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# Aromatic diglycosides from *Cladogynos orientalis*

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**Abstract**

Two unusual aromatic diglycosides with galloyl substitution, 4″-*O*-galloyl-violutoside and 4″-*O*-galloyl-benzyl-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside, were isolated from the aerial portion of *Cladogynos orientalis* along with isovitexin, apigenin 6-*C*-(2″-*O*-galloyl)-β-D-glucopyranoside, apigenin 8-*C*-(2″-*O*-galloyl)-β-D-glucopyranoside, syringic acid β-D-glucopyranoside, 3,4,5-trimethoxyphenyl β-D-glucopyranoside, (6*S*,9*R*)-roseoside, and violutioside. The structural elucidations were based on analyses of chemical and spectroscopic data by including 1D and 2D NMR analyses.


*Keywords:* *Cladogynos orientalis*; Euphorbiaceae; Aromatic diglycoside; Violutoside; 4″-*O*-galloyl-violutoside; Galloyl substitution

## 1. Introduction

*Cladogynos orientalis* Zipp. Ex Span. (Thai name: Chetta-phang-khi), a member of the family Euphorbiaceae of the monotypic genus, is a shrub up to 2 m high native in tropical regions of Asia. It is used in Thai traditional medicine for the relief of stomach-ache and abdominal pain. In continuing studies on Thai medicinal plants from this family (Kanchanapoom et al., 2002, 2003), the constituents of this plant were investigated, following plant collection from the Chaiyaphum province, Thailand. Pervious investigations of this plant resulted in *ent*-halimane diterpenes and guainane sesquiterpene being reported (Sato et al., 1970, 1971; Kanlayavattanakul et al., 2005). The present paper deals with the isolation and structural determination of nine polar compounds, including three flavone *C*-glycosides (**1**–**3**), two aromatic glucosides (**4**, **5**), one megastigmane glucoside (**6**), as well as two new unusual aromatic diglycosides bearing with a galloyl moiety (**8**, **9**) from the aerial part of this plant.

## 2. Results and discussion

The methanolic extract of the aerial portion of *C. orientalis* was partitioned with $Et_2O$, *n*-BuOH, and $H_2O$. The *n*-BuOH soluble fraction was subjected to using a column chromatography highly porous copolymer resin of styrene and divinylbenzene, with $H_2O$, MeOH and $Me_2CO$ as eluants, successively. The portion eluted with MeOH was repeatedly subjected to silica gel, RP-18, and preparative HPLC-ODS chromatography to provide nine compounds. Compounds **1**, **2** and **3** have been assigned as the flavone *C*-glycosides; isovitexin, apigenin 6-*C*-(2″-*O*-galloyl)-β-D-glucopyranoside, apigenin 8-*C*-(2″-*O*-galloyl)-β-D-glucopyranoside, respectively (Markham and Chari, 1982; Lin et al., 2000; Latté et al., 2002). The $^1H$ and $^{13}C$ NMR spectroscopic data of compounds **4** and **5** were coincident with those of syringic acid β-D-glucopyranoside (Inoshiri et al., 1987), and 3,4,5-trimethoxyphenyl β-D-glucopyranoside (Shimomura et al., 1988), respectively. Compound **6** was elucidated as a megastigmane glucoside, (6*R*,9*S*)-3-oxo-α-ionol-β-D-glucopyranoside, by comparison of its physical and NMR spectroscopic data with reported data (Pabst et al., 1992).

Compound **7** was isolated as an amorphous powder and determined as $C_{19}H_{26}O_{12}$ by high-resolution (HR)-FAB

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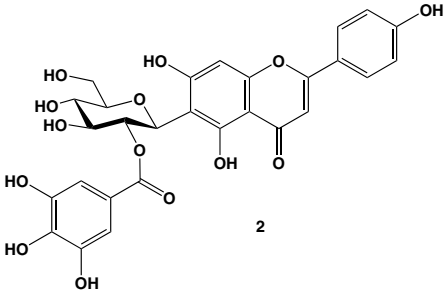
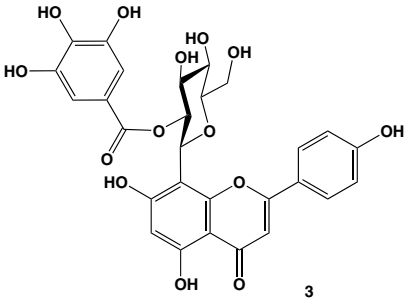
mass spectrometric analysis. The $^1$H NMR spectroscopic data showed the characteristic of a 1,2-disubstituted aromatic ring system from the chemical shifts at $\delta_H$ 7.38 (1H, *br d*, $J = 8.3$ Hz), 7.51 (1H, *br dd*, $J = 8.3$, 6.8 Hz), 7.06 (1H, *br dd*, $J = 7.8$, 6.8 Hz), and 7.69 (1H, *br d*, $J = 7.8$ Hz), together with a singlet methoxyl signal at $\delta$ 3.83 (3H) for an aglycone moiety. The $^{13}$C NMR spectrum displayed 19 carbon signals, of which eight were assignable to one oxy-aryl carbon at $\delta_C$ 158.2, four aryl-methines at $\delta_C$ 119.2, 123.6, 132.0 and 135.3, one non-protonated carbon at $\delta_C$ 122.4, and two carbon signals of a carbomethoxyl group at $\delta_C$ 168.5 and 52.8 for an aglycone, indicative of a methyl salicylate derivative. The remaining carbon signals belonged to the sugar moiety, and could be identified as α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranosyl unit by comparing chemical shifts with the reported data (Matsuda et al., 1997). From these spectroscopic data, compound **7** could be identified as methyl salicylate α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside. In order to confirm the absolute configurations of the sugar units, compound **7** was hydrolyzed with sulfuric acid to give the sugar fraction from an aqueous layer. The absolute configurations of glucose and arabinose were determined to be D- and L-forms, respectively; by comparison of the optical rotations with those of authentic samples. The structure of compound **7** was identical to violutoside, isolated compound from *Viola cornuta* L. in 1926 (Picard, 1926a,b) and was reported as a synthetic compound in 1932 (Robertson and Waters, 1932). So far this compound was not been reported since then; therefore the physical and spectroscopic data were given as shown in Table 1.

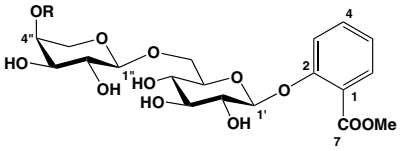
Table 1
NMR spectroscopic data of violutoside (**7**) and compound **8**

| No. | **7** | | **8** | |
|---|---|---|---|---|
| | $\delta_C$ | $\delta_H$ | $\delta_C$ | $\delta_H$ |
| 1 | 122.4 | | 122.3 | |
| 2 | 158.5 | | 158.6 | |
| 3 | 119.2 | 7.38 (1H, *br d*, $J = 8.3$ Hz) | 119.2 | 7.42 (1H, *dd*, $J = 8.3$, 2.2 Hz) |
| 4 | 135.3 | 7.51 (1H, *br dd*, $J = 8.3$, 6.8 Hz) | 135.4 | 7.40 (1H, *br dd*, $J = 8.3$, 6.6 Hz) |
| 5 | 123.6 | 7.06 (1H, *br dd*, $J = 7.8$, 6.8 Hz) | 123.7 | 7.00 (1H, *ddd*, $J = 7.8$, 6.6, 2.2 Hz) |
| 6 | 132.0 | 7.69 (1H, *br d*, $J = 7.8$ Hz) | 132.0 | 7.68 (1H, *br d*, $J = 7.8$ Hz) |
| 7 | 168.5 | | 168.6 | |
| 8 | 52.8 | 3.83 (3H, *s*) | 52.8 | 3.83 (3H, *s*) |
| Glc | | | | |
| 1′ | 103.8 | 4.83 (1H, $J = 7.1$ Hz) | 103.9 | 4.83 (1H, *d*, $J = 7.5$ Hz) |
| 2′ | 74.9 | 3.47 (1H)[a] | 74.9 | 3.49 (1H, *dd*, $J = 9.0$, 7.5 Hz) |
| 3′ | 77.4 | 3.45 (1H)[a] | 77.5 | 3.43 (1H, *dd*, $J = 9.0$, 8.8 Hz) |
| 4′ | 71.5 | 3.37 (1H, *dd*, $J = 9.3$, 8.8 Hz) | 71.5 | 3.35 (1H, *dd*, $J = 9.3$, 8.8 Hz) |
| 5′ | 77.4 | 3.65 (1H, *m*) | 77.5 | 3.65 (1H, *m*) |
| 6′ | 69.6 | 3.78 (1H)[a]; 4.08 (1H, *br d*, $J = 11.5$ Hz) | 70.4 | 3.78 (1H, *dd*, $J = 11.7$, 6.6 Hz); 4.12 (1H, *br d*, $J = 11.7$ Hz) |
| Ara | | | | |
| 1″ | 105.0 | 4.27 (1H, *d*, $J = 6.6$ Hz) | 105.6 | 4.35 (1H, *d*, $J = 6.6$ Hz) |
| 2″ | 74.1 | 3.55 (1H)[a] | 73.0 | 3.69 (1H)[a] |
| 3″ | 72.4 | 3.55 (1H)[a] | 72.7 | 3.67 (1H)[a] |
| 4″ | 69.4 | 3.74 (1H)[a] | 72.8 | 5.12 (1H, *br s*) |
| 5″ | 66.6 | 3.44 (1H)[a]; 3.80 (1H, *dd*, $J = 11.9$, 2.0 Hz) | 64.9 | 3.59 (1H, *br d*, 11.9 Hz); 3.95 (1H, *dd*, 11.9, 2.2 Hz) |
| Galloyl moiety | | | | |
| 1‴ | | | 121.6 | |
| 2‴, 6‴ | 110.4 | 7.08 (2H, *br s*) | | |
| 3‴, 5‴ | 146.5 | | | |
| 4‴ | | | 139.9 | |
| 7‴ | | | 168.0 | |

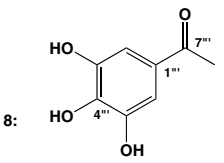
[a] Chemical shifts obtained approximately by HSQC.

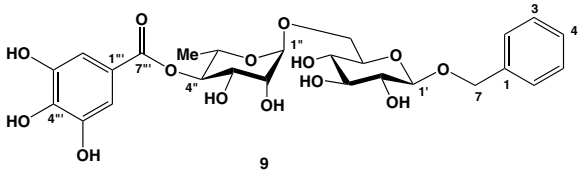



7: H



The molecular formula of compound **8** was determined as $C_{26}H_{30}O_{16}$ by HR-FAB mass spectrometric analysis. The $^1$H NMR spectroscopic data also showed the presence of a set of 1,2-disubstituted aromatic ring systems from the chemical shifts at 7.42 (1H, *dd*, $J = 8.3$, 2.2 Hz), 7.40 (1H, *br dd*, $J = 8.3$, 6.6 Hz), 7.00 (1H, *ddd*, $J = 7.8$, 6.6, 2.2 Hz), and 7.68 (1H, *br d*, $J = 7.8$ Hz), as well as two anomeric protons at $\delta_H$ 4.83 (1H, *d*, $J = 7.5$ Hz) and 4.35 (1H, *d*, $J = 6.6$ Hz) and a methyl singlet signal at $\delta_H$ 3.83 (3H). The $^1$H and $^{13}$C NMR spectroscopic data were very similar to those of compound **7**. In addition, the signals of a galloyl moiety were observed from the chemical shifts at $\delta_H$ 7.08 (2H) in the $^1$H NMR spectrum, and at $\delta_C$ 110.4 (2C), 121.6, 139.9, 146.5 (2C), and 168.0 in the $^{13}$C NMR spectrum. Therefore, the structure of compound **8** was assumed to be a galloyl derivative of violutoside (**7**). This functional group was assigned to be linked to C-4″, since the chemical shift of H-4″ appeared downfield at $\delta_H$ 5.12, and the chemical shifts of C-4″ and C-5″ were significantly changed to $\delta_C$ 72.8 and 64.9, respectively, as compared to violutoside (**7**). The assignment was supported by the results from analyses of COSY, HSQC and HMBC experiments. In the HMBC spectrum, three bond correlations were found between (i) H-4″ and C-7‴, (ii) H-1″ and C-6′, and (iii) H-1′ and C-2 as illustrated in Fig. 1. Accordingly the structure of compound **8** was elucidated to be 4″-*O*-galloyl-violutoside.

The molecular formula of compound **9** was determined as $C_{26}H_{32}O_{14}$ by HR-FAB mass spectrometric analysis. The NMR spectroscopic data displayed the presence of characteristic signals of benzyl alcohol part as an aglycone from the chemical shifts of five protons in the aromatic region at $\delta_H$ 7.24 (2H, *m*), 7.27 (1H, *m*), 7.38 (2H, *br d*, $J = 7.8$ Hz), and two methylene protons at $\delta_H$ 4.65 and 4.88 (each 1H, *d*, $J = 11.8$ Hz) in the $^1$H NMR spectrum, together with the results from the chemical shifts of five aryl-methines at $\delta_C$ 128.8, 129.2 (2C), and 129.3 (2C), one non-protonated carbon at $\delta_C$ 138.8, and one oxy-methylene carbon at $\delta_C$ 71.8 in the $^{13}$C NMR spectrum. The remaining signals could be assigned to a galloyl moiety as compared to compound **8**, and the sugar moiety was identified as an α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl unit (De Tommasi et al., 1996). The chemical shifts of compound **9** were closely related to those of benzyl-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside (De Tommasi et al., 1996), except for the occurrence of additional signals of a galloyl moiety. This functional group was located at C-4″ of the rhamnopyranosyl unit due to the downfield shift of C-4″ and the upfield shifts of C-3″ and C-5″ by +0.8, −1.7, and −1.8 ppm, respectively. The HMBC experiments provided further confirmation of the structure by detection of long range correlations between (i) H-4″ and C-7‴, (ii) H-1″ and C-6′, and (iii) H-1′ and C-2 as shown in Fig. 2. Therefore, the structure of compound **9** was determined to be 4″-*O*-galloyl-benzyl-O-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside.

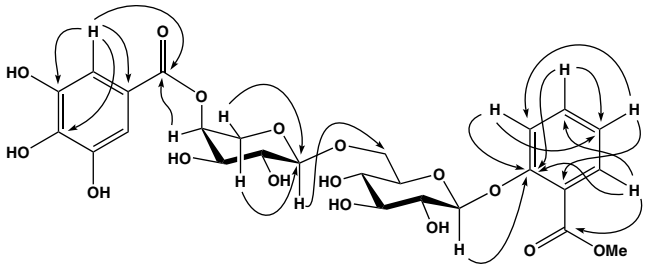


Fig. 1. The significant HMBC correlation of compound **8**.

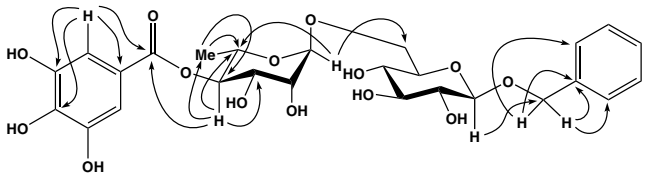


Fig. 2. The significant HMBC correlation of compound **9**.

## 3. Concluding remarks

*Cladogynos* is a monotypic genus in the tribe Epiprineae, together with the genera *Cleidiocarpon*, *Epiprinus*, and *Koilodepas* which is found in Thailand. Only the chemical investigations of *C. orientalis* have been reported. Among the compounds isolated from this species, the present study reported polar compounds bearing galloyl moieties attached to the sugar part, which were quite rare to find in plants. Other examples include: apigenin 6-*C*-(2″-*O*-galloyl)-β-D-glucopyranoside (**2**), apigenin 8-*C*-(2″-*O*-galloyl)-β-D-glucopyranoside (**3**), 4″-*O*-galloyl-violutoside (**8**) and 4″-*O*-galloyl-benzyl-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside (**9**). Compounds **2** and **3** have previously been isolated from *Terminalia catappa* (Combretaceae) (Lin et al., 2000), and from *Pelargonium reniforme* (Geraniaceae) (Latté et al., 2002). Only compound **3** has been identified before from the family Euphorbiaceae, *Conceveiba guianensis* (tribe Acalyphae) (Braca et al., 2004). The occurrence of the constituents with galloyl substitution might be useful for further chemotaxonomic studies of tribe Epiprineae.

## 4. Experimental

### 4.1. General procedures

NMR spectra were recorded in $CD_3OD$ using a JEOL JNM α-400 spectrometer (400 MHz for $^1$H NMR and 100 MHz for $^{13}$C NMR). UV spectra were recorded on a Shimadzu UV-1700 spectrophotometer. MS values were obtained on a JEOL JMS-SX 102 spectrometer. Optical rotations were measured with a Jasco P-1020 digital polarimeter. For column chromatography, silica gel 60 (70–230 mesh, GE0049, Scharlau Chemie SA), RP-18 (50 μm,

YMC), and Diaion HP-20 (Mitsubishi Chemical Industries Co. Ltd.) were used. Preparative HPLC (Jasco PU-980 pump) was carried out on an ODS column (250 × 20 mm i.d., YMC) with a Jasco RI-2031 refractive index detector. The flow rate was 6 ml/min. The solvent systems were: (I) EtOAc–MeOH (9:1); (II) EtOAc–MeOH–$H_2O$ (40:10:1); (III) EtOAc–MeOH–$H_2O$ (70:30:3); (IV) 10–80% aqueous MeOH; (V) 10% aqueous MeCN; (VI) 15% aqueous MeCN; (VII) 20% aqueous MeCN; and (VIII) 40% aqueous MeOH. The spraying reagent used for TLC was 10% $H_2SO_4$ in 50% EtOH.

### 4.2. Plant material

The aerial portion of *C. orientalis* Zipp. Ex Span. was collected in March 2005 from Chaiyaphum Province, Thailand. The identification of the plant was confirmed by Dr. Thaweesak Thitimetharoch, Department of Pharmaceutical Botany and Pharmacognosy, Faculty of Pharmaceutical Sciences, Khon Kaen University. A voucher specimen (TK-PSKKU-0055) was deposited in the Herbarium of the Faculty of Pharmaceutical Sciences, Khon Kaen University.

### 4.3. Extraction and isolation

The aerial portion of *C. orientalis* (3.4 kg) was extracted three times with hot MeOH (8 l for each extraction, under reflux). The MeOH extract was concentrated in vacuo to give a powder (381.9 g). This residue was suspended in $H_2O$ (1.0 l), and then partitioned with $Et_2O$ (1.0 l) and *n*-BuOH (1.0 l), successively. The *n*-BuOH soluble fraction (106.4 g) was subjected to highly porous synthetic resin column chromatography (Diaion HP-20), and eluted with $H_2O$, MeOH and $(CH_3)_2CO$, successively. The fraction eluted with MeOH (65.9 g) was subjected to a column of silica gel using solvent systems I (6.5 l), II (6.0 l) and III (4.0 l), to provide six fractions (Fr. a–f), monitored by TLC. Fraction b (32.1 g) was subjected to a column of RP-18 using solvent system IV to give nine fractions (fr. b-1 to b-9). Fraction b-7 was purified by preparative HPLC-ODS with solvent systems VII and VIII, respectively, to afford compounds **2** (65.9 mg) and **3** (43.1 mg). Fraction c (4.8 g) was subjected to a column of RP-18 using solvent system V to provide seven fractions (fr. c-1 to c-7). Fraction c-3 was purified by preparative HPLC-ODS with solvent system V to give compounds **4** (9.0 mg) and **5** (20.9 mg). Fraction c-5 was purified by preparative HPLC-ODS using solvent system VI to provide compound **1** (123.5 mg). Similarly, fraction c-6 was purified by preparative HPLC-ODS using solvent system VII to afford compounds **6** (35.2 mg) and **9** (5.6 mg). Fraction d (6.5 g) was subjected to a column of RP-18 using solvent system IV, giving nine fractions (fr. d-1 to d-9). Fraction d-8 was semi-purified by preparative HPLC-ODS using solvent system VII, and followed by solvent system VIII to provide compound **8** (9.8 mg). Finally, fraction e was separated by a column of RP-18 using solvent system IV to provide six fractions (fr. e-1 to e-6). Fraction e-4 provides the major constituent, compound **7** (1.2 g) by precipitation.

Table 2
NMR spectroscopic data of compound **9**

| No. | $\delta_C$ | $\delta_H$ |
|---|---|---|
| 1 | 138.8 | |
| 2, 6 | 129.3 | 7.38 (2H, *br d*, $J = 7.8$ Hz) |
| 3, 5 | 129.2 | 7.24 (2H, *m*) |
| 4 | 128.8 | 7.27 (1H, *m*) |
| 7 | 71.8 | 4.65 (1H, *d*, $J = 11.8$ Hz) 4.88 (1H, *d*, $J = 11.8$ Hz) |
| Glc | | |
| 1′ | 103.2 | 4.35 (1H, *d*, $J = 7.8$ Hz) |
| 2′ | 75.2 | 3.26 (1H, *dd*, $J = 8.3$, 7.8 Hz) |
| 3′ | 78.1 | 3.31 (1H, *dd*, $J = 9.3$, 8.3 Hz) |
| 4′ | 71.6 | 3.33 (1H, *dd*, $J = 9.3$, 9.3 Hz) |
| 5′ | 76.9 | 3.39 (1H, *m*) |
| 6′ | 67.9 | 3.70 (1H, *dd*, $J = 11.3$, 5.6 Hz) 4.02 (1H, *br d*, $J = 11.3$ Hz) |
| Rha | | |
| 1″ | 102.3 | 4.84 (1H, *br s*) |
| 2″ | 72.4 | 3.94 (1H, *br d*, $J = 3.4$ Hz) |
| 3″ | 70.6 | 3.98 (1H, *dd*, $J = 9.8$, 3.4 Hz) |
| 4″ | 75.7 | 5.10 (1H, *dd*, $J = 9.8$, 9.8 Hz) |
| 5″ | 68.2 | 3.96 (1H, *m*) |
| 6″ | 18.0 | 1.15 (3 H, *d*, $J = 6.3$ Hz) |
| Galloyl moiety | | |
| 1′ | 121.6 | |
| 2‴, 6‴ | 110.3 | 7.09 (2H, *br s*) |
| 3‴, 5‴ | 146.5 | |
| 4‴ | 139.9 | |
| 7‴ | 168.2 | |

### 4.4. Violutoside (7)

Amorphous powder, $[\alpha]_D^{29} - 50.4°$ (MeOH *c* 0.50); UV $\lambda_{max}$MeOH (nm): 284; for $^1H$ and $^{13}C$ NMR ($CD_3OD$) spectra, see Table 1; negative HR-FAB-MS, *m/z*: 445.1357 M–H]– (calcd. for $C_{19}H_{25}O_{12}$, 445.1346).

### 4.5. Acid hydrolysis of violutoside (7)

A solution of compound **7** (20 mg) in 1,4-dioxane (1 ml) and 5% $H_2SO_4$ (1 ml) was heated at 90 °C for 3 h. After cooling, $H_2O$ (2 ml) was added and the whole extracted with EtOAc. The aqueous layer was neutralized with saturated $NaHCO_3$ and concentrated to dryness. The residue was applied to a silica gel column, using $CHCl_3$–MeOH–$H_2O$ (40:10:1) as solvent system to obtain L-arabinose (2 mg, $[\alpha]_d^{29} + 98.8$) and D-glucose (3 mg, $[\alpha]_d^{29} + 49.5$) in comparison with authentic samples.

### 4.6. 4″-O-galloyl-violutoside (8)

Amorphous powder, $[\alpha]_D^{28} + 19.4°$ (MeOH *c* 0.63); UV $\lambda_{max}$MeOH (nm): 279.5; for $^1H$ and $^{13}C$ NMR ($CD_3OD$) spectra, see Table 1; negative HR-FAB-MS, *m/z*: 597.1457 $[M–H]^-$ (calcd. for $C_{26}H_{29}O_{16}$, 597.1456).

### *4.7. 4″-O-galloyl-benzyl-O-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside (**9**)*

Amorphous powder, $[\alpha]_D^{28} - 25.7°$ (MeOH *c* 0.37); UV $\lambda_{max}$MeOH (nm): 277; for $^1$H and $^{13}$C NMR ($CD_3OD$): Table 2; negative HR-FAB-MS, *m/z*: 567.1721 $[M–H]^-$ (calcd. for $C_{26}H_{31}O_{14}$, 567.1714).

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