1H, *dd*, $J = 11.6$, 1.7 Hz, H-6'), 4.92 (1H, *dd*, $J = 11.6$, 7.2 Hz, H-6'), 4.55 (1H, *dd*, $J = 11.8$, 1.7 Hz, H-6), 4.37–4.20 (7H, overlapping, H-2-4 and H-2′–5′), 4.39 (IH, dd, $J = 11.8, 5.2$ Hz, H-6), 4.11 (1H, *m*, H-5).

Alkaline hydrolysis *of* **7** with NaOMe. 7 (11 .1 mg) was treated in the same manner as 6 to give 4, 5, **6a** and methyl 2-$\beta$-D-glucopyranosyloxy-6-hydroxybenzoate **(7a).** These compounds were identified by TLC comparison with authentic samples. 4: $R_f$ ***0.1, 5:*** $R_f$ 0.75. **6a:** ***R,*** 0.34, 7a: $R_f$ 0.58, $CHCl_3$–MeOH (4: 1) on silica gel.

*Acetylation of* **7**. Compound 7 (5.1 mg) was acetylated in the same manner as 6 to give the octaacetate **7b** (5.0 mg) as a colourless amorphous powder; IR $\nu_{max}^{KBr}$ cm$^{-1}$: 1755, 1605; EIMS *m/z* (rel. int.): 1024 [M]' (80), 966 (10), 759 (7), 681(6),652(S), 571 (40), 509 (100); $^1$H NMR ($CHCl_3$): 68.06 (2H, d-like, $J$ = 7.5 Hz, H-Z" and H-6"), 7.60 (1 H, t-like, J = 7.5 Hz. H-4"), 7.49-7.45 (3H, overlapping, H-3', H-3", and H-5"), 7.35 (1H, ı, $J$ = 8.3 Hz, H-4), 7.12-7.08 (3H, overlapping, H-4′–6'), 6.99 (1 H, d-like, J = 8.3 Hz, H-3 or H-5), 6.87 (1 H, d-like, J = 8.3 Hz, H-3 or H-5). 5.40–5.01 (2H, overlapping to glucose signals, H-7'). glucose moiety: $\delta$5.40–5.01 (8H, overlapping, H-l-4 and H-1′–4′), 4.56 (1H, dd, J = 12.1, 2.5 Hz, H-6'), 4.38 (1H, ***dd***, $J = 12.1, 6.5$ Hz, H-6'). 4.28 (1H, *dd*, $J = 12.3$, 5.6 Hz, H-6), 4.17 (1H, *dd*, $J = 12.3$, 2.4 Hz, H-6), 4.04 (1H, ***m,*** H-5'), 3.85 (1H, m, H-S), acetoxy groups: 62.09, 2.07, 2.05, 2.04. 2.03, 2.02, 2.00. 1.93 (each 3H. *s*, –OAc).

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