Pergamon

PII: S0031-9422(98)00019-3

Phytochemistry, Vol. 48, No. 4, pp. 711–717, 1998

Printed in Great Britain
0031-9422/98 $19.00+0.00

LIGNAN AND ACETYLENIC GLYCOSIDES FROM *ASTER AURICULATUS*

CHANG ZENG WANG and DE QUAN YU*

Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, 1 Xian Nong Tan Street, Beijing 100050, P.R. China

(*Received in revised form* 9 *December* 1997)

Key Word Index—*Aster auriculatus*; Compositae; roots; lignan glucosides; acetylenic glycosides; decaene; syringaresinol; 2D NMR.

Abstract—One new lignan glucoside, *erythro*-1-(4-*O*-*β*-D-glucopyranosyl-3,5-dimethyoxyphenyl)-2-syringaresinoxyl-propane-1, 3-diol, four new acetylenic glycosides, 8*E*-decaene-4,6-diyn-1-*O*-*β*-D-glucopyranosyl-(1″–2′)-*β*-D-glucopyranoside, 8*E*-decaene-4,6-diyn-1-*O*-*β*-D-apiofuranosyl-(1″–6′)-*β*-D-glucopyranoside, 8*E*-decaene-4,6-diyn-1-*O*-*β*-D-glucopyranoside and 2*E*-decaene-4,6-diyn-1-*O*-*β*-D-glucopyranoside, as well as the known syringaresinol-4′-*O*-*β*-D-glucopyranoside were isolated from roots of *Aster auriculatus*. They were identified on the basis of spectral data and chemical evidence.

INTRODUCTION

Although many acetylenic compounds have been isolated from the Compositae [1–4], acetylenic glycosides are very limited in occurrence [5, 6]. In continuation of our chemical investigation on the glycosidic constituents from the roots of *Aster auriculatus* [7], we have isolated four new C_{10}-acetylenic glycosides (**3**–**6**). In addition, one new sesquilignan glucoside (**1**) and the known syringaresinol-4′-*O*-*β*-D-glucopyranoside (**2**) were also obtained from the *Aster* genus for the first time. This paper describes their isolation and structural elucidation.

RESULTS AND DISCUSSION

The 70% ethanol extract from roots was chromatographed over a highly porous polymer column eluting successively with water, 30%, 60% and 95% ethanol. The 60% ethanol eluate was then subjected to repeated CC over silica gel to obtain compounds **1**–**6**.

Compound **2** was identified as syringaresinol-4-′-*O*-*β*-D-glucopyranoside by comparison of its spectral data with those reported in the literature [8].

Compound **1**, obtained as a white amorphous powder, gave a positive response with $FeCl_3$ and Molish tests, indicating that it was a glycoside with a phenolic hydroxyl group. Its FAB mass spectrum showed a $[M+H]^+$ at *m/z* 807, which suggested the molecular formula of $C_{39}H_{50}O_{18}$, compatible with the results of elemental analysis. The IR spectrum of **1** showed the presence of hydroxyl at 3418 cm^{-1}, a phenyl ring at 1595, 1500 and 1462 cm^{-1} and a C—O—C bond at 1124–1000 cm^{-1}. The NMR data clearly indicated the presence of six aromatic methoxyl groups, one unit of *β*-glucose, a *bis*-tetrahydrofuran ring [9], a 1-phenyl-2-aryloxypropane-1, 3-diol moiety [10] and three sets of 3, 5-dimethoxy-4-oxygenated phenyls [11, 12] (Table 1). This suggested that **1** was a sesquilignan monoglucoside, with an overall structure shown in Fig. 1, the chemical shifts of which were assigned from the analysis of the 2D NMR spectral data, including ^1H-^1H COSY, ^{13}C-^1H COSY and HMBC spectra.

The relatively small coupling constant between H-7″ and H-8″ (5.3 Hz) and the chemical shift of C-7″ (*δ* 74.04), indicated that the 1-phenyl-2-aryloxypropane-1,3-diol moiety was in the *erythro*-configuration [12–16]. Comparison between the NMR data of **1** and syringaresinol-4′-*O*-D-monoglucopyranoside (**2**), showed that in **1**, H-7 and H-7′ were both axial, i.e. the *β*-configuration [8, 17–19].

From the well resolved resonance of H-7″ (*δ* 4.96, *d*, *J* = 5.3 Hz), the ^{13}C NMR chemical shift assignments from C-1″ to C-4″ were proved by analysis of the correlation in the HMBC spectrum between the resonance of H-7″ and C-1″ (*δ* 139.49), H-7″ and C-2″/6″ (*δ* 106.05), C-1″ and H-2″/H-6″ (*δ* 6.78), H-2″/6″ and C-3″/5″ (*δ* 153.83), H-2″/6″ and C-4″ (*δ* 135.51). With the signal of *δ* 135.51 assigned to C-4″, the glucosyl linkage could be assigned to this position from the cross-peak between Glu H-1 (*δ* 4.86, *d*, *J* = 7.8 Hz)

* Author to whom correspondence should be addressed.

Table 1. NMR chemical shifts (δ) of compounds **1** and **2** (125 MHz for ^{13}C and 500 MHz for ^{1}H)

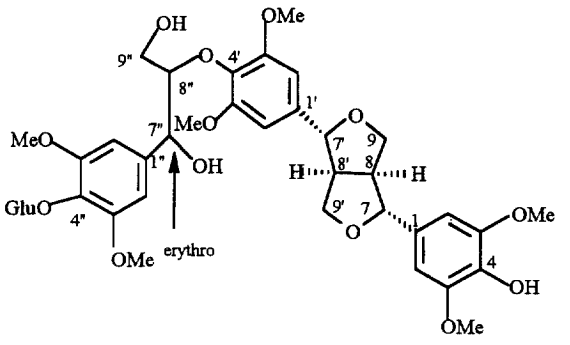
Position	**1** (CD_3OD)		**2** (CD_3OD)		DEPT
1	133.1		133.2		C
2, 6	104.6	6.69 *s*	105.0	6.68 *s*	CH
3, 5	149.4		149.4		C
4	136.3		136.4		C
7	87.2	4.79 *d* (3.1)	87.2	4.79 *d* (4.0)	CH
8	55.7	3.17 *m*	55.7	3.15 *m*	CH
9	72.8	4.31 *m*, 3.95 *m*	72.9	4.31 *m*, 3.93 *m*	CH_2
3,5-OMe	56.9	3.88 *s*	56.9	3.88 *s*	CH_3
1′	139.0		139.6		C
2′, 6′	104.4	6.72 *s*	104.8	6.74 *s*	CH
3′, 5′	154.6		154.4		C
4′	136.1		135.8		C
7′	87.6	4.75 *d* (4.0)	87.6	4.74 *d* (4.4)	CH
8′	55.5	3.17 *m*	55.5	3.15 *m*	CH
9′	72.9	4.32 *m*, 3.95 *m*	73.0	4.31 *m*, 3.93 *m*	CH_2
3′,5′-OMe	57.0	3.87 *s*	57.2	3.87 *s*	CH_3
1″	139.5				C
2″, 6″	106.1	6.78 *s*			CH
3″, 5″	153.8				C
4″	135.5				C
7″	74.0	4.96 *d* (5.3)			CH
8″	87.0	4.30 *m*			CH
9″	61.6	3.64 *dd* (8.0, 3.6) 3.94 *d* (8.0)			CH_2
3″,5″-OMe	56.8	3.84 *s*			CH_3
Glu					
1	105.6	4.86 *d* (7.8)	105.4	4.89 *d* (7.9)	CH
2	75.8	3.51 *dd* (7.8, 9.0)	75.8	3.51 *dd* (7.9, 8.8)	CH
3	78.3	3.25 *m*	78.3	3.23 *m*	CH
4	71.4	3.45 *m*	71.4	3.44 *m*	CH
5	77.8	3.46 *m*	77.9	3.45 *m*	CH
6	62.6	3.70 *dd* (12.1, 4.9) 3.81 *dd* (12.1, 2.2)	62.7	3.69 *dd* (12.0, 5.1) 3.80 *dd* (12.0, 2.4)	CH_2

and C-4″ (δ 135.51). This conclusion was further confirmed by the fragment ions in the FAB mass spectrum (Fig. 2). From the above results, **1** was identified as *erythro*-1-(4-*O*-β-D-glucopyranosyl-3,5-dimethoxyphenyl)-2-syringaresinoxyl-propane-1, 3-diol.

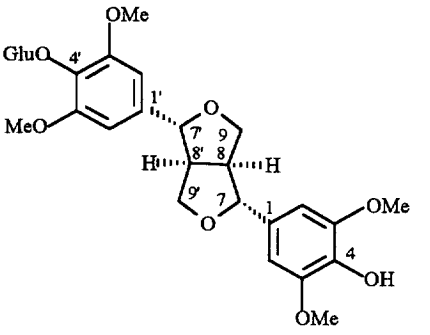
Compound **3** was obtained as a white amorphous powder. Its IR spectrum showed absorptions for hydroxyl at 3406 cm^{-1}, C≡C at 2368–2153 cm^{-1}, a double bond at 1628 cm^{-1} and a C—O—C bond at 1076–1000 cm^{-1}. The ^{1}H NMR spectrum showed one methyl group at δ 1.54 (*dd*, J = 6.9, 1.4 Hz), two *trans*-double bond protons at δ 6.22 (*dq*, J = 15.9, 6.9 Hz) and 5.55 (*d*, J = 15.9 Hz) and 16 protons resonating in the region of δ 3.65–5.28, including two anomeric protons at δ 5.27 (*d*, J = 7.7 Hz) and 4.83 (*d*, J = 7.7 Hz). The ^{13}C NMR and DEPT spectra revealed the presence of one methyl group at δ 18.5, two olefinic carbons at δ 143.5 and 110.3, four C≡C bonded quaternary carbons at δ 84.5, 74.7, 74.0 and 66.2, five methylenes at δ 16.6, 29.2, 62.6, 62.8 and 68.2, and ten methines in the region δ 107–71, including two anomeric carbons at δ 106.6 and 102.9. These spectral data suggested that compound **3** was a C_{10}-acetylene diglycoside. The FAB mass spectrum showed a $[M+H]^+$ at m/z 473, suggesting the molecular formula $C_{22}H_{32}O_{11}$, compatible with its NMR data.

Acid hydrolysis of **3** with 2N HCl-MeOH produced sugar components, which were identified as glucose by PC comparison with an authentic sample. The two glucose units had β-configurations, based on the coupling constants of their anomeric protons.

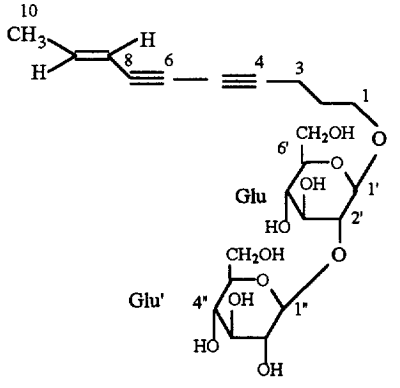
The ^{1}H NMR spectrum of the aglycone moiety of **3** showed two separate spin systems. The first was a $CH_3CH{=}CH$— unit related to five protons at δ 1.54 (3H), 5.55 (1H) and 6.22 (1H), respectively, the second, a —$CH_2CH_2CH_2O$— unit, which corresponded with the six protons at δ 1.88 (2H, *t*, J = 6.5 Hz), 2.61 and 2.69 (each 1H, *m*), 3.85 and 3.93 (each 1H, *m*), the chemical shifts of the last two protons showing that this methylene must be bounded to an oxygen atom. The two units were linked through two acetylenic bonds; therefore, the aglycone was deter-



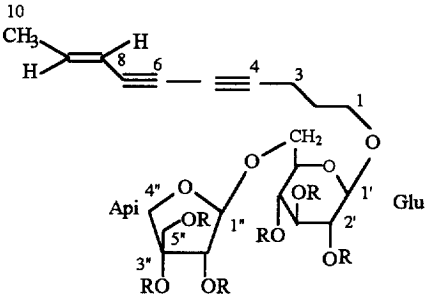
1



2

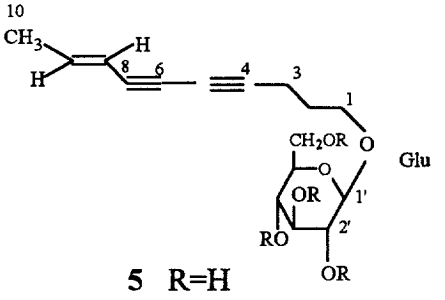


3



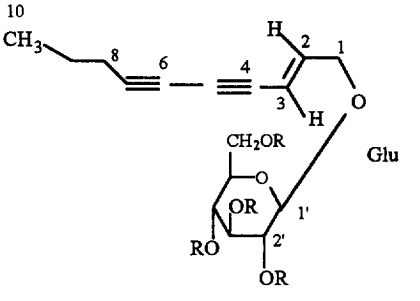
4 R=H

4a R=Ac



5 R=H

5a R=Ac



6 R=H

6a R=Ac

Fig. 1.

mined to be CH_3—CH=CH—C≡C—C≡C—CH_2 CH_2CH_2O—.

The ^{13}C NMR spectrum of **3** displayed signals at δ 106.6, 76.8, 78.6, 71.4, 78.3 and 62.6, attributable to C-1 to C-6 of a terminal glucose, respectively. The signals observed at δ 102.9, 84.4, 78.0, 71.7, 78.0 and 62.8 were due to C-1 to C-6 of the inner glucose. The glycosylation shifts of +10.3 ppm for the C-2 of the

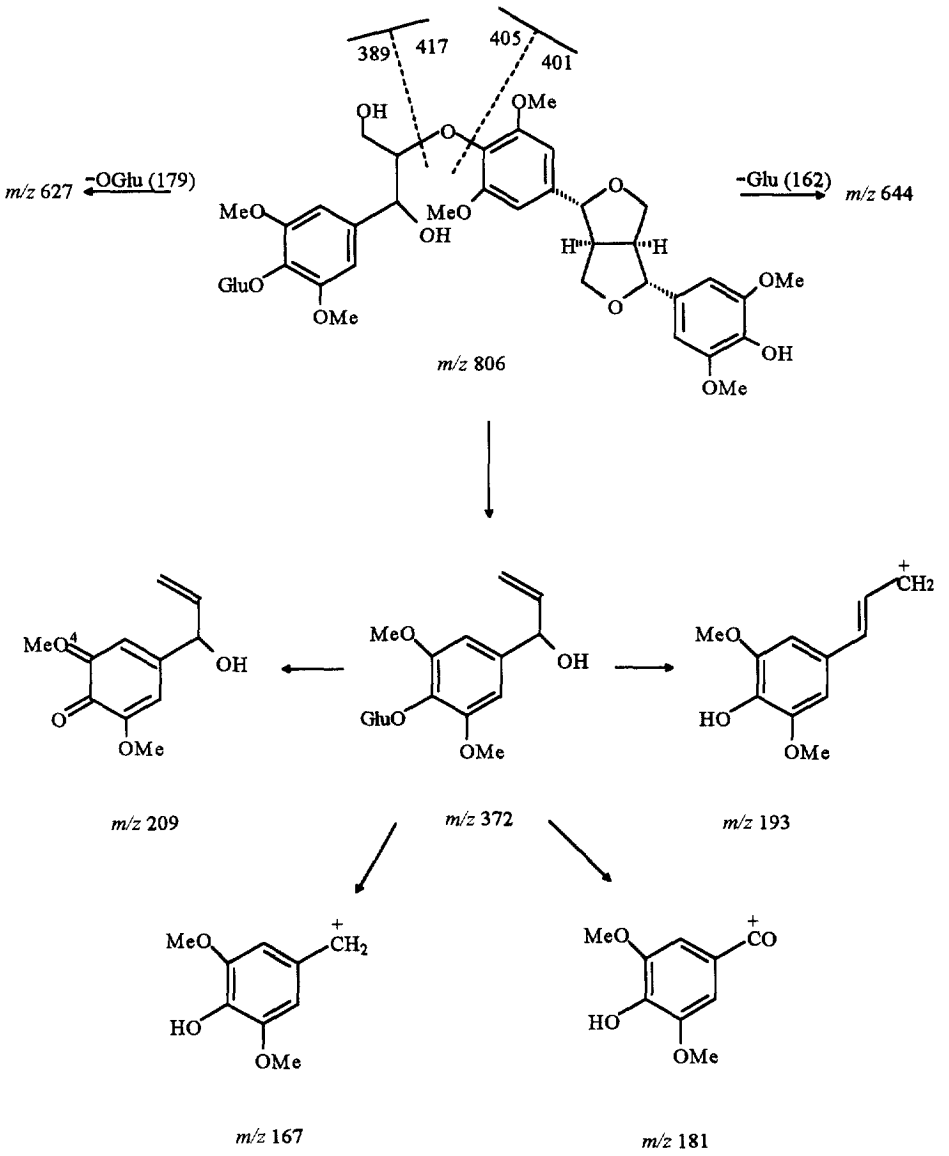


Fig. 2. FAB mass spectral fragment ions of compound **1**.

inner glucose in comparison with that of methyl-β-D-glucopyranoside [20] showed that the terminal glucose was connected to C-2 of the inner glucose.

Taken together, this evidence gave the structure shown for **3** and this conclusion was confirmed by 2D NMR experiments, including ^{1}H-^{1}H COSY, ^{13}C-^{1}H COSY and HMBC, which demonstrated the various chemical shift assignments and their connectivities. Thus, compound **3** was established as 8*E*-decaene-4,6-diyn-1-*O*-β-D-glucopyranosyl-(1″–2″)-β-D-glucopyranoside.

Compound **4** was obtained as its corresponding peracetate **4a**. The IR spectrum showed the presence of a —C≡C— bond at 2230 and 2130 cm^{-1}, a double bond at 1630 cm^{-1} and a C—O—C bond at 1038 cm^{-1}. The ^{1}H NMR spectrum of **4a** showed two separate spin moieties for $CH_3CH{=}CH{-}$ [δ 1.79 (3H, *dd*, J = 6.9, 1.8 Hz), 6.28 (1H, *dq*, J = 15.9, 6.9 Hz) and 5.57 (1H, *d*, J = 15.9 Hz)] and $-CH_2CH_2CH_2O-$ [δ 2.39 (2H, *t*, J = 7.0 Hz), 1.73–1.81 (2H, *m*), 3.63 and 3.88 (each 1H, *m*)], as well as two anomeric protons at δ 4.69 (1H, *d*, J = 8.0 Hz) and 5.04 (1H, *s*). The ^{13}C NMR data of the aglycone part of **4a** was almost superposable on that of **3**, which indicated that it was also a 4,6-diyn-8*E*-decaene diglycoside.

Acid hydrolysis of **4a** afforded glucose and apiose as sugar components, identified by PC comparison with authentic samples. Comparison between the ^{13}C NMR data of **4a** and those of methyl-β-D-glucopyranosepentaacetate [20], showed that in the acetyl glucose moiety of the former, the C-6 resonance (δ 67.1) was shifted downfield by +5.5 ppm and the C-5 (δ 72.2) shifted upfield by −0.8 ppm, owing to the glycosylation effect. This showed that the terminal

Table 2. NMR chemical shifts (δ) of the aglycone moieties of compounds **3**, **4a**, **5**, **5a**, **6** and **6a**. (500 MHz for ^1H and 125 MHz for ^{13}C)

Position	**3** (C_5D_5N)	**4a** (CD_3COCD_3)	**5** ($CDCl_3$)	**5a** (CD_3OD)	**6** ($CDCl_3$)	**6a** (CD_3OD)
1	68.2	68.6	68.7	69.3	69.0	69.8
	3.85 *m*	3.63 *m*	3.53 *m*	3.69 *m*	3.50–3.65	4.25 *ddd* (1.7, 5.6, 15.5)
	3.93 *m*	3.88 *m*	3.62 *m*	3.95 *m*	3.92 *m*	4.42 *ddd* (1.9, 5.0, 15.5)
2	29.2	29.1	28.4	29.4	141.5	144.2
	2.61 *m*	1.73–1.8 *m*	2.40–2.50 *m*	1.77–1.87 *m*	6.30 *m* (16.0)	6.32 *m* (16.0)
	2.69 *m*					
3	16.6	16.2	16.2	16.5	111.2	110.8
	1.88 *t* (6.5)	2.39 *t* (7.0)	1.83 *t* (6.3)	2.43 *t* (6.9)	5.85 *d* (16.0)	5.59 *d* (16.0)
4	66.2	66.2	65.7	66.0	84.8	85.2
5	74.04	73.3	72.6	73.5	75.2	75.9
6	74.7	74.8	74.3	74.8	72.2	73.4
7	84.5	84.7	82.7	83.0	65.2	66.6
8	110.3	110.4	109.8	111.4	21.0	22.0
	5.55 *d* (15.9)	5.57 *d* (15.9)	5.49 *d* (15.8)	5.80 *d* (15.9)	2.29 *t* (7.3)	2.35 *t* (7.0)
9	143.5	144.2	143.2	142.7	21.7	22.9
	6.22 *dq* (15.9, 6.9)	6.28 *dq* (15.9, 6.9)	6.28 *dq* (15.8, 6.9)	6.29 *m* (15.9, 7.0)	1.24 *m* (7.3)	1.60 *m* (7.0)
10	18.5	18.7	18.8	18.8	14.2	13.7
	1.54 *dd* (1.4, 6.9)	1.78 *dd* (1.8, 6.9)	1.80 *dd* (1.6, 6.9)	1.85 *dd* (1.8, 7.0)	0.99 *t* (7.3)	1.04 *t* (7.0)

apiose unit was connected to the C-6 of the inner glucose unit.

The FAB mass spectrum of **4a** showed an $[M+H]^+$ at *m/z* 695, which was consistent with the molecular formula $C_{33}H_{42}O_{16}$. The observation of fragment ion peaks at *m/z* 259 $[Api(OAc)_3]^+$, 289 $[Glu(OAc)_3]^+$ and 547 $[Api(OAc)_3Glu(OAc)_3]^+$ provided additional evidence for the sequence of the sugar moiety. Therefore, compound **4** was proved to be 8*E*-decaene-4,6-diyn-1-*O*-β-D-apiofuranosyl-(1″–6′)-β-D-glucopyranoside.

Compounds **5** and **6** were obtained as a mixture (ca 2:1) after analysis of ^1H and ^{13}C NMR data. They gave only one red spot on HPTLC eluting with general solvent systems; acetylation failed to resolve them. The quasi-molecular ion peaks at *m/z* 311 $[M+H]^+$ and 333 $[M+Na]^+$ in the FAB mass spectrum suggested the molecular formula $C_{16}H_{22}O_6$, which was supported by the ^1H NMR, ^{13}C NMR and DEPT data (Tables 2 and 3). Most NMR signals from the mixture were double, but due to the different amounts of **5** and **6**, it was possible to identify the individual signals for the two compounds. It was evident that both **5** and **6** contained four *sp*-bonded carbon signals and that both were β-monoglucopyranosides. The difference between **5** and **6** was only due to their aglycone moieties. The ^1H NMR spectra showed the presence of two separate units of $CH_3CH{=}CH{-}$ and $-CH_2CH_2CH_2O-$ in **5**, but $CH_3CH_2CH_2-$ and $-CH{=}CHCH_2O-$ in **6** [21, 22] (Table 2), which indicated that the *trans*-double bond in **5** was at C-8/9 and in **6**, at C-2/3. The glucosyl linkages at C-1 in **5** and **6** were determined from the signals of δ 68.7 (C-1 of **5**) and 69.0 (C-1 of **6**). The FAB mass spectrum of peracetylated **5a** and **6a** also showed quasi-molecular ions at 479 $[M+H]^+$, 501 $[M+Na]^+$ and 331 $[Glu(OAc)_4]^+$. Thus, compound **5** and **6** were elucidated as 8*E*-decaene-4, 6-diyn-1-*O*-β-D-glucopyranoside and 2*E*-decaene-4, 6-diyn-1-*O*-β-D-glucopyranoside, respectively.

EXPERIMENTAL

General

Mps are uncorr. NMR spectra were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C. TLC was on silica gel GF_{254} and HPTLC on silica gel H (5–7 μm). Separation and purification were performed by CC on silica gel (300–400 mesh and 180–200 mesh).

Plant material. Roots of *A. auriculatus* were collected in Sichuan Province, P. R. China. A voucher specimen (880801) was identified by Prof. W. Z. Song and is deposited in the Herbarium of the authors' Institute.

Extraction and purification. Air-dried roots (2.5 kg) were extracted with 70% EtOH (5 × 5 l) under reflux. The combined extracts were evapd under red. pres. to obtain a crude syrup (500 g), which was chromatographed over a highly porous polymer column (RA, Seventh Chemical and Industrial Factory, Beijing) (9.5 × 50 cm, 2 × 750 g) eluting successively with H_2O, 30%, 60% and 95% EtOH. The 60% EtOH eluate (250 g) was subjected to CC over silica gel (8.0 × 64 cm, 180–200 mesh, 2 kg) eluting with $CHCl_3$–MeOH (9:1 → 1:1) gradient to afford eight crude frs after monitoring by HPTLC. Fr. 1 (14–20), elution

Table 3. NMR chemical shifts (δ) of sugar moieties of compounds **3**, **4a**, **5**, **5a**, **6** and **6a**. (500 MHz for ^1H and 125 MHz for ^{13}C)

Position	**3** (C_5D_5N)	**4a** (CD_3COCD_3)	**5** ($CDCl_3$)	**5a** (CD_3OD)	**6** ($CDCl_3$)	**6a** (CD_3OD)
	Glu					
1	102.9	101.3	102.8	101.3	102.1	101.9
	4.83 *d* (7.7)	4.69 *d* (8.0)	4.31 *d* (7.0)	4.74 *d* (8.0)	4.34 *d* (7.0)	4.70 *d* (8.0)
2	84.4	73.6	73.3	72.8	72.9	72.8
	4.11 *dd* (7.7, 9.0)	4.86 *dd* (8.0, 9.6)		4.92 *dd* (8.0, 9.7)		4.95 *dd* (8.0, 9.7)
3	78.0	73.7	76.3	74.2	77.0	74.3
		5.21 *dd* (9.6, 9.6)		5.30 *dd* (9.7, 9.7)		5.30 *dd* (9.7, 9.7)
4	71.7	69.8	69.2	69.9	69.8	69.9
		4.92 *dd* (9.6, 9.6)		5.06 *t* (9.7)		5.06 *t* (9.7)
5	78.0	72.2	75.5	72.9	76.1	72.9
	3.67 *m*	3.76 *m*		3.93 *m*		3.95 *m*
6	62.8	67.1	61.2	63.1	60.4	63.1
	4.42 *dd* (11.6, 4.6)	4.66 *d* (12.1)		4.17 *dd* (12.3 2.3)		4.17 *dd* (12.3, 2.3)
	4.53 *dd* (11.6, 2.4)	4.62 *d* (12.1)		4.32 *dd* (12.3, 4.5)		4.32 *dd* (12.3, 4.5)
	Glu	Api				
1′	106.6	106.9				
	5.27 *d* (7.7)	5.04 *s*				
2′	76.8	76.8				
	4.18 *dd* (7.7, 8.5)	5.28*s*				
3′	78.6	83.5				
	4.10 *t* (8.5)					
4′	71.4	73.2				
	4.25 *t* (8.5)	2.83 *d* (15.5)				
5′	78.3	63.8				
	4.05 *m*	4.24 *d* (10.3)				
		4.06 *d* (10.3)				
6′	62.6					
	4.33 *dd* (11.6, 5.3)					
	4.48 *dd* (11.6, 2.1)					
CH_3 (Ac)		2.00 (12H)		2.10 (9H)		2.01 (9H)
		1.98 (6H)		1.96 (3H)		1.98 (3H)
		1.95 (6H)				
$COCH_3$		20.1–20.6		20.2–20.8		20.2–20.8
		167.8–170.8		168.2–170.5		168.2–170.5

with $CHCl_3$–MeOH, 9:1, 500 ml frs) was separated by silica gel CC eluting with EtOAc-95% EtOH (12:1) to obtain pure **1** (35 mg) and **2** (90 mg). Fr. 2 (21–25, eluting with $CHCl_3$–MeOH, 9:1, 500 ml frs) was also chromatographed over silica gel eluting with $CHCl_3$–MeOH (8:1) and then subjected to CC over silica gel eluting with EtOAc–95% EtOH (9:1) to obtain a mixt. of **5** and **6** (80 mg). This (60 mg) was acetylated with Ac_2O (2 ml) and dry pyridine (2 ml) at room temp. overnight. The soln was evapd *in vacuo* and the residue purified by CC over silica gel eluting with petrol Me_2CO (4:1) followed by recrystallization from MeOH at 0–5°, to obtain a mixt. of **5a** and **6a**. Mixts of **5** and **6**, and **5a** and **6a**, both showed one clear red spot with 5% H_2SO_4-EtOH on HPTLC (silica gel 5–7 μm) eluting with EtOAc–95% EtOH (6:1) and petrol–Me_2CO (4:1), respectively; R_fs 0.52 for **5** and **6**; 0.29 for **5a** and **6a**. Furthermore, **5** and **6**, and **5a** and **6a** could not be separated by HPLC or HPTLC eluting with any other solvent systems. Fr. 4 (47–61, elution with $CHCl_3$–MeOH, 4:1, 500 ml frs) was separated by repeated chromatography over a silica gel eluting with $CHCl_3$–MeOH–H_2O (5:1:0.1) to obtain crude compound **4**, which was acetylated with Ac_2O-pyridine (1:1) at room temp. overnight. After concn under red. pres., the residue was subjected to CC over silica gel eluting with petrol Me_2CO (5:1) to obtain pure **4a** R_f 0.33 on HPTLC in petrol–Me_2CO, 5:1. Fr. 5 (62–64, elution with $CHCl_3$–MeOH, 7:3, 500 ml frs) was subjected to CC over silica gel eluting with EtOAc-*n*-BuOH-H_2O (4:1:0.2) to obtain crude compound **3**, which was purified by CC over silica gel eluting with $CHCl_3$–MeOH–H_2O (7:1:0.1) to give pure **3** (150 mg).

Compound **1**. Amorphous powder, mp 121–123°. $[\alpha]_D^{31}$ +15.85° (MeOH, *c* 0.057). $C_{39}H_{50}O_{18}$, elemental analysis: found: C 54.30%, H 6.49%; Calcd: C 54.40%, H 6.56% for $C_{39}H_{50}O_{18}$. $3H_2O$. FAB-MS *m/z*: 807 $[M+H]^+$, 644, 627, 597, 444, 417, 405, 401, 387,

372, 282, 229, 209, 193, 181, 167. IR ν_{max}^{KBr} (cm^{-1}): 3418, 2932, 1595, 1500, 1462, 1225, 1124–1063–1000. ^1H and ^{13}C NMR: Table 1.

Compound **2**. Amorphous powder. $C_{28}H_{36}O_{13}$. FAB-MS *m/z*: 581 $[M+H]^+$, 418 $[M-162]^+$. ^1H and ^{13}C NMR: Table 1.

Compound **3**. Amorphous powder, mp 160–163°. $[\alpha]_D^{31}$ 0° (MeOH, *c* 0.052). $C_{22}H_{32}O_{11}$. FAB-MS *m/z*: 473 $[M+H]^+$, 325 [Glu-Glu]$^+$, 309 [M-Glu]$^+$, 255, 235, 207, 186, 163 [Glu]$^+$, 145, 131, 115, 85, 69. EI-MS *m/z*: 309 $[M-Glu]^+$, 292, 256, 235, 218, 191, 163, 148, 145, 127, 115, 91, 85, 73, 57. IR ν_{max}^{KBr} (cm^{-1}): 3406, 2922, 2368, 2230, 2153, 1628, 1375, 1076–1032. ^1H and ^{13}C NMR: Tables 2 and 3.

Compound **4a**. Solid. $C_{33}H_{42}O_{16}$. FAB-MS *m/z*: 695 $[M+H]^+$, 547 $[Api(OAc)_3Glu(OAc)_3]^+$, 505, 407, 289 $[Glu(OAc)_3]^+$, 259 $[Api(OAc)_3]^+$, 217, 169, 139. IR ν_{max}^{KBr} (cm^{-1}): 2957, 2230, 2130, 1751, 1630, 1433, 1371, 1221, 1038. ^1H and ^{13}C NMR: Tables 2 and 3.

Compounds **5** *and* **6**. Liquid. $C_{16}H_{22}O_6$. FAB-MS *m/z*: 311 $[M+H]^+$, 333 $[M+Na]^+$, 147 $[M-Glu]^+$. ^1H and ^{13}C NMR: Tables 2 and 3.

Compounds **5a** *and* **6a**. Amorphous powder, mp 105–107°. $[\alpha]_D^{31}$ −17.1° (MeOH, *c* 0.050). $C_{24}H_{30}O_{10}$. FAB-MS *m/z*: 501 $[M+Na]^+$, 479 $[M+H]^+$, 331 $[Glu(OAc)_4]^+$, 285, 169 $[M+Na-Glu(OAc)_4-H]^+$, 109. IR ν_{max}^{KBr} (cm^{-1}): 2230, 2150, 1747, 1632, 1367, 1230, 1040. ^1H and ^{13}C NMR: Tables 2 and 3.

REFERENCES

1. Christensen, L. P. and Lam, J., *Phytochemistry*, 1990, **29**, 2753.
2. Christensen, L. P. and Lam, J., *Phytochemistry*, 1991, **30**, 11.
3. Christensen, L. P. and Lam, J., *Phytochemistry*, 1991, **30**, 2453.
4. Christensen, L. P., *Phytochemistry*, 1992, **31**, 7.
5. Rucker, G., Kehrbaum, S., Sakulas, H., Lawong, B. and Goeltenboth, F., *Planta Medica*, 1992, **58**, 266.
6. Shao, Y., Zhou, B. N., Gao, J. H., Lin, L. Z. and Cordell, G. A., *Phytochemistry*, 1995, **38**, 675.
7. Wang, C. Z. and Yu, D. Q., *Phytochemistry*, 1997, **45**, 1483.
8. Lanni, I., Kadota, S., Kikuchi, T. and Momose, Y., *Chem. Pharm. Bull.*, 1991, **39**, 1551.
9. Macreae, W. E. and Towers, G. H. N., *Phytochemistry*, 1985, **24**, 561.
10. Popoff, T. and Theander, O., *Acta Chem. Scand B*, 1977, 329.
11. Deyama, T., Ikawa, I. and Nishibe, S., *Chem. Pharm. Bull.*, 1985, **33**, 3651.
12. Wang, C. Z. and Jia, Z. J., *Planta Medica*, 1997, **63**, 241.
13. Fang, J. M., Lee, C. K. and Cheng, Y. S., *Phytochemistry*, 1992, **31**, 3659.
14. Hattori, M., Hada, S., Shu, Y. S., Kakiuchi, N. and Namba, T., *Chem. Pharm. Bull.*, 1987, **35**, 668.
15. Braga, A. C. H., Zacchino, S., Badano, H., Sierra, M. G. and Ruveda, E. A., *Phytochemistry*, 1984, **23**, 2025.
16. Miki, K., Takehara, T., Sasaya, T. and Sakakibara, A., *Phytochemistry*, 1980, **19**, 449.
17. Pelter, A., Ward, R. S., Rao, E. V. and Sastry, K. V., *Tetrahedron*, 1976, **32**, 2783.
18. Pelter, A., Ward, R. S. and Nishino, C., *Tetrahedron Letters*, 1977, **47**, 4137.
19. Russel, G. B. and Fenemore, P. G., *Phytochemistry*, 1973, **12**, 1799.
20. Wang, X. K., *Medicinal Chemistry of Natural Products*, Public Health Press, Beijing, 1989, p. 220.
21. Bohlmann, F., Zdero, C., Robinson, H, and King, R. M., *Phytochemistry*, 1979, **18**, 1519.
22. Bohlmann, F., Zdero, C. and Kapteyn, H., *Chem. Ber.*, 1969, **102**, 1682.