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Two New Triterpenoids from *Gelsemium elegans* and *Aglaia odorata*

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Eleganoside A (**1**) and odoratanone A (**15**), a triterpenoid trisaccharide glycoside and a nortriterpenoid, together with twelve known compounds (**2-13**) and a mixture of cerebrosides (**14**) were isolated from *Gelsemium elegans* and *Aglaia odorata*. Their structures were elucidated by extensive spectroscopic and spectrometric analysis. Eleganoside A (**1**) features a 3-*O*-*α*-L-rhamnopyranosyl (1→4)-*β*-D-glucopyranosyl (1→4)-*β*-D-glucopyranoside of a peculiar 3,16-dihydroxyl-lanosta-8,24-dien-26-oic acid triterpenoid skeleton, and odoratanone A (**15**) is a 29-norcycloartane−type triterpenoid bearing an unusual five-membered methyl acetal ring. Anti-acetylcholinesterase/butyrylcholinesterase (AChE/BChE) assay indicated that at 50 μM, ethyl caffeate (**5**) was promising as a dual inhibitor of AChE and BChE, and paeonol (**3**) and 24-hydroperoxy-24-vinylcholesterol (**9**) exhibited BChE-selective inhibition.

Keywords: *Gelsemium elegans*, *Aglaia odorata*, Eleganoside A, Odoratanone A, AChE/BchE.

Gelsemium elegans Benth. (Loganiaceae), a well-known poisonous evergreen perennial vine, has long been used as a Chinese folk medicine for the relief of rheumatoid and nervous pains and the treatment of skin ulcers and cancers [1]. The structurally complex and diversified alkaloids in this species have attracted the attention of natural products chemists in the past several decades [2], but the non-alkaloids were rarely reported [1, 3]. In our previous studies, some *Gelsemium* alkaloids with either anticancer or immunosuppressive activity have been reported from the stems and leaves of *G. elegans* [4]. Herein we report the isolation from the stems and leaves of *G. elegans* and structural elucidation of a new triterpenoid saponin, odoratanone A (**1**) together with twelve known compounds 2-*β*-D-glucopyranosyloxy-5-methoxy methyl benzoate (**2**) [5], paeonol (**3**) [6], ethyl vanillate (**4**) [7], ethyl caffeate (**5**) [8], stigmastane-3,6-dione (**6**) [9], *β*-sitosterol (**7**), *β*-daucosterol (**8**), 24-hydroperoxy-24-vinylcholesterol (**9**) [10], lupeol (**10**) [11], *α*-amyrin (**11**) [12], ursolic acid (**12**) [12], *α*-amyrin margarate (**13**) [13], and a mixture of cerebrosides (**14**) [14].

Aglaia odorata Lour. (Meliaceae) is a common spice from which many dammarane triterpenoids have been isolated [15]. In the current investigation, a new cycloartane triterpenoid (**15**) was also isolated from the root barks (Figure 1). The results of the anti-acetylcholinesterase/butyrylcholinesterase activities of these isolated compounds were also determined.

Compound **1** was obtained as a white solid. Its molecular formula was deduced to be $C_{48}H_{78}O_{18}$ from the HRESI-MS (*m/z* 941.5121, $[M-H]^-$; calcd. for 941.5110) and confirmed by ^{13}C NMR and DEPT spectra (Table 1). The IR spectrum showed absorptions for hydroxyl (3440, 3426 cm^{-1}), carbonyl (1682 cm^{-1}) and glycosidic C─O (1068, 1043 cm^{-1}) groups. The ^1H NMR spectrum of **1** exhibited six singlet methyls at δ 0.80, 0.99, 1.07, 1.35, 1.47, and 2.15, and one olefinic proton at δ 7.33 (t, J = 6.7 Hz). Initial

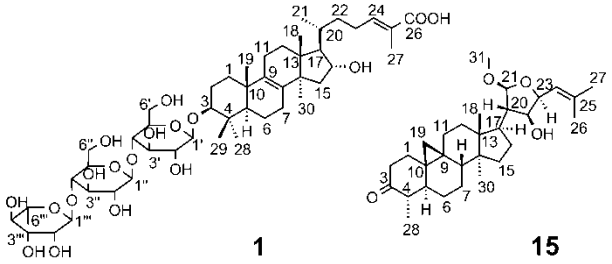

Figure 1: Structures of compounds **1** and **15**.

inspection of the ^{13}C NMR and DEPT data indicated that **1** possessed, except for three hexosyl residues (three distinguishable anomeric carbons at δ_C 107.2, 105.3, 103.1), a 30-carbon skeleton, which suggested that **1** might be a triterpenoid trisaccharide glycoside. Observation of the $[M+Cl-146]^-$ ion at *m/z* 831 suggested the presence of a deoxyhexosyl residue in **1**, which was possibly a rhamnosyl residue, as indicated by the doublet methyl at δ_H 1.74 [16]. Although exact assignments of the NMR data were still not possible at this stage, further analysis of the ^{13}C NMR and DEPT spectra showed that the triterpenoid backbone contained two double bonds with one trisubstituted and the other tetrasubstituted (δ_C 143.6 *CH*, 135.4 *C*, 135.2 *C*, 129.2 *C*), a carboxyl (δ_C 171.2), seven methyls (five tertiary on saturated carbons, one olefinic, and one secondary on a saturated carbon), nine methylenes, five methines (two oxygenated), and four quaternary carbons. These observations suggested that compound **1** was possibly a lanosta-8,24-dien-26-oic acid trisaccharide glycoside.

Confirmation of the lanosta-8,24-dien-26-oic acid triterpenoid backbone and sequential identification of H-1 to H-6 within each sugar unit was then accomplished through interpretation of the HSQC, HMBC, ^1H-^1H-COSY, HSQC-TOCSY and ROESY data (Figure 2) and by comparison of these with those reported in the

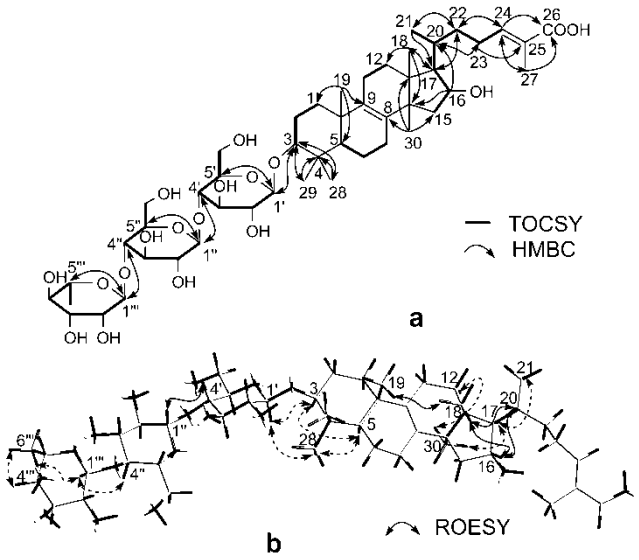

Figure 2: (a) TOCSY and selected HMBC correlations of **1**; (b) Key ROESY correlations of **1**.

literature [16]. In particular, the two hydroxymethines at δ_H 3.37 (δ_C 89.6) and δ_H 4.35 (δ_C 77.5) were located at C-3 and C-16, respectively, by the spin systems [CH_2(1)-CH_2(2)-CH(3) and CH_2(15)-CH(16)-CH(17)-CH(20)] established by HSQC-TOCSY and the HMBC correlations from H-3 to C-28 and C-29 and from H-16 to C-14 and C-20. The proton signals resonating at δ 4.91 (d, *J* = 7.8 Hz), 5.21 (d, *J* = 7.9 Hz), and 5.86 (s), which correlated with the anomeric carbon signals at δ 107.2, 105.3 and 103.1, respectively, in the HSQC spectrum, were three anomeric protons. The three sugar residues were further identified as *β*-D-glucopyranosyl (I), *β*-D-glucopyranosyl (II), and *α*-L-rhamnopyranosyl (III), respectively by detailed analysis of their 2D NMR spectroscopic data (Figure 2). The1→4-interglycosidic and sugar–aglycone linkages were deduced from the long range HMBC correlations (Figure 2a). The HMBC correlations between H-1′ of glucopyranosyl (I) (δ_H 4.91) and C-3 (δ_C 89.6) of the aglycone, H-1″ of the glucopyranoside (II) (δ_H 5.21) and C-4 of glucopyranosyl (I) (δ_C 81. 6), and H-1‴ of rhamnopyranosyl (III) (δ_H 5.86) and C-4 (δ_C 78.3) of glucopyranosyl (II) allowed the establishment of a triglycosyl moiety at C-3 as *O*-*α*-L-rhamnopyranosyl-(1→4)-*β*-D-glucopyranosyl-(1→4)-*β*-D-glucopyranoside.

The stereochemistry of **1** was determined by ROESY correlation analysis (Figure 2b). H-3 is *α*-oriented as it correlated with H-5 and H-28. H-16 is *β*-oriented as it correlated with H-18, H-20 and H-23. The remaining 2D NMR data were consistent with the structure depicted in Figure 2 for **1**. From the above mentioned information, compound **1** could be identified as 3*β*,16*α*-dihydroxyl-lanosta-8,24-dien-26-oic 3-*O*-*α*-L-rhamnopyranoside (1→4)-*β*-D-glucopyranoside (1→4)-*β*-D-glucopyranoside, and named eleganoside A.

Compound **15** was obtained as pale yellow oil. The molecular ion $[M]^+$ at *m/z* 470.3376 in the HR-EIMS was in agreement with the molecular formula $C_{30}H_{46}O_4$ (calcd. for 470.3396). The EIMS spectrum gave a fragmentation peak at $[M–18]^+$, suggesting the presence of a hydroxyl. The IR spectrum showed absorptions for hydroxyl (3443 cm^{-1}), carbonyl (1711 cm^{-1}) and methoxyl (2923 cm^{-1}) groups. The ^{13}C NMR spectrum showed, except for the signal for a methoxyl (δ_C 55.2), signals for 29 carbons as five methyls, nine methylenes, nine methines (one olefinic and three oxygenated) and six quaternary carbons (one carbonyl and one olefinic), which suggested that compound **15** was possibly a nortriterpenoid. The

Table 1: ^1H NMR spectroscopic data[a] of **1** (500 MHz in C_5D_5N) and **15** (600 MHz in $CDCl_3$).

No.	1	2	No.	Sugar of 1
1	1.14, 1.59 (m)	1.52, 1.80 (m)	**Glc I**	
2	1.84, 2.24 (m)	2.36 (m, 2H)	**1'**	4.91 (d, 7.8)
3	3.37 (dd, 11.8, 4.1)		**2'**	4.06[b]
4		2.17 (dd, 6.5, 11.6)	**3'**	4.25 (t, 8.7)
5	1.14 (m)	1.52 (m)	**4'**	4.35[b]
6	1.51, 1.69 (m)	1.63 (t, 3.5)	**5'**	3.97 (dt, 9.4, 3.1)
		0.67 (dq, 2.7, 12.7)	**6'**	4.64 (dd, 12.0, 3.1)
7	2.05 (m, 2H)	1.07 (dd, 2.7, 12.7)		4.56 (br d, 12.0)
		1.32 (m)	**Glc II**	
8		1.59 (d, 4.9)	**1''**	5.21 (d, 7.9)
11	1.97, 2.05 (m)	1.24 (t, 4.4), 2.01 (m)	**2''**	4.08[b]
12	1.72, 1.97 (m)	1.61 (d, 4.4), 1.51 (m)	**3''**	4.21 (t, 9.2)
15	1.65 (d, 12.9), 2.29[b]	1.32 (m, 2H)	**4''**	4.46 (t, 9.2)
16	4.35[b]	1.89, 1.51 (m)	**5''**	3.79 (dt , 2.7, 9.2)
17	1.94 (dd, 5.6, 9.8)	1.77 (m)	**6''**	4.24 (d, 9.2)
18	0.80 (s)	1.04 (s)		4.07[b]
19	0.99 (s)	0.35, 0.58 (d, 4.0)	**Rha**	
20	1.77 (m)	2.29 (br d, 11.6)	**1'''**	5.86 (s)
21	1.10 (d, 6.1)	4.82 (br s)	**2'''**	4.68 (br s)
22	1.76[b], 2.26[b]	3.84 (dd, 4.4, 10.6)	**3'''**	4.58 (dd, 9.4, 3.4)
23	2.61 (m), 2.27[b]	4.73 (dd, 4.4, 9.0)	**4'''**	4.38 (t, 9.4)
24	7.33 (t, 6.7)	5.35 (dt, 1.1, 9.0)	**5'''**	5.03 (dt, 6.2, 15.5)
26		1.67 (d, 1.1)	**6'''**	1.74 (d, 6.2)
27	2.15 (s)	1.75 (d, 1.1)		
28	1.35 (s)	0.93 (d, 6.5)		
29	1.07 (s)			
30	1.47 (s)	0.86 (s)		
31		3.31 (s)		

[a]Assignments based on 2D experiments. [b]Overlapping signals.

Table 2: ^{13}C NMR spectroscopic data of **1** (125 MHz in C_5D_5N) and **15** (150 MHz in $CDCl_3$).

No.	1	2	No.	Sugar of 1
1	36.2	33.0	**Glc I**	
2	27.6	41.1	**1'**	107.2
3	89.6	213.5	**2'**	75.5
4	40.1	50.1	**3'**	77.3
5	51.4	46.1	**4'**	81.6
6	18.9	25.9	**5'**	76.8
7	27.3	25.3	**6'**	62.6
8	135.4	47.2	**Glc II**	
9	135.2	24.9	**1''**	105.3
10	37.4	29.5	**2''**	75.7
11	21.5	27.1	**3''**	76.8
12	32.0	32.5	**4''**	78.3
13	46.7	45.9	**5''**	77.7
14	49.5	48.9	**6''**	61.7
15	44.3	35.4	**Rha**	
16	77.5	27.2	**1'''**	103.1
17	60.5	44.9	**2'''**	73.1
18	17.8	19.3	**3'''**	73.2
19	19.8	27.5	**4'''**	74.4
20	36.0	57.7	**5'''**	70.9
21	19.7	107.2	**6'''**	19.1
22	35.7	77.3		
23	26.6	79.7		
24	143.6	121.0		
25	129.2	137.9		
26	171.2	26.4		
27	13.4	18.7		
28	28.5	10.9		
29	17.3			
30	25.8	19.3		
31		55.2		

^{1}HNMR spectrum (Table 1) contained two upfield doublets at δ 0.35 (*J* = 4.0 Hz) and δ 0.58 (*J* = 4.0 Hz), characteristic of a C-9, C-10 cyclopropyl methylene group. These observations indicated that compound **15** was likely to be a cycloeucalenone type nortriterpenoid [17]. A vinyl proton at δ 5.35 (dt, *J* = 1.1, 9.0 Hz, H-24) and two geminal vinyl methyls at δ_H 1.67 and δ 1.75 (δ_C 26.4 and δ 18.7) were indicative of the presence of a Δ^{24} double bond rather than a $\Delta^{24(25)}$ double bond in the side chain. 2D NMR spectroscopic experiments (^1H-^1H COSY, HMQC, HMBC and NOESY) were then conducted to figure out the structural details of the compound. Four spin systems (CH-1−CH-2; CH-28−CH-8; CH-11−CH-12; CH-15−CH-24), drawn with bold bonds, were easily identified in the ^1H-^1H COSY spectrum, and HMBC correlation analysis further established the structure for **15** (Figure 3a). In

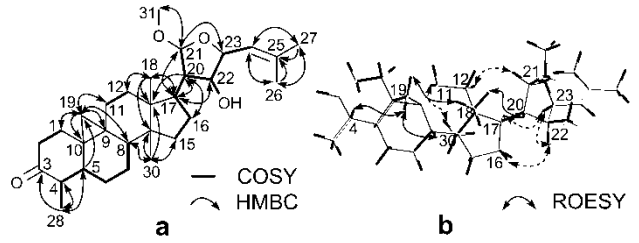

Figure 3: (a) COSY and selected HMBC correlations of **15**; (b) Key ROESY correlations of **15**.

particular, HMBC correlation from H_3-28 to C-3, C-4, and C-5 indicated that the carbonyl was at C-3, while HMBC correlations from H_2-19 to C-1, C-10, C-9, C-8, and C-10, as well as from H-5 to C-19 not only confirmed the cyclopropyl methylene group, but allowed establishment of the left-side substructure (C-1 through C-12, C-19 and C-28) of **15**. HMBC correlation from the methoxyl (δ_H 3.31) to the dioxygenated methine (C-21, δ_C 107.2) suggested that the methoxyl was located at C-21, while correlation from H-21 to C-23 suggested the presence of an oxygen bridge between carbons 21 and 23, and a five-membered methyl acetal ring in **15**. HMBC correlations from H_3-26 to C-24, C-25, and C-27 were also in agreement with a 2, 2-dimethylvinyl group in the side chain.

The stereochemistry of **15** was determined by ROESY correlation analysis (Figure 3b). H-21 is *α*–oriented (21*S*) as it correlated with H-12. This conclusion was also supported by the downfield chemical shift of C-21 (δ 107.2), which is typical of a 1,2 antisubstituted furanoside [18]. The ROESY correlations H-16/H-22, H-17/H-23 and H-22/H-23 suggested that both H-22 and H-23 are *α*–oriented (22*S*, 23*S*). The remaining 2D NMR data were consistent with the structure depicted in Figure 1 for **15**. Compound **15** was therefore determined to be 21*S*, 22*S*, 23*S*-epoxy-21-methoxycycloart-24en-3-one-22-ol, and was named odoratanone A.

Table 3: Acetylcholinesterase/ butyrylcholinesterase inhibitory activity of compounds isolated[a].

	Inhibition rate, %			Inhibition rate, %	
Compds	AChE	BChE	Compds	AChE	BChE
1	2.0	− 29.4	**9**	− 16.7	15.6
2	4.6	10.0	**11**	− 2.8	2.9
3	4.3	20.5	**12**	42.6 [19]	64.5 [19]
5	18.6	16.8	**13**	− 13.1	2.2
6	− 11.8	1.0	**14**	10.3	− 0.6
8	1.1	−10.3	TA[b]	47.9	85.5

[a]Evaluated at the concentration of 50 μM.
[b]Tacrine, used as the positive control.

Compounds **1**–**3**, **5**–**6**, **8**–**9**, **11** and **13**–**14** were evaluated for the acetylcholinesterase/butyrylcholinesterase (AChE/BChE) inhibitory activity by the spectrophotometric method developed by Ellman et al [20]. As shown in Table 3, except that compounds **1**, **8** and **11** were inactive against both enzymes, other tested compounds showed varying degrees of inhibition in the tests. It was reported that compound **12** possessed overt dual AChE/BChE inhibitory activity at 50 μM, comparable with the potency of galantamine, which is used in the treatment of mild to moderate AD and has been previously investigated by Kolak *et al.* [19]. In the current investigation, we found that though not very strong, compound **5** was also promising as a dual inhibitor of AChE and BChE, and compounds **3** and **9** exhibited BChE-selective inhibiton.

Experimental

General: IR spectra were measured using a Bruker Tensor 27 instrument with a KBr disc; UV spectra were recorded in MeOH on a Shimadzu UV-2401PC spectrometer; HREIMS were measured on an AutoSpec Premier P776 spectrometer; HRESIMS data was obtained on a Waters-Micromass Q-TOF electrospray; 1D and 2D-NMR spectra were recorded on a Bruker DRX-500 or Bruker AM-400 spectrometer with TMS as internal standard. Silica gel (200–300 mesh, Qingdao Marine Chemical, P.R. China), Lichroprep RP-18 (40–65 μm, Merck, Darmstadt, Germany) and Sephadex LH-20 (Pharmacia Fine Chemical Co., Ltd.) were used for CC.

Plant material: The stems and leaves of *G. elegans* and the root barks of *A. odorata* were collected in Xishuangbanna, Yunnan Province, China, in August, 2010 and authenticated by one of the authors (Y-K Xu) of Xishuangbanna Tropical Botanical Garden. Voucher specimens of *G. elegans* (No. 102243) and *A. odorata* (No. 148199) have been deposited in the Herbarium of the Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences.

Extraction and isolation: The air-dried and powdered stems and leaves of *G. elegans* (14.8 kg) were extracted 3 times (each for 6 days) with 95% ethanol in water at room temperature. The extract was filtered and concentrated under reduced pressure until only H_2O remained. The remaining solution was adjusted to pH 3 using 10% H_2SO_4 and then extracted with EtOAc to give EtOAc and water extracts, after concentration. The EtOAc extract (350 g) was then subjected to silica gel CC eluted with a light petroleum/ethyl acetate (v/v 7:3 to 2:8) gradient to yield 5 fractions (Fr. 1–5). Fraction 1 (5 g) was subjected to silica gel CC using a gradient solvent system containing lght petroleum/acetone (19:1 to 5:1) to yield **3** (14 mg), **4** (6 mg), **10** (5 mg) and **11** (5 mg). Fraction 2 (6 g) was separated on a silica gel column eluted with light petroleum/ethyl acetate/acetone (6:3:1 to 2:6:2) to yield **6** (8 mg), **7** (39 mg), **9** (7 mg), **12** (21 mg) and a subfraction Fr.2-1. Fr. 2-1 was subjected to Sephadex LH-20 CC using a gradient solvent system containing water/methanol (40:60 to 10:90) to yield **13** (10 mg). Fr. 4 and Fr. 5 were separated by a reversed phase (RP_{18}) silica gel column eluted by water/methanol (40:60 to 0:100) to yield **1** (18 mg), **2** (7 mg), **5** (11 mg), **8** (23 mg) and **14** (22 mg).

The air-dried and powdered root bark of *A. odorata* (3.7 kg) was extracted 3 times (each for 6 days) with 95% ethanol in water at room temperature. The combined extracts were concentrated under reduced pressure to give a semi-solid dark brown ethanol extract (238 g). The ethanol extract (230 g) was then dispersed in water and fractionated sequentially with light petroleum, chloroform, and *n*-butanol to yield light petroleum ether (63 g), chloroform (50 g) and butanol fractions (15 g), respectively. The light petroleum fraction was separated by silica gel CC eluted with light petroleum/EtOAc (from 50:1 to 0:1) through EtOAc/MeOH (from 10:1 to 3:1) to give 7 major fractions (Fr. 1–7). Silica gel CC (petroleum ether/EtOAc, 20:1 to 0:1) and Sephadex LH-20 CC (water/methanol, 30:70 to 0:100) of Fr. 3 afforded compound **15** (3 mg).

Anti-AChE/BChE assay: Acetylcholinesterase/ butyrylcholinesterase (AChE/BChE) inhibitory activity of the isolated compounds was assayed using the Ellman method [20]. *S*-Acetylthiocholine iodide, *S*-butyrylthiocholineiodide, 5,5'-dithio-bis-(2-nitrobenzoic) acid (DTNB, Elman's reagent), acetylcholinesterase and butyrylcholinesterase derived from human erythrocytes were purchased from Sigma Chemical. Compounds were dissolved in DMSO. The reaction mixture (totally 200 μL) containing phosphate buffer (pH 8.0), test compound (50 μM), and either acetylcholinesterase (0.02 U/mL) or butyrylcholinesterase (0.016 U/mL), was incubated for 20 min (37°C). Then, the reaction was initiated by the addition of 40 μL of solution containing DTNB (0.625 mM) and either acetylthiocholine iodide (0.625 mM) or butyrylthiocholine iodide (0.625 mM) for AChE or BChE inhibitory

activity assay, respectively. The hydrolysis of acetylthiocholine or butyrylthiocholine was monitored at 405 nm every 30 seconds for one hour. Tacrine was used as positive control with final concentration of 0.333 μM. All these actions were performed in triplicate. The percentage inhibition was calculated as follows: % inhibition = (E - S)/E × 100 (E is the activity of the enzyme without test compound and S is the activity of enzyme with test compound).

Eleganoside A (**1**)
White solid.
$[\alpha]_D^{15.2}$: +85.25 (*c* 0.058, $CHCl_3$).
IR (KBr) ν_{max} (cm^{-1}): 3440, 3426, 2921, 2876, 2853, 1682, 1639, 1462, 1456, 1376, 1068, 1043.
UV (MeOH) λ_{max} nm (log ε): 208 (4.07).
^{1}H NMR: Table 1.
^{13}C NMR: Table 2.
HRESIMS *m/z*: 941.5121 $[M-H]^-$ (calcd. for $[C_{48}H_{78}O_{18}-H]^-$, 941.5110).

Odoratanone A (**15**)
Pale yellow oil.
$[\alpha]_D^{23.5}$: − 6.67 (*c* 0.21, MeOH).
IR (KBr) ν_{max} (cm^{-1}): 3564, 3443, 3398, 2923, 1711, 1642, 1631.
^{1}H NMR: Table 1.
^{13}C NMR: Table 2.
HREIMS *m/z*: 470.3376 $[M]^+$ (calcd. for $[C_{30}H_{46}O_4]^+$, 470.3396).

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