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New Cucurbitacine Glycosides from *Gratiola officinalis* L.

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Summary. Eight new cucurbitacine glycosides were isolated from "hedgehyssop" *Gratiola officinalis* L. Their structures were determined by two-dimensional NMR techniques and mass spectrometry. For the first time cucurbitacine I derivatives with an acetyl group in position 16 are described.

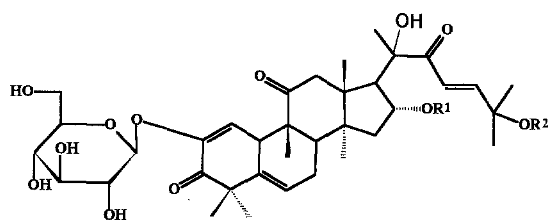
Keywords. *Gratiola officinalis* L; Cucurbitacines; Gratiogenin; Glycosides.

Neue Cucurbitacinglycoside aus *Gratiola officinalis* L.

Zusammenfassung. Acht neue Cucurbitacinglycoside wurden aus der Droge *Gratiola officinalis* L. isoliert. Ihre Strukturen wurden durch zweidimensionale NMR-Spektroskopie und Massenspektrometrie geklärt. Erstmalig wurden Cucurbitacin I-Derivate mit einer Acetylgruppe an C 16 identifiziert.

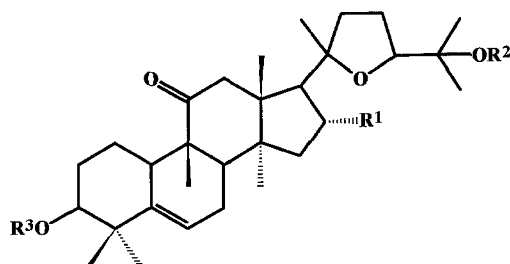
Introduction

Gratiola officinalis L. is a plant which belongs to the family of cucurbitaceae. It grows in moist surroundings of rivers and seas, mostly in south-eastern Europe. In Germany it has become rare because of drainage of valleys and marshes. The dried aboveground parts ("herba gratiolae") were used in medicine as a purgative and anthelmintic as well as to cure gout and liver diseases. Today it is used in homeopathic doses for the treatment of inflammatory affections of the digestive system [1]. In early publications [2], compounds with cardiotoxic effects similar to cardenolides were described, but these results could not be confirmed by recent studies [3–5]. A number of different cucurbitacine derivatives have been isolated [6, 7], including elaterinide (**1**), which is supposed to be responsible for the cardiotoxic activity of herba gratiolae [7]. Other cucurbitacine derivatives are desacetyl-elaterinide (**2**) and the aglycones of **1** and **2**, cucurbitacine E and cucurbitacine I. Gratiogenine (**3**) and 16-β-hydroxy-gratiogenine (**4**) were up to now only isolated from *Gratiola officinalis* L. Two glycosides of **3** were isolated and identified as a monoglucoside and a diglucoside [3, 4] by hydrolysis. The exact structure of the disaccharide chain, however, remained unclear. Until now, no glycosides of **4** have been found, although Herba gratiolae has been shown to contain a variety of other types of glycosides. Relative large amount of different flavonoid glycosides [8–10], which are most likely respon-



	R^1	R^2
1	H	$COCH_3$
2	H	H
5	$COCH_3$	$COCH_3$
6	$COCH_3$	H

Fig. 1



<table>
<tr><th></th><th>R1</th><th>R2</th><th>R3</th></tr>
<tr><td>3</td><td>H</td><td>H</td><td>H</td></tr>
<tr><td>4</td><td>β-OH</td><td>H</td><td>H</td></tr>
<tr><td>7</td><td>H</td><td>β-D-Glcp (2)</td><td>β-D-Glcp (1)</td></tr>
<tr><td>8</td><td>H</td><td>β-D-Glcp (2)</td><td>||</td></tr>
<tr><td>9</td><td>H</td><td>β-D-Glcp (2)</td><td>|</td></tr>
<tr><td>10</td><td>β-OH</td><td>H</td><td>β-D-Glcp (1)</td></tr>
<tr><td>11</td><td>β-OH</td><td>H</td><td>|</td></tr>
<tr><td>12</td><td>β-OH</td><td>β-D-Glcp</td><td>|</td></tr>
</table>

Fig. 2

sible for the antiinflammatory effect of the drug, and caffeic acid glycoside esters, which are known to have similar antibiotic properties, have been described [11].

Cucurbitacines, first isolated from species belonging to the curcurbitaceae [12], are the common bitter principle of many plants of different families. They are pharmacologically active compounds, and diuretic and laxative effects [13] as well as a strong cancerostatic activity [12, 13] have been observed.

Results and Discussion

Isolation

Commercially available dried plant material, "herba gratiolae" was extracted with methanol and the solution distributed between water and *n*-butanol. The residue from the butanolic phase was subjected to column chromatography (CC) on silica

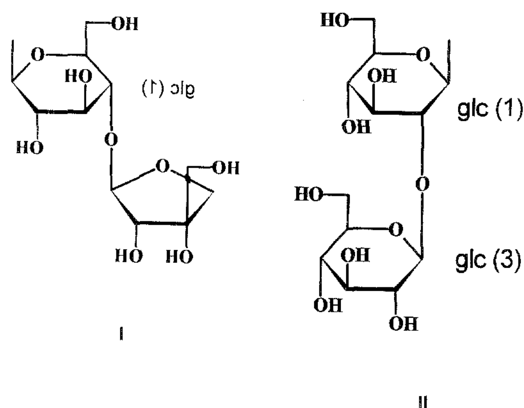


Fig. 3

gel, followed by CC on Sephadex LH-20-100. The resulting crude glycoside mixtures were purified by gradient HPLC on RP-18. Crude **5** thus obtained was further purified by HPLC on a RP-4-column. Other fractions of the first HPLC separation were mixtures of **6** with **12**, of **7** with **9**, and of **8** with **10** and **11**. The glycosides were isolated from these mixtures by HPLC chromatography on a RP-8-column with methanol/water using two different gradient programs.

Structure determination

The structures of **6** to **12** were determined by two-dimensional NMR experiments. Unambiguous assignments were made by ^{1}H,^{1}H-COSY, HMQC, HMBC spectra. We used ROESY correlations to determine the relative configurations of the aglycone units **5** and **6** and to confirm the assignments of the methyl groups. ROE signals were obtained between 8-H and the methyl groups 18-H and 19-H. Methyl group 30 (connected to C-14) shows ROE-correlations with 10-H and 17-H. The latter shows further correlations with 21-H and 12-H_{ax}. The presence of an acetyl group at C-16 is indicated by the downfield shift of 16-H and established by a HMBC signal between 16-H and the acetyl carbonyl C. A negative FAB-MS of **6** shows a fragment at $m/z = 603$ (loss of mass 114) which is the result of cleavage between C-20 and C-22 in α-position to the carbonyl group. It shows that the side chain and hence C-25 of **6** is not acetylated. The second acetyl group of **5** is attached to C-25, because the ^{13}C NMR shift of this carbon atom is observed at lower field (9.4 ppm) than in the NMR spectrum of **6**. A ROE correlation between 1-H of the aglycone and 1-H of the glucose unit shows that the glucose unit is attached to C-2 of the aglycone **5** resp. **6**. This is confirmed by a HMBC signal, showing a connection between 1-H of glucose and C-2 of the aglycone.

The structures of the gratiogenine derivatives were determined by similar experiments. In all spectra, the signals of the glucose residues show a large coupling, proving an axial-axial arrangement of 1-H and 2-H. All glucose units have therefore β-configuration. Additional glycosidation at C-25 is indicated by a ROE signal between 1-H of glucose 2 and 24-H of the aglycone. This is confirmed by the HMBC signal between 1-H of glucose 2 and C-25 of the aglycone.

The bisdesmosidic compounds **8**, **9**, **11**, and **12** contain a disccharide chain. In **8**, this chain consists of two β-*D*-glycopyranosyl units which are connected by a $(1 \rightarrow 2)$ glycosidic bond. This is recognized by the glycosidation shift of C-2 of glucose 1 and confirmed by a ROE correlation between 1-H of glucose 3 and 2-H of glucose 1 as well as by HMBC signals between 2-H of glucose 1 and C-1 of glucose 3. In compounds **9**, **11**, and **12**, the disaccharide chain consists of a β-*D*-glucopyranosyl residue and a terminal apiose unit connected by a $(1 \rightarrow 4)$ glycosidic bond. This is proven by the glycosidation shift of C-4 of glucose as well as by a HMBC signal between 1-H of apiose and C-4 of glucose 1.

A ROE signal between 2-H of apiose and the exocyclic methylene group (5-H of apiose) indicates the relative configuration of C-3 of the apiofuranosyl unit. No ROE correlation between 1-H of apiose and other protons of the apiosyl units is observed. The ^{13}C NMR shift of the apiose C-1 correlates well with data given for β-apiose in the literature [14, 15]. We therefore assume a β configuration for the apiose unit.

The *D* configuration of the glucose residue was determined by chemical derivatization. After acid hydrolysis, the monosaccharides were glycosidated with *S*-(+)-2-butanol [11], and the resulting diastereomer was identified gas-chromatographically by coinjection with a standard sample prepared from authentic *D*-(+)-glucose.

Experimental

NMR spectra were recorded with a Bruker AMX 500 NMR spectrometer at 500 MHz for ^{1}H and at 125 MHz for ^{13}C; solvent: CD_3OD (also used as internal reference). FT-IR spectra: Bruker IFS 113 V (Sektion Schwingungsspektroskopie, Univ. Ulm). FAB-mass spectra were measured at Sektion Massenspektrometrie, Univ. Ulm, with a Finnigan TSQ 7000 spectrometer. Optical rotation: Perkin-Elmer Polarimeter 241. Melting points are uncorrected and were determined with a Leitz SM-LUX heating stage microscope. HPLC: Beckman gradient pump 126, diode array detector 168, UV detection at 210 nm. TLC: *a*: silica gel ($CHCL_3$/MeOH, 3:1); *b*: silica gel-RP-8 (MeOH/H_2O, 2:1). Spots containing glycosides were detected by spraying with EtOH/H_2SO_4/anisaldehyde (17:2:1) and heating to 120 °C. Compounds **5** and **6** gave violet spots, **7** to **9** turned into a greenish yellow, and **10** to **12** showed a blue-green color.

Isolation of glycosides **5** *to* **12**

Plant material from "Herba gratiolae" was obtained from Caesar & Loretz, Hilden. 200 g were treated with 5.3 l of $CHCl_3$ to remove unpolar substances. Then the solution was extracted with 6.7 l of MeOH at room temperature. The methanolic solution was concentrated *in vacuo*, the residue suspended in 600 ml of H_2O, and the suspension extracted with 1.2 l of water-saturated *n*-BuOH. The extract was concentrated and the residue was subjected to CC on Matrex silica (60, Å, eluent: $CHCl_3$/MeOH/H_2O, 8:5:1), followed by CC on Sephadex LH-20-100 with MeOH, yielding fractions containing glycoside mixtures. These were separated by HPLC on a silica gel RP-18 5-μ, column (1.0 × 25.0 cm) by using the following gradient program: start with 60% MeOH, 40% H_2O, after 10 min change to 100% MeOH during 15 min, isocratic for additional 15 min (constant flow of 1 ml eluent/min). The glycosides, eluting after 29 minutes, were separated into 4 crude fractions (1–4). Fraction 1 contained **6** and **12** which were separated and purified on a silica gel RP-8 5-μ column (1.0 × 25.0 cm) with the following gradient program: start with 70% MeOH, 30% H_2O; after 10 min change to 90% MeOH during 10 min, then isocratic for 5 min (constant flow of 1 ml eluent/min).

Fraction 2 consisted of crude **5** which was purified by isocratic elution with 1 ml/min of

Table 1. ^{1}H NMR data of aglycone moieties of glycosides **5** to **12** (500 MHz, CD_3OD)

	5	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1a	6.18	6.17	1.30	1.30	1.31	1.33	1.33	1.32
e			1.61	1.61	1.62	1.63	1.63	1.62
2a	–	–	2.05	2.04	2.05	2.06	2.06	2.05
e			1.79	1.80	1.80	1.79	1.81	1.78
3	–	–	3.45	3.47	3.45	3.45	3.45	3.44
6	5.87	5.88	5.66	5.65	5.66	5.67	5.67	5.66
7a	2.08	2.08	2.03	2.00	2.01	2.04	2.02	2.04
e	2.45	2.45	2.43	2.43	2.42	2.44	2.42	2.42
8	2.14	2.14	1.99	1.99	2.00	2.09	2.09	2.08
10	3.71	3.73	2.42	2.44	2.44	2.42	2.41	2.41
12a	3.49	3.51	3.06	3.08	3.08	3.14	3.14	3.15
e	2.75	2.76	2.63	2.61	2.62	2.60	2.60	2.65
15	2.10	2.05	1.41	1.41	1.42	2.12	2.11	2.12
	1.47	1.47	1.46	1.46	1.46	1.48	1.48	1.47
16	5.44	5.38	1.92	1.92	1.92	4.74	4.70	4.74
			1.96	1.96	1.96			
17	2.84	2.87	2.33	2.34	2.35	2.43	2.42	2.45
18	1.04	1.06	0.92	0.92	0.93	1.19	1.19	1.18
19	1.08	1.08	1.10	1.14	1.10	1.13	1.13	1.13
21	1.45	1.46	1.27	1.26	1.26	1.34	1.35	1.34
22	–	–	1.64	1.62	1.63	1.76	1.76	1.81
			1.94	1.93	1.94	2.24	2.24	2.23
23	6.82	6.88	1.78	1.79	1.80	1.95	1.95	1.96
			1.93	1.94	1.95	1.95	1.95	1.96
24	7.12	7.09	4.04	4.04	4.05	3.87	3.86	3.93
26	1.60	1.38	1.29	1.28	1.28	1.15	1.15	1.29
27	1.61	1.38	1.31	1.30	1.32	1.24	1.24	1.33
28	1.33	1.34	1.28	1.29	1.26	1.27	1.26	1.27
29	1.31	1.31	1.08	1.08	1.09	1.07	1.07	1.07
30	1.41	1.41	1.14	1.15	1.16	1.13	1.12	1.12
16-Ac 2	1.92	1.89	–	–	–	–	–	–
25-Ac 2	2.04	–						

$MeOH/H_2O$ (2:1) on a silica gel RP-4 5-μ column (1.0 × 25.0 cm).

Compounds **8**, **10**, and **11**, contained in fraction 3, were separated by chromatography on a silica gel RP-8 5-μ column (1.0 × 25.0 cm, isocratic elution with 1 ml/min $MeOH/H_2O = 9:1$). Compounds **7** and **9** from fraction 4 were separated using a silica gel RP-8 5-μ column (1.0 × 25.0 cm). Elution program: start: 80% MeOH, 20% H_2O; after 5 min change to 90% MeOH during 5 min, then isocratic for 15 min (constant flow of 1 ml eluent/min).

Chemical degradation and determination of sugar configuration

Acid hydrolysis: 2 mg of glycoside were heated with 5 ml 2 *N* HCl (100 °C) for 2 h. The solvent was removed *in vacuo* at 40 °C. The residue was extracted three times with 1 ml of Et_2O each and the sugar was derivatized and analyzed as described in Ref. [11].

Table 2. ^{1}C NMR data of aglycone moieties of glycosides **5** to **12** (125 MHz, CD_3OD)

	5	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1	124.5	124.4	22.4	22.4	22.4	22.4	22.4	22.4
2	148.2	148.2	28.8	28.6	28.7	28.8	28.7	28.8
3	200.6	200.6	88.0	88.0	88.1	88.0	88.1	88.1
4	51.2	51.2	42.6	42.6	42.6	42.6	42.6	42.6
5	138.4	138.4	142.1	141.9	142.0	142.1	142.0	141.9
6	123.2	123.2	119.5	119.9	119.8	119.7	119.7	119.7
7	25.5	25.5	24.8	24.8	24.8	24.7	24.7	24.6
8	43.7	43.7	44.9	44.9	44.9	44.8	44.8	44.7
9	51.0	51.0	50.3	50.4	50.3	50.4	50.4	50.3
10	37.4	37.3	36.9	36.8	36.9	36.8	36.8	36.8
11	216.8	216.7	218.3	218.4	218.3	217.2	217.2	216.8
12	51.0	51.0	49.6	49.7	49.6	50.3	50.2	50.2
13	52.2	52.2	51.4	51.4	51.3	51.3	51.3	51.2
14	50.0	50.2	49.9	49.9	49.9	48.1	48.1	46.0
15	45.4	45.4	35.1	35.1	35.1	47.9	47.9	47.9
16	76.1	76.2	23.4	23.4	23.4	73.7	73.7	73.9
17	57.2	56.8	53.3	53.4	53.3	54.6	54.6	53.8
18	21.5	21.5	19.3	19.3	19.3	20.8	20.8	20.6
19	21.5	21.5	20.2	20.3	20.2	20.3	20.3	20.4
20	80.6	80.4	86.5	86.5	86.5	87.5	87.5	88.5
21	25.7	25.6	26.6	26.6	26.0	26.7	26.7	25.6
22	205.3	205.0	38.0	38.0	38.0	38.2	38.2	37.7
23	122.8	121.5	26.6	26.6	26.6	24.9	24.9	24.8
24	153.7	157.4	84.1	84.1	84.1	85.6	85.6	86.2
25	81.8	72.4	80.2	80.2	80.2	71.6	71.6	79.0
26	27.7	30.3	23.4	23.5	23.4	26.0	25.9	23.6
27	27.8	30.3	23.7	23.7	23.7	27.5	27.5	24.2
28	21.7	21.7	26.8	26.8	26.8	26.3	26.3	25.9
29	29.1	29.1	28.7	28.7	28.7	28.6	28.6	28.6
30	19.5	19.5	18.9	18.9	18.9	20.1	20.1	20.2
16-Ac 1	173.3	173.1	–	–	–	–	–	–
16-Ac 2	22.1	22.0	–	–	–	–	–	–
25-Ac 1	172.6	–	–	–	–	–	–	–
25-Ac 2	22.7		–	–	–	–	–	–

2-(O-β-D-glucopyranosyl)-16,25-diacetyl-cucurbitacine I (**5**)

$[\alpha]_D^{20} = -16.0$ ($c = 0.1$, MeOH); mp = 154 °C; IR: $\tilde{\nu}$(KBr): 3442, 2974, 2934, 1734, 1690, 1635, 1384, 1260, 1078, 1027 cm^{-1}; FAB-MS (pos.): *m/z* = 539, 479, 471, 455, 437, 203; FAB-MS (neg.): *m/z* = 759(M-H$^+$), 701, 538, 326, 311; TLC: *a*: $R_f = 0.86$; *b*: $R_f = 0.40$.

2-(O-β-D-glucopyranosyl)-16-acetyl-cucurbitacine I (**6**)

$[\alpha]_D^{20} = -57.6$ ($c = 0.096$, MeOH); mp = 149 °C; IR: $\tilde{\nu}$(KBr): 3434, 2974, 2932, 1738, 1690, 1633, 1463, 1449, 1431, 1378, 1252, 1224, 1078, 1029 cm^{-1}; FAB-MS (pos.): *m/z* = 741 (MNa$^+$), 701, 539, 479, 443, 341, 309; FAB-MS (neg.): *m/z* = 717 (M-H$^+$), 603, 555; TLC: *a*: $R_f = 0.78$; *b*: $R_f = 0.50$.

Table 3. ^1H NMR data of sugar moieties of glycosides **5** to **12** (500 MHz, CD_3OD)

	5	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Glucose 1								
1	4.69	4.69	4.31	4.43	4.34	4.31	4.34	4.33
2	3.43	3.45	3.23	3.62	3.27	3.22	3.27	3.28
3	3.47	3.47	3.36	3.54	3.48	3.34	3.48	3.48
4	3.54	3.56	3.35	3.33	3.48	3.31	3.48	3.48
5	3.40	3.39	3.28	3.26	3.35	3.26	3.36	3.34
6	3.90	3.90	3.70	3.69	3.75	3.69	3.76	3.76
	4.07	4.08	3.86	3.85	3.83	3.86	3.84	3.84
Glucose 2								
1			4.62	4.63	4.63			4.48
2			3.17	3.15	3.16			3.21
3			3.42	3.41	3.48			3.40
4			3.35	3.33	3.33			3.32
5			3.28	3.26	3.30			3.29
6			3.70	3.69	3.69			3.68
			3.86	3.85	3.85			3.87
Glucose 3								
1				4.67				
2				3.28				
3				3.38				
4				3.32				
5				3.26				
6				3.69				
				3.85				
Apiose								
1					5.11		5.12	5.11
2					3.94		3.94	3.94
4					3.83		3.83	3.83
					4.17		4.17	4.18
5					3.57		3.57	3.57
					3.60		3.60	3.59

3-O-β-D-glucopyranosyl-(25-O-β-D-glucopyranosyl)-gratiogenine (**7**)

$[\alpha]_D^{20} = +95.0$ ($c = 0.1$, MeOH); mp = 215 °C; IR: $\tilde{\nu}$(KBr): 3420, 2970, 2928, 2876, 1691, 1653, 1465, 1449, 1385, 1374, 1165, 1075, 1030 cm^{-1}; FAB-MS (pos.): $m/z = 797$ (MH^+), 635, 473, 455, 437,; FAB-MS (neg.): $m/z = 795$ (M-H^+), 633; TLC: *a*: R_f: = 0.31; *b*: $R_f = 0.33$.

3-O-(β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl)-25-O-β-D-glucopyranosyl-gratiogenine (**8**)

$[\alpha]_D^{20} = +52.5$ ($c = 0.1$, MeOH); mp = 185 °C; IR: $\tilde{\nu}$(KBr): 3427, 2969, 2928, 2876, 1684, 1635, 1457, 1385, 1161, 1077, 1033 cm^{-1}; FAB-MS (pos.): $m/z = 981$ (MNa^+), 635, 473, 455, 437; FAB-MS (neg.): $m/z = 957$ (M-H^+), 795, 633, 249, 221; TLC: *a*: $R_f = 0.15$; *b*: $R_f = 0.15$; *b*: $R_f = 0.45$.

Table 4. ^{13}C NMR data of sugar moieties of glycosides **5** to **12** (125 MHz, CD_3OD)

	5	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Glucose 1								
1	102.2	102.1	106.6	105.0	106.4	106.6	106.4	106.4
2	75.3	75.2	75.6	80.9	75.4	75.6	75.4	75.3
3	78.6	78.5	78.4	78.3	76.7	78.4	76.7	76.7
4	71.7	71.6	71.8	71.8	80.1	71.8	80.1	80.1
5	79.1	79.1	77.7	77.6	76.5	77.7	76.5	76.5
6	63.0	62.9	62.9	62.9	62.0	63.0	62.0	61.9
Glucose 2								
1			98.4	98.4	98.4			99.0
2			75.4	75.4	75.4			75.0
3			78.3	78.3	78.3			77.6
4			71.7	71.8	71.8			71.8
5			77.7	77.7	76.5			77.6
6			62.9	63.1	62.9			62.9
Glucose 3								
1				104.3				
2				76.3				
3				78.2				
4				71.8				
5				77.7				
6				62.9				
Apiose								
1					111.2		111.2	111.1
2					77.7		77.8	77.7
3					80.1		80.1	80.0
4					75.0		75.0	74.9
5					64.8		64.8	64.7

3-O-(apiofuranosyl-(1→4)-β-D-glucopyranosyl)-25-β-D-glucopyranosyl-gratiogenine (**9**)

$[\alpha]_D^{20} = +42.2$ ($c = 0.1$, MeOH); mp = 245 °C; IR: $\tilde{\nu}$ (KBr): 3447, 2969, 2933, 2875, 1696, 1653, 1457, 1385, 1076, 1032 cm^{-1}; FAB-MS (pos.): $m/z = 951$ (MNa^+), 797, 767, 635, 473, 455, 437; FAB-MS (neg.): $m/z = 927$ (M-H^+), 795, 765, 633; TLC: *a*: $R_f = 0.48$; *b*: $R_f = 0.33$.

3-O-β-D-glucopyranosyl-16β-hydroxy-gratiogenine (**10**)

$[\alpha]_D^{20} = +81.4$ ($c = 0.1$, MeOH); mp = 154 °C; IR: $\tilde{\nu}$ (KBr): 3420, 2967, 2925, 2879, 1690,1638, 1465, 1431, 1385, 1265, 1168, 1099, 1075, 1043, 1022 cm^{-1}; FAB-MS (pos.): $m/z = 651$ (MH^+), 489, 471, 453, 435; FAB-MS (neg.): $m/z = 649$ (M-H^+), 487, 255; TLC: *a*: $R_f = 0.75$; *b*: $R_f = 0.33$.

3-O-(apiofuranosyl-(1→4)-β-D-glucopyranosyl)-16β-hydroxy-gratiogenine (**11**)

$[\alpha]_D^{20} = +50.3$ ($c = 0.1$, MeOH); mp = 167 °C; IR: $\tilde{\nu}$ (KBr): 3433, 2967, 2926, 2879, 1690, 1635, 1465, 1385, 1265, 1097, 1076, 1045, 1027 cm^{-1}; FAB-MS (pos.): $m/z = 805$ (MNa^+), 651, 489, 471, 453, 435; FAB-MS (neg.): $m/z = 781$ (M-H^+), 649, 487, 309, 265, 233; TLC: *a*: $R_f = 0.70$; *b*: $R_f = 0.35$.

3-O-(apiofuranosyl-(1→4)-β-D-glucopyranosyl-))-(25-O-β-D-glucopyranosyl-)-16β-hydroxy gratiogenine (**12**)

$[\alpha]_D^{20} = +34.8$ ($c = 0.023$, MeOH); mp = 164 °C; IR: $\tilde{\nu}$ (KBr): 3428, 2966, 2924, 2877, 1691, 1606, 1464, 1385, 1265, 1164, 1099, 1077, 1040, 1022 cm^{-1}; FAB-MS (pos.): $m/z = 945$ (MH^+), 651, 489, 471, 453, 435; FAB-MS (neg.): $m/z = 943$ ($M\text{-}H^+$), 811, 781, 649; TLC: *a*: $R_f = 0.48$; *b*: $R_f = 0.56$.

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