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Eudesmane and megastigmane glucosides from *Laggera alata*

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This paper is dedicated to Professor Dr. Xiao-Tian Liang on the occasion of his 80th birthday.

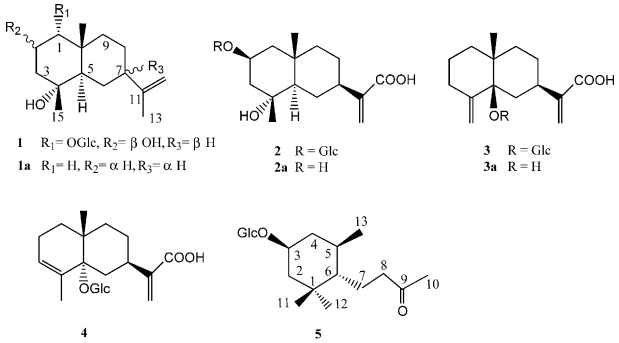
Abstract

Four eudesmane glucosides, alatosides A–D (**1**–**4**), and one megastigmane glucoside, alatoside E (**5**), were isolated from the BuOH fraction of *Laggera alata* along with six known compounds. Structures of the new compounds were elucidated by a combination of chemical and spectroscopic methods. Alatosides A–E were characterized as: 1α-*O*-(β-D-glucopyranosyloxyl)-7-*epi*-eudesma-11-en-2β,4α-diol (**1**), 2β-*O*-(β-D-glucopyranosyloxyl)-eudesma-4α-hydroxyl-11(13)-en-12-oic-acid (**2**), 5β-*O*-(β-D-glucopyranosyloxyl)-eudesma-4(15),11(13)-dien-12-oic-acid (**3**), 5α-*O*-(β-D-glucopyranosyloxyl)-eudesma-3,11(13)-dien-12-oic acid (**4**) and 3β-*O*-(β-D-glucopyranosyloxyl)-megastigma-9-one (**5**), respectively. Based on the chemical characteristics of eudesmane derivatives isolated from the *Laggera* genus, it was suggested that there are probably two different biogenetic pathways for these secondary metabolites in this genus.

Keywords: *Laggera alata*; Compositae; Eudesmane; Megastigmane; Alatoside

1. Introduction

Laggera (Astereae, Trib. Plucheae Cass.) is a small genus of about 20 species, mainly found in tropical Africa and Southeast Asia. *Laggera alata* and *Laggera pterodonta* are the only two *Laggera* species found in China. Both are employed as traditional herbal medicines for their anti-inflammatory and anti-bacterial activities (Deng, 1963). Previous investigation of *L. pterodonta* led to the isolation of 20 eudesmane sesquiterpenes and eudesmane glucosides, including some cytotoxic ones (Zhao et al., 1997a, b). These interesting findings on *L. pterodonta* along with pertinent research reports about *L. alata* (Bohlmann et al., 1985; Zdero and Bohlmann, 1989; Onayade et al., 1990; Rahar-ivelomanana et al., 1998) have prompted a thorough phytochemical examination of *L. alata* scattered in China. As a result, four new sesquiterpene glucosides (**1**–**4**) of the eudesmane type and one megastigmane glucoside (**5**), along with six known compounds, isocostic acid (Zdero et al., 1987), 2,5-dihydrocinnamic acid (Cannon et al., 1973), 3-oxoisocostic acid (Bohlmann et al., 1977), ilicic acid (Herz et al., 1966), artemitin (Li and Ding, 1994), and 3,3′-dimethoxyquercetagetin (Masayuki et al., 1977) were obtained from the BuOH fraction of



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the title plant. The present paper reports the isolation and structure elucidation of these new compounds.

2. Result and discussion

The positive ion HRFAB-MS of **1** showed a molecular ion peak $[M+H]^+$ at *m/z*: 417.2528, in agreement with the molecular formula of $C_{21}H_{36}O_8$. The ^{13}C NMR spectrum of **1** exhibited 21 signals, of which eight resonated in the region corresponding to oxygenated carbon (60–90 ppm), as well as a methine signal at δ 105.4 suggesting the presence of an anomeric carbon (Table 1). This gave support to **1** being a sesquiterpene glucoside. Acid hydrolysis of **1** gave D-glucose (identified by PC and TLC). Furthermore, the EIMS of **1** exhibiting fragments pattern at *m/z*: 254 $[M–Glc]^+$, 236 $[M–Glc–H_2O]^+$, 218 $[M–Glc–2\times H_2O]^+$ and *m/z*: 200 $[M–Glc–3\times H_2O]^+$ disclosed the presence of three hydroxyl groups in the aglycone part of **1**. The ^{13}C NMR spectrum of **1** was close to that of eudesma-11-en-2α,4α-diol (**1a**) (Masuyama et al., 1993), suggesting that **1** is an eudesmane glucoside. The diagnostic changes of C-1, C-2 and C-10 between these two analogues by their ^{13}C NMR spectra (Table 1) indicated that the glucosyl group of **1** was attached to the hydroxyl group at C-1. The relative configuration of H-1β, H-2α, and H-7β was deduced from the observed coupling constants (Table 2), and was confirmed by the correlations between H-1β and H-14, H-5α and H-3α, H-3α and H-2α, H-14 and H-8β, as well as H-8β and H-7β in the ROESY spectrum of **1** (Fig. 1). Moreover, the characteristic coupling constant of the anomeric hydrogen of **1** ($J=7.6$ Hz) indicated the presence of a β-D-glucoside. Therefore, the structure of **1** was 1α-*O*-(β-D-glucopyranosyloxyl)-7-*epi*-eudesma-11-en-2β,4α-diol.

The molecular formula of alatoside B (**2**) was deduced as $C_{21}H_{34}O_9$ from its HRFAB-MS data (see Experimental section). The ^1H and ^{13}C NMR spectra of **2** (Tables 1 and 2) suggested that it was also an eudesmane glucoside. Acid hydrolysis of **2** gave D-glucose and a known aglycone, namely 2β-hydroxyilicic acid (**2a**) (Zhao et al., 1997a), which was identified by comparison of its physical and spectroscopic properties (R_f, IR, EIMS, NMR and $[\alpha]_D$) with the authentic sample isolated from *L. pterodonta*. Characteristic shifts in some specific signals were noticed (Table 1) in the ^{13}C NMR spectrum of **2** by comparison to that of **2a**. A significant downfield shift (ca. 11 ppm, from δ 67.8 in **2a** to δ 78.9 in **2**) was observed for the signals of C-2, while the signals of C-1 and C-3 shifted (by 3–4 ppm) slightly to a higher field. This suggested that the glucosyl group was bound to the hydroxyl group at C-2. The coupling constant of the anomeric hydrogen ($J=8.0$ Hz in **2**) indicated that it was a β-glucoside. According to the above information, compound **2** was 2β-*O*-(β-D-glucopyranosyloxyl)-eudesma-4α-hydroxyl-11(13)-en-12-oic-acid.

The ^1H and ^{13}C NMR spectral data of alatoside C (**3**) suggested that it was another eudesmane glucoside. Its molecular formula was deduced as $C_{21}H_{32}O_8$ from the HRFAB-MS data of **3** (see Experimental section). Acid hydrolysis of **3** gave D-glucose and an aglycone, which was identified as 5β-hydroxycostic acid (**3a**), a natural product isolated from *Jasonia montana* (Ahmed and Jakupovic, 1990). By comparing the ^{13}C NMR spectral data of **3** and **3a** (Table 1), the characteristic shifts of C-4, C-5 and C-6 of the two compounds indicated that the glucosyl group was bound to the hydroxyl group at C-5. The coupling constant of the anomeric hydrogen ($J=7.6$ Hz in **3**) indicated that it was a β-glucoside. Therefore, **3** was 5β-*O*-(β-D-glucopyranosyloxyl)-eudesma-4(15),11(13)-dien-12-oic-acid.

Eudesmane glucoside **4**, after acid hydrolysis, yielded D-glucose and a known eudesmane derivative, 5α-hydroxyisocostic acid (Ahmed and Jakupovic, 1990), by comparing its IR, MS, ^1H NMR and $[\alpha]_D$ spectral data

Table 1
^{13}C NMR (100 MHz in δ from TMS) spectral data of compound **1–5**

Position	**1**[a]	**1a**[b]	**2**[a]	**2a**[c]	**3**[b]	**3a**[c]	**4**[b]	**5**[b]
1	90.7 *d*	51.2 *t*	46.5 *t*	50.2	34.9 *t*	34.9	33.2 *t*	36.7 *s*
2	69.4 *d*	65.9 *d*	78.9 *d*	67.8	23.6 *t*	22.3	28.4 *t*	48.4 *t*
3	49.6 *t*	52.9 *t*	45.2 *t*	47.8	38.2 *t*	37.1	117.0 *d*	75.6 *d*
4	74.1 *s*	73.3 *s*	70.4 *s*	70.9	151.1 *s*	151.9	135.1 *s*	44.6 *t*
5	57.0 *d*	55.1 *d*	54.9 *d*	55.6	76.7 *s*	72.5	79.5 *s*	34.9 *d*
6	24.6 *t*	27.8 *t*	27.0 *t*	27.4	39.4 *t*	36.1	40.6 *t*	53.5 *d*
7	47.1 *d*	47.8 *d*	41.4 *d*	41.4	38.5 *d*	37.7	41.9 *d*	23.9 *t*
8	27.2 *t*	27.1 *t*	27.5 *t*	27.6	27.7 *t*	26.3	29.3 *t*	46.3 *t*
9	35.9 *t*	45.9 *t*	44.2 *t*	45.9	35.0 *t*	34.3	33.5 *t*	210.0 *s*
10	35.9 *s*	35.1 *s*	34.4 *s*	34.8	40.0 *s*	39.1	41.1 *s*	29.8 *t*
11	145.4 *s*	151.6 *s*	146.4 *s*	148.4	146.4 *s*	145.8	146.9 *s*	21.3 *t*
12	114.8 *t*	108.8 *t*	166.7 *s*	170.0	168.0 *s*	167.9	167.6 *s*	21.2 *t*
13	25.9 *t*	21.2 *t*	120.5 *t*	121.5	125.4 *t*	123.0	125.4 *t*	31.3 *t*
14	19.1 *t*	20.1 *t*	20.2 *t*	20.8	23.5 *t*	22.4	18.4 *t*	–
15	20.0 *t*	23.5 *t*	25.2 *t*	25.6	112.3 *t*	109.8	19.7 *t*	–
1′	105.4 *d*		96.7 *d*		96.4 *d*		96.4 *d*	102.7 *d*
2′	75.1 *d*		74.6 *d*		74.4 *d*		74.5 *d*	75.1 *d*
3′	79.0 *d*		78.8 *d*		78.6 *d*		78.8 *d*	78.1 *d*
4′	72.0 *d*		72.0 *d*		71.5 *d*		71.5 *d*	71.7 *d*
5′	78.8 *d*		79.9 *d*		79.3 *d*		78.6 *d*	77.8 *d*
6′	62.9 *t*		62.5 *t*		62.7 *t*		62.8 *t*	62.8 *t*

[a] Taken in C_5D_5N.
[b] Taken in CD_3OD.
[c] Taken in $CDCl_3$.

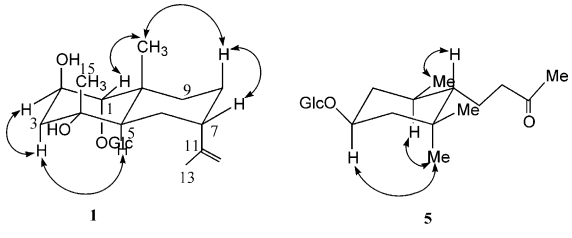

Fig. 1. Selected correlations in ROESY spectra of **1** and **5**.

Table 2
^{1}H NMR (400 MHz in δ from TMS) spectral data of compound **1–5**[c]

Position	**1**[a]	**2**[a]	**3**[b]	**4**[b]	**5**[b]
1α-H	–	2.19 (*dd*, 13.5, 3.6)	1.12 *m*	1.55 *m*	–
1β-H	3.75 (*d*, 3.1)	2.59 (*brd*, 13.5)	1.02 *m*	1.35 *m*	–
2α-H	3.58 *brs*	4.56 (*brt*, 3.3)	1.50–1.65 *m*	2.08 *m*	1.08 *m*
2β-H	–	–	1.50–1.65 m	1.95 *m*	1.69 (*dd*, 13.4, 4.8)
3α-H	2.47 (*brd*, 13.8)	1.49 (*dd*, 13.9, 3.6)	2.45 (*ddd*, 13.7, 12.5, 5.2)	5.50 (*d*, 7.5)	3.78 (*br t*, 12.0)
3β-H	1.99 m	1.96 (*brd*, 13.9)	2.10 (*ddd*, 13.7, 4.8, 4.8)	–	–
4α	–	–	–	–	1.01 *m*
4β	–	–	–	–	1.93 *m*
5α-H	1.30 (*dd*, 12.5, 4.6)	1.85 *m*	–	–	1.38 (*dt*, 12.5, 3.8)
6α-H	2.01 (*ddd*, 13.2, 4.6, 3.8)	2.75 (*brd*, 12.4)	2.12 (*dd*, 13.5, 4.8)	1.96 *m*	0.55 (*dt*, 12.5, 3.8)
6β-H	1.27 (*ddd*, 13.2, 12.5, 3.8)	1.72 *m*	1.80 m	1.53 *m*	–
7α-H	–	2.98 (*dddd*, 12.5, 12.5, 3.4, 3.4)	2.82 (*dddd*, 12.5, 12.5, 4.8, 4.8)	2.28 (*dddd*, 12.5, 12.5, 4.8, 4.8)	1.20 *m*
7β-H	2.91 *brs*	–	–	–	1.55 *m*
8α-H	1.76 *m*	1.72 *m*	1.50–1.65 *m*	1.50–1.62 *m*	2.40 *m*
8β-H	1.68 *m*	1.84 *m*	1.50–1.65 m	1.50–1.62 *m*	2.50 *m*
9α-H	1.02 *m*	1.32 (*ddd*, 12.6, 12.6, 4.3)	1.72 *m*	1.10 *m*	–
9β-H	1.58 *m*	1.54 *m*	1.32 *m*	0.88 *m*	–
10-H	–	–	–	–	2.05 (3H, *s*)
11-H	–	–	–	–	0.76 (3H, *s*)
12-H	5.71 *brs*	–	–	–	0.88 (3H, *s*)
12′-H	5.17 *brs*	–	–	–	–
13-H	1.97 *s*	6.52 (*d*, 1.1)	6.25 *brs*	6.25 *brs*	0.90 (3H, *d*, 6.4)
13′-H	–	5.72 *brs*	5.68 *brs*	5.56 *brs*	–
14-H	0.92 (3H, *s*)	1.54 (3H, *s*)	0.97 (3H, *s*)	0.95 (3H, *s*)	–
15-H	1.30 (3H, *s*)	1.79 (3H, *s*)	5.19 (1H, *s*)	1.49 (3H, *s*)	–
15′-H	–	–	4.90 (1H, *s*)	–	–
1′-H	4.88 (*d*, 7.6)	4.85 (*d*, 8.0)	5.40 (*d*, 7.6)	4.84 (*d*, 8.0)	4.25 (*d*, 8.0)
2′-H	3.89 (*t*, 8.0)	4.00 (*t*, 8.2)	3.22 (*t*, 8.0)	3.22 (*t*, 8.0)	3.12 (*t*, 8.0)
3′-H	3.99 (*t*, 8.2)	4.10 (*t*, 8.2)	3.31 (*t*, 8.2)	3.34 (*t*, 8.2)	3.34 (*t*, 8.6)
4′-H	4.24 *m*	4.27 *m*	3.38 *m*	3.30 *m*	3.22 *m*
5′-H	4.20 *m*	4.24 *m*	3.40 *m*	3.26 *m*	3.18 *m*
6′a-H	4.52 (*dd*, 11.8, 2.0)	4.86 (*brd*, 11.5)	3.76 (*dd*, 12.0, 2.0)	3.65 (*dd*, 12.0, 3.5)	3.58 (*dd*, 11.8, 2.0)
6′b-H	4.38 (*dd*, 11.8, 3.7)	4.70 (*brd*, 11.5)	3.62 (*dd*, 12.0, 3.2)	3.82 (*dd*, 12.0, 4.5)	3.82 (*dd*, 11.8, 2.2)

[a] Taken in C_5D_5N.
[b] Taken in CD_3OD.
[c] Multiplicity and *J* values (Hz) shown in parentheses.

with those reported in the literature. The fact that only one oxygenated quaternary carbon signal appeared at δ 79.5 in the ^{13}C NMR spectrum of **4** indicated that the glucosyl group could only be connected to the hydroxyl group at C-5. The coupling constant of the anomeric hydrogen ($J = 8.0$ Hz in **4**) suggested that it was also a β-glucoside. Therefore, **4** was 5α-*O*-(β-D-glucopyranosyloxyl)-eudesma-3,11(13)-dien-12-oic acid.

The ^{13}C NMR spectrum of **5** showed 19 resonances, including six typical carbon systems attributable to a glucose, a carbonyl, an oximethine, four methylenes, two methines, and four methyls. Combined with molecular weight exhibited in the HRFAB-MS of **5** $[M]^+$ at *m*/*z* 375.2316, the molecular formula $C_{19}H_{34}O_7$ was deduced.

The 2D ^{1}H–^{1}H COSY spectrum of **5** disclosed the presence of $H_3C-\underset{|}{CH}-\underset{|}{CH}-$, $-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$, $-H_2C-\underset{CH_3}{\underset{|}{C}}-CH_3$, and $-CH_2-\underset{O}{\underset{\|}{CH}}-CH_2-$ moieties. These results together with the HMBC spectrum (Fig. 2) indicated the presence of a megastigmane skeleton (Ngo and Brown, 1999). The 2D NMR spectra further suggested that glucosyl group was connected to the hydroxyl group at C-3 and that a carbonyl group was located at C-9. The relative configuration of H-3 was presumed to be axial from the coupling constant (br *t*, $J = 12.0$ Hz). This was confirmed by clear NOE correlations between H-3α and H-12, H-5α and H-12, as well as between H-6β and H-13 (Fig. 2). Based on the above

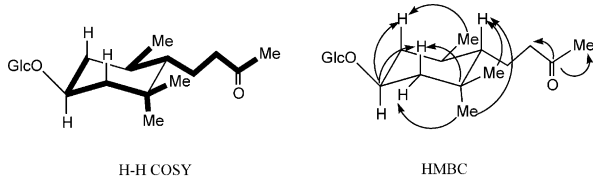

Fig. 2. H–H COSY and HMBC correlation of **5**.

information, **5** was elucidated as 3β-*O*-(β-D-glucopyranosyloxyl)-megastigma-9-one.

Among the about 20 species of the genus *Laggera*, only *L. aurita* (Zutshi and Bokadia, 1976), *L. pterodonta* (Zhao et al., 1997a, b), *L. crispate* (Ahmed et al., 1998) and *L. alata* (also reported as *Blumea alata*) (Bohlmann et al., 1985; Zdero and Bohlmann, 1989; Onayade et al., 1990; Raharivelomanana et al., 1998) have been chemically investigated. All of the eudesmane derivatives isolated from the *Laggera* genus appear to contain the following characteristic. H-7 always occurs in an α-orientation when the isopropyl side chain attached to C-7 exists as an allylic acid moiety. On the other hand, a β-orientation of H-7 is always present when the isopropyl exists as an allyl group or as a propenol group. This fact suggested that there are probably two different biogenetic pathways for these secondary metabolites in this genus.

3. Experimental

3.1. General

Optical rotations were measured on a Perkin-Elmer 341 polarimeter. IR spectra were obtained on a Perkin-Elmer 577 spectrometer using KBr pellets. EIMS data were obtained on a Finnigan-4510 spectrometer at 70 ev, and HRFAB-MS spectra were recorded on a VG ZAB-HS spectrometer. The NMR spectra were obtained using a Bruker AM-400 MHz spectrometer with TMS as the internal standard. CC was performed on silica gel (300–400 mesh, Ocean Chemical Plant of Qingdao, China), RP-18 gel (75 μm, Merck) and Sephadex LH-20 (Pharmacia).

3.2. Plant material

Whole plants of *Laggera alata* (D. Don) Sch.-Bip. Ex Oliv. were collected in November of 1994, at Quibei county, Yunnan Province of China, and identified by Professor Zhong-wen Lin. A voucher specimen (No. 941102) was deposited at the State Key Laboratory of Phytochemistry and Plant Resource in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

3.3. Extraction and isolation

The air-dried aerial parts of the *Laggera alata* (5.8 kg) were powdered and extracted twice with 95% EtOH at 70 °C, 2 h each time, and the alcoholic extracts were combined and evaporated to dryness (426 g). The residue was suspended in H_2O and then partitioned with petroleum ether (60–90 °C), EtOAC and BuOH, respectively. Saccharidic compounds in the BuOH extract (89 g) were removed by passage over a Diaion HP-50 macroporous resin column, eluted with MeOH–H_2O (1:1). The residue (53 g) was subjected to silica gel CC (1 kg), and then eluted by $CHCl_3$ with increasing concentrations of MeOH to afford 9 fractions (F_A–F_I). Five of the fractions (F_D–F_H) were repeatedly subjected to Sephadex LH-20 CC eluted with $CHCl_3$–MeOH (1:1), and then applied to a RP-18 gel column eluted with MeOH–H_2O (3:2), and finally purified by passage over silica gel column eluted with a gradient of benzene–MeOH (from 8:1 to 2:1, containing 0.5% HCOOH). As a result, F_D afforded 38 mg of 2,5-dihydrocinnamic acid. F_E afforded 21 mg of **1** and 28 mg of **2**. F_F afforded 17 mg of **3**. F_G afforded 34 mg of **4**, and 14 mg of **5** was obtained from F_H, respectively.

3.4. Acid hydrolysis of *1*–*4*

A solution of **1**–**4** (8–10 mg for each sample, respectively) in 5% H_2SO_4–MeOH (10 ml) was heated under reflux for 2 h under an Ar atmosphere. After cooling, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The aglycones were purified by prep. TLC, some of which were compared with an authentic sample by TLC. The H_2O layer was neutralized with $BaCO_3$ before subjected to a Co–TLC and a Co–PC comparing with the standard D-glucose.

3.5. Alatoside A (*1*)

Gum, $[\alpha]_D^{20} = -93.1°$ (*c* 0.44, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3600, 3341, 3010, 2950, 1030, 930. HRFAB-MS *m/z*: 417.2528 $[M+H]^+$ (calc. for $C_{21}H_{36}O_8$: 417.2534). EIMS 70 eV, *m/z*: 416 $[M]^+$ (2), 254 $[M\text{-Glu}]^+$ (20), 236 $[M–Glu–H_2O]^+$ (22), 218 $[M–Glu–2\times H_2O]^+$ (24), 212 (60), 201 (28), 175 (44), 167 (48), 73 (100).

3.6. Alatoside B (*2*)

Gum, $[\alpha]_D^{20} = -108.4°$ (*c* 0.20, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3423, 3340, 1698, 1437, 1172, 1140, 905. HRFAB-MS *m/z*: 431.2214 $[M+H]^+$ (calc. for $C_{21}H_{34}O_9$: 431.2203). EIMS 70 eV, *m/z*: 268 $[M–Glu]^+$(40), 250 $[M–Glu–H_2O]^+$ (14), 232 $[M–Glu–2\times H_2O]^+$ (42), 217 (14), 167 (56), 149 (46), 121 (52), 84 (88), 55 (100).

3.7. Alatoside C (*3*)

Gum, $[\alpha]_D^{20} = -88°$ (*c* 0.17, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3600, 3335, 1710, 1204, 928. HRFAB-MS *m/z*: 413.2103 $[M+H]^+$ (calc. for $C_{21}H_{32}O_8$: 413.2097). EIMS 70 eV, *m/z*: 250 $[M–Glu]^+$ (58), 232 $[M–Glu–H_2O]^+$ (100), 217 (30), 204 (35), 109 (50), 95 (47).

3.8. Alatoside D (*4*)

Gum, $[\alpha]_D^{20} = -16.5°$ (*c* 0.24, MeOH). IR ν_{max}^{KBr} cm^{-1}; 3616, 3348, 1706, 1243, 917. HRFAB-MS: 413.2143 $[M+H]^+$ (calc. for $C_{21}H_{32}O_8$: 413.2158). EIMS 70 eV,

m/z: 250 $[M–Glu]^+$ (30), 232 $[M–Glu–H_2O]^+$ (65), 217 (22), 204 (18), 162 (33), 145 (55), 55 (100).

3.9. Alatoside E (5)

Gum, $[\alpha]_D^{20} = -18^\circ$ (c 0.20, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3360, 2928, 1721, 1042, 925. HRFAB-MS: 375.2316 $[M+H]^+$ (calc. for $C_{19}H_{34}O_7$: 375.2383). EIMS m/z: 374 $[M]^+$ (2), 212 $[M–Glu]^+$ (26), 195 (72), 177 (70), 155 (24), 137 (66), 95 (84), 69 (97), 55 (100).

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