Monoterpene Glycosides and Triterpene Acids from *Eriobotrya deflexa*

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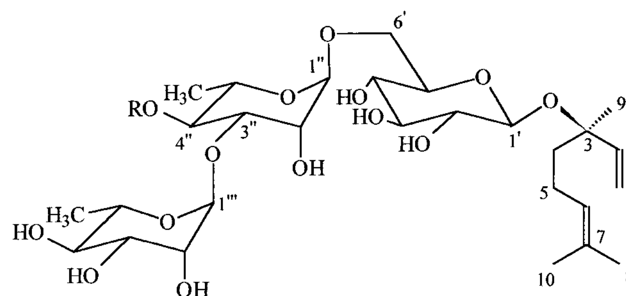
A phytochemical study on a methanolic extract of leaves of *Eriobotrya deflexa* led to the isolation and characterization of nine terpenoid compounds. Four of these are new chemical entities, including two monoterpene glycosides, (3*S*)-*O*-α-L-rhamnopyranosyl-(1→3)-[4-*O*-(*E*)-coumaroyl]-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-linalool (**1**) and (3*S*)-*O*-α-L-rhamnopyranosyl-(1→3)-[4-*O*-(*Z*)-coumaroyl]-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-linalool (**2**), and two triterpene acids, 1β,2α,19α-trihydroxy-3-oxo-12-ursen-28-oic acid (**3**) and 2α,3α,19α-trihydroxy-12-oleanen-28-oic acid (**4**). Their structures were elucidated on the basis of spectroscopic analysis. The activities of these isolates in an *in vitro* antiproliferation test were also determined.

Eriobotrya deflexa N. (Rosaceae), an erect shrub indigenous to Taiwan, is widely distributed in hardwood forests at about 1500 m in elevation throughout the island.[1] Leaves of *E. deflexa* have been used in traditional Chinese medicine as an expectorant and antitussive.[2] A closely related species, *E. japonica*, is commonly known as "loquat".[3] A series of sesquiterpene glycosides,[4−6] triterpene acids,[7] and triterpene esters[7,8] have been isolated from *E. japonica*, and among them, several components were found to show significant bioactivities including antiviral,[8] antiinflammatory,[9] and hypoglycemic properties.[10,11] To determine if *E. deflexa* can be used as a substitute for *E. japonica*, its leaf chemical constituents were investigated. Additionally, to determine the immunomodulatory activity of the *E. deflexa* isolates obtained, these substances were evaluated in an *in vitro* antiproliferation assay.

Results and Discussion

A methanolic extract of the dried leaves of *E. deflexa* was fractionated by liquid−liquid partitioning into fractions soluble in *n*-hexane, chloroform, and *n*-butanol. The *n*-butanol- and chloroform-soluble fractions were then subjected to Sephadex LH-20 column chromatography and HPLC to give two monoterpene glycosides (**1** and **2**) and seven triterpene acids (**3**−**9**), respectively. Of these, compounds **5**−**9** were found to be known, based on spectral comparison with reported data. Compounds **5**−**8** are ursolic acid analogues and were identified as euscaphic acid (**5**), obtained previously from *E. japonica*[7] and *Rosa laevigata*,[12] 1β-hydroxy-2-oxopomolic acid (**6**) and 2-oxopomolic acid (**7**), both isolated from *R. woodsii*,[13] and 2α,19α-dihydroxy-3-oxo-12-ursen-28-oic acid (**8**), a constituent of *Geum japonicum*.[14] Compound **9** is an oleanolic acid analogue and was identified as arjunic acid, having been isolated from the bark of *Terminalia arjuna*[15] and *T. macroptera*.[16]

The molecular formula for **1**, $C_{37}H_{54}O_{16}$, was determined by ^{13}C NMR, DEPT, and FABMS data. The ^{1}H NMR spectrum of **1** (Table 1) indicated that the molecule contained three sugar units, as evident from the presence of three anomeric proton signals at δ 4.33 (d, J = 7.8 Hz), 4.77 (brs), and 4.82 (d, J = 1.5 Hz). Of these three sugars, two were assigned as α-L-rhamnose units, supported by signals typical for anomeric protons and two secondary methyl signals (δ 1.16 and 1.24, d, J = 6.2 Hz). Besides the sugar proton regions, the ^{1}H NMR spectrum of **1** showed signals for a *trans*-coumaroyl moiety,[8] an AA′XX′ system at δ 6.80 (H-6′′′′ and H-8′′′′) and 7.47 (H-5′′′′ (J_{AX} = 8.6 Hz), and an AX system at δ 6.33 (H-2′′′′) and 7.65 (H-3′′′′) (J_{trans} = 15.9 Hz). In addition, this spectrum also displayed signals for a linalool moiety,[17] three methyl singlets at δ 1.34, 1.56, and 1.61, two methylenes at δ 1.62 and 2.04 (2H, m), and four olefinic protons at δ 5.08 (1H, t, J = 7.0 Hz), 5.21 (2H, m), and 6.06 (1H, dd, J = 10.7, 18.0 Hz). The presence of this moiety was supported by the ^{13}C NMR and DEPT data, in which the C-3 signal in linalool was significantly shifted downfield (δ 81.4 vs 72.9), suggesting that the hydroxy group at C-3 is glycosylated. Acid hydrolysis of **1** yielded *S*-(+)-linalool,[18] rhamnose, and glucose, with the sugars being analyzed as their TMS derivatives by GC−MS.[19] The HMBC spectrum of **1** showed the anomeric proton signal H-1′ (glc) (δ 4.33, d, J = 7.8 Hz) coupled to C-3 of linalool (δ 81.4, s), the H-1′′ (rha-1) (δ 4.77) signal coupled to C-6′ (glc) (δ 68.0, t), and the H-1′′′ (rha-2) (δ 4.82) signal coupled to C-3′′ (rha-1) (δ 78.5, d). These correlations helped to determine the main part of the structure of **1** as (3*S*)-*O*-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyllinalool. The coumaroyl moiety in **1** was assigned at C-4′′ of the central



1 R = *trans*-coumaroyl
2 R = *cis*-coumaroyl

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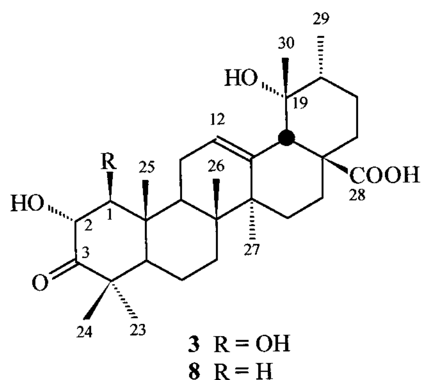
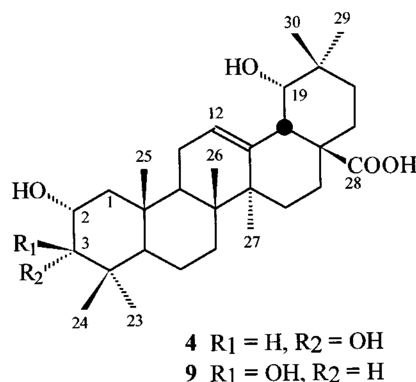
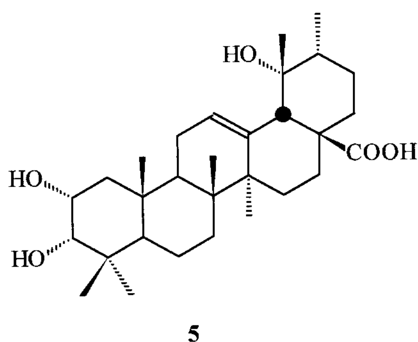


3 R = OH
8 R = H



4 R1 = H, R2 = OH
9 R1 = OH, R2 = H



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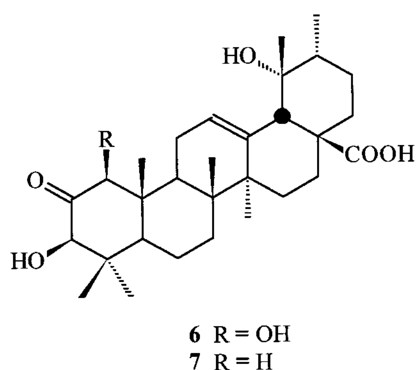

6 R = OH
7 R = H

rhamnose residue (rha-1) on the basis of observation of the downfield-shifted signal of the H-4″ (δ 5.18 vs 3.35) with respect to the corresponding signal of the nonsubstituted rhamnose unit (rha-2). This proposal was also confirmed by the HMBC spectrum, which revealed a three-bond coupling between H-4″ and C-1″″ (δ 168.4) of the coumaroyl unit. In addition, this coumaroyl moiety was in the *trans* form, deduced from the coupling constant between H-2″″ and H-3″″ (J = 15.9 Hz). Hence, **1** was established to be (3*S*)-*O*-α-L-rhamnopyranosyl-(1→3)-[4-*O*-(*E*)-coumaroyl]-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyllinalool. This structure was supported by the FABMS data, which showed prominent fragments at *m*/*z* 639, 439, 293, and 147. Complete ^{1}H and ^{13}C NMR data (Table 1) assignment of **1**, especially in the sugar region, was accomplished by analysis of two-dimensional COSY-45, NOESY, TOCSY, HMQC, and HMBC NMR spectra.

Compound **2** was assigned the same molecular formula as **1**, as deduced from its FABMS and ^{13}C NMR data. It possessed spectroscopic data closely comparable to those of **1** except for those in the coumaroyl part of the molecule. Its ^{1}H NMR exhibited signals for two *cis*-conjugated olefinic protons at δ 5.77 and 6.92 (J = 12.9 Hz) in contrast to the *trans*-conjugated signals (δ 6.33 and 7.65, J = 15.9 Hz) observed for **1**. Hence, **2** contained a *cis*-coumaroyl moiety, which was also supported by the evidence that H-5″″ and H-9″″ appeared at a lower field in the ^{1}H NMR spectrum relative to those same signals in **1** (Table 1).[8] Therefore, the structure of **2** was established as (3*S*)-*O*-α-L-rhamnopyranosyl-(1→3)-[4-*O*-(*Z*)-coumaroyl]-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyllinalool.

Compound **3** was assigned a molecular formula of $C_{30}H_{46}O_6$, as deduced from the HREIMS and ^{1}H and ^{13}C NMR data, one more oxygen atom than that of **8**. Its IR spectrum indicated the presence of a carbonyl (1716 cm^{-1}), a carboxylic acid group (1688 cm^{-1}), and a double bond (1653 cm^{-1}). The ^{1}H NMR spectra of both **3** and **8** showed characteristic signals for the olefinic proton H-12 (δ 5.73, brs), H-18 (δ 3.08, s), and seven methyls including six singlets and one doublet (H_3-29), consistent with a 19α-hydroxyursolic acid skeleton.[20] In addition, the ^{1}H NMR spectrum of **3** exhibited two mutually coupled carbinoyl protons at δ 3.70 (d) and 4.88 (d), instead of only one carbinoyl proton (H-2) in **8**, which appeared as a double doublet (δ 4.84, J = 6.4, 12.6 Hz). This difference was also reflected in their ^{13}C NMR spectra, which indicated that a methylene signal (C-1, δ 50.6, t) in **8** was replaced by an oxygenated methine (δ 87.1, d) in **3**. To account for this difference, C-1 of **3** must be hydroxylated, and OH-1 and OH-2 should be β- and α-oriented, respectively, to fit the diaxial coupling constant between H-1 and H-2 (J = 9.6 Hz). The NOESY spectrum of **3** exhibited mutual correlations between H-2, H_3-24, and H_3-25, confirming H-2 to be axially oriented. The HMBC spectrum revealed a three-bond coupling of H_3-25 (δ 1.43) to C-1 (δ 87.1), which was directly coupled to H-1, as observed in the HMQC spectrum, confirming C-1 to be hydroxylated. Furthermore, correlations between the carbonyl carbon (δ 214.1) and two methyl protons (δ 1.02, H_3-24; δ 1.24, H_3-23) in the HMBC spectrum confirmed the ketone group to be located at the C-3 position. Further analysis of 2D NMR data allowed the complete assignments of the ^{1}H and ^{13}C NMR spectra of **3**, and the results are listed in Table 2. Thus, compound **3** was established as 1β,2α,19α-trihydroxy-3-oxo-12-ursen-28-oic acid.

Compound **4** was assigned a molecular formula of $C_{30}H_{48}O_5$, by HREIMS, the same as that of **9**. Similar to that of **9**, its ^{1}H NMR spectrum exhibited characteristic signals for a 19α-hydroxyoleanolic acid skeleton,[20] namely, seven methyl singlets and signals for an olefinic H-12 (δ 5.57, brs), and the mutually coupled H-18 (δ 3.64, brs) and H-19 (δ 3.61, brs), as determined by the COSY-45 spectrum. Both spectra also displayed another two carbinoyl proton signals, however, having quite different coupling patterns. These two protons, H-2 and H-3, in **9** are diaxially oriented, thus having a large coupling constant (J = 9.5 Hz), with the corresponding signals in **4** exhibiting a much smaller coupling constant. In addition, the coupling con-

Table 1. ^{1}H and ^{13}C NMR and 2D NMR Data for Compound **1** (methanol-d_4, 500 MHz)

position	δ_C (ppm) mult.[a]	δ_H mult. (J/Hz)[b]	HMBC (H→C)	NOESY (H→H)
linalool				
1	115.3 t	5.21 m	2,3	2
2	144.4 d	6.06 dd (10.7, 18.0)	3,4,9	1
3	81.4 s			
4	41.8 t	1.62 m	2,3,6,9	
5	23.7 t	2.04 m	3,4,6,7	
6	125.7 d	5.08 t (7.0)	4,5,8,10	
7	132.1 s			
8	17.8 q	1.56 s	6,7,10	
9	23.6 q	1.34 s	2,3,4	
10	25.9 q	1.61 s	6,7,8	
3-*O*-glc				
1′	99.2 d	4.33 d (7.8)	2′, 3′,3	2′, 3′, 5′
2′	75.1 d	3.18 dd (7.8, 8.9)	1′,3′	1′
3′	78.3 d	3.32	2′,4′	1′
4′	71.7 d	3.27	3′, 5′	
5′	76.4 d	3.27	3′, 4′, 6′	1′, 6′a, 6′b
6′a	68.0 t	3.56 dd (6.0, 10.4)	1″,5′	1″,5′, 6′b
6′b		3.93 dd (3.6, 10.4)	1″,5′	1″,5′, 6′a,
6′-*O*-rha				
1″	101.9 d	4.77 brs	2″,3″,5″,6′	2″,5″,6′a,6′b
2″	72.0 d	3.98	3″, 4″	1″
3″	78.5 d	4.00	1‴,4″	1‴, 4″,5‴
4″	74.2 d	5.18 t (9.6)	1⁗,3″, 5″, 6″	3″,5″, 6″
5″	67.9 d	3.95 dq (9.6, 6.2)	4″,3″, 6″	1″, 4″,6″
6″	17.9 q	1.16 d (6.2)	4″,5″	4″,5″
3″-*O*-rha				
1‴	104.1 d	4.82 d (1.5)	3″,3‴,5‴	2‴,3″
2‴	72.4 d	3.68 dd (1.5, 3.3)	3‴, 4‴	1‴
3‴	72.1 d	3.70 dd (3.3, 9.4)	4‴	4‴
4‴	73.9 d	3.35	2‴, 6‴	3‴,5‴, 6‴
5‴	70.2 d	3.77 dq (9.4, 6.2)	3‴, 4‴,6‴	3″,4‴
6‴	18.1 q	1.24 d (6.2)	4‴, 5‴	4‴, 5‴
4″-coumaroyl				
1⁗	168.4 s			
2⁗	114.6 d	6.33 d (15.9)	1⁗, 3⁗, 4⁗	3⁗, 5⁗, 9⁗
3⁗	147.4 d	7.65 d (15.9)	1⁗,2⁗, 4⁗, 5⁗, 9⁗	2⁗,5⁗, 9⁗
4⁗	127.1 s			
5⁗	131.4 d	7.47 d (8.6)	3⁗,6⁗, 7⁗,8⁗, 9⁗	2⁗,3⁗, 6⁗
6⁗	116.8 d	6.80 d (8.6)	4⁗,7⁗,8⁗	5⁗
7⁗	161.5 s			
8⁗	116.8 d	6.80 d (8.6)	4⁗, 6⁗,7⁗	9⁗
9⁗	131.4 d	7.47 d (8.6)	3⁗,5⁗,6⁗,7⁗,8⁗	2⁗,3⁗, 8⁗

[a] Multiplicities were obtained from DEPT experiments. [b] Signals without multiplicity were picked up from COSY-45 or HMQC spectra.

stants between H-2 and H_2-1 were found to be 12.1 and 3.9 Hz, corresponding to a diaxial and an axial−equatorial coupling, respectively. Thus, H-2 was axially oriented. Consequently, H-3 was deduced to be equatorially oriented. In the NOESY spectrum, the signal of H-2 showed correlations with those of H-3, H_3-24, and H_3-25, confirming both H-2 and H-3 to be β-oriented. Its HMBC spectrum displayed the correlation of H-3 to C-1, C-2, C-4, C-5, C-23, and C-24, confirming H-3 to be hydroxylated. Further analysis of these 2D NMR data allowed the complete assignment of its ^{1}H and ^{13}C NMR spectra, and the results are listed in Table 2. Accordingly, compound **4** was assigned as 2α,3α,19α-trihydroxy-12-oleanen-28-oic acid.

The inflammatory response is a nonspecific immune response triggered by pathogenic microorganism infection or tissue injury and provides early protection in restricting the tissue damage to the site of infection or tissue injury.[21] Several immune cells including lymphocytes, neutrophils, monocytes, eosinophils, and basophils are involved in the inflammatory response, which in response to invasive organisms, if sufficiently intense or inappropriately prolonged, could paradoxically aggravate the injury or even cause death. The use of antiinflammatory medications must therefore be discreet. Blockade of the lymphocyte activation and proliferation is an antiinflammatory mechanism.[22] In this investigation the isolated pure compounds from *E. deflexa* were tested for their antiproliferation activity on human mononuclear cells involving T lymphocytes, B lymphocytes, and macrophages isolated from peripheral blood.[23] Compounds **3**, **5**, **6**, **7**, and **8**, having IC_{50} values of 26.9, 28.8, 32.5, 38.1, and 40.0 μM, respectively, were found to be moderately active in contrast to cyclosporin A, with a IC_{50} value of 0.012 μM. However, compounds **1** and **2** did not show any activity up to 100 μM concentration. The quantities of **4** and **9** obtained were insufficient to perform this biological investigation.

Experimental Section

General Experimental Procedures. Optical rotations were measured using a JASCO DIP-180 digital spectropolarimeter. UV spectra were measured in MeOH on a Hitachi U-2000 spectrophotometer. The IR spectra were recorded on a Nicolet 510P FT-IR spectrometer. The NMR spectra were recorded in MeOH-d_4 or pyridine-d_5 at room temperature on a Bruker DMX-500 SB spectrometer, and the solvent resonances were used as internal shift references. The 2D NMR spectra were recorded using standard pulse sequences. FABMS were recorded on a JEOL SX-102A instrument using *m*-nitrobenzyl alcohol (NBA) as the matrix. Sephadex LH-20 (Pharmacia Biotech) was used for open column chromatography. TLC was performed using silica gel 60 F_{254} plates (200 μm, Merck). HPLC was performed using an ODS column (Hyperprep ODS, 10 mm i.d. × 250 mm, Keystone Scientific

Table 2. ^{1}H and ^{13}C NMR Data for Compounds **3** and **4** (pyridine-d_5, 500 MHz)

	3		4	
position	δ_C (ppm) mult.[a]	δ_H mult. (J/Hz)[b]	δ_C (ppm) mult.[a]	δ_H mult. (J/Hz)[b]
1	87.1 d	3.70 d (9.6)	43.1 t	1.80 t (12.1) 1.95 dd (3.9, 12.1)
2	76.4 d	4.88 d (9.6)	66.6 d	4.34 dt (3.9, 12.1)
3	214.1 s		79.9 d	3.79 brs
4	48.5 s		39.4 s	
5	53.9 d	1.16	49.4 d	1.69
6	19.5 t	1.52 m 1.59 m	19.1 t	1.42 m 1.58 m
7	33.9 t	1.41 m 1.57 m	33.8 t	1.39 m 1.61 m
8	41.5 s		40.7 s	
9	48.9 d	2.23 dd (7.4, 10.8)	48.7 d	2.13
10	44.0 s		39.3 s	
11	28.4 t	2.65 m 3.28 m	24.7 t	2.12 m
12	129.8 d	5.73 brs	124.0 d	5.57 brs
13	139.4 s		145.4 s	
14	42.6 s		42.7 s	
15	29.9 t	1.31 m 2.35 m	29.6 t	2.10−2.20
16	26.9 t	2.10 m 3.15 m	28.9 t	2.16 m 2.83 m
17	48.8 s		46.5 s	
18	55.0 d	3.08 s	45.3 d	3.64 brs
19	73.1 s		81.7 d	3.61 brs
20	42.8 d	1.50 m	36.2 s	
21	27.4 t	1.36 m 2.12 m	29.7 t	2.10−2.20
22	38.9 t	2.08 m 2.18 m	34.2 t	2.05 m 2.21m
23	25.9 q	1.24 s	29.9 q	1.28 s
24	22.1 q	1.02 s	22.7 q	0.93 s
25	13.3 q	1.43 s	17.0 q	1.02 s
26	18.2 q	1.23 s	18.1 q	1.09 s
27	25.2 q	1.70 s	25.3 q	1.39 s
28	181.2 s		181.5 s	
29	17.2 q	1.13 d (6.5)	29.3 q	1.20 s
30	27.5 q	1.45 s	25.3 q	1.13 s

[a] Multiplicities were obtained from DEPT experiments. [b] Signals without multiplicity were picked up from COSY-45 or HMQC spectra.

Inc., Bellefonte, PA; detector, UV 254 nm) and a silica column (Hyperprep HS silica, 10 mm i.d. × 250 mm, ThermoQuest Hypersil, Runcorn, UK; detector, RI). GLC: HP gas chromatograph 6890; MS, HP 5973 mass selective detector; column, HP-5MS fused silica capillary column, 0.25 mm i.d. × 30 m, carrier gas, He; flow rate, 1 mL/min.

Plant Material. Leaves of *E. deflexa* were collected from Central Cross Island Road in central Taiwan in April 2000 and were identified by Chii-Cheng Liao, a Ph.D. candidate in the Department of Botany of National Taiwan University. Voucher specimens (No. 20000405) have been deposited at the Institute of Botany, Academia Sinica, Nankang, Taipei, Taiwan.

Extraction and Isolation. Dried leaves (500 g) were ground into a powder and extracted three times with 500 mL of MeOH for 2 days. The methanolic extract was adjusted to 85% in aqueous solution for an *n*-hexane partition, which generated two fractions soluble in methanol and *n*-hexane. Subsequently, the methanol-soluble fraction was then vacuum-evaporated to dryness (75 g) and further partitioned between chloroform and water, and the remaining water solution was extracted three times with *n*-butanol. Both the *n*-butanol and chloroform layers were evaporated to dryness and redisssolved in MeOH for individual chromatographic separation. The first separation step was carried out using gel filtration chromatography on a Sephadex LH-20 column (3 × 55 cm) and eluted by MeOH with a flow rate of 13 mL/min.

Fractions collected from the *n*-butanol layer were checked for their compositions by TLC using CH_2Cl_2−EtOAc−HCO_2H−H_2O (15:70:5:1) for development. Vanillin−sulfuric acid (yellow-green spots) and observation under long-wave UV were used in the detection of monoterpene glycosides. Subsequently, the monoterpene glycoside fractions from the above separation were combined and rechromatographed on a reversed-phase HPLC column with MeCN−H_2O (40:60) as eluent to yield **1** (360 mg) and **2** (195 mg).

Fractions collected from the chloroform layer were further purified by repetitive HPLC separations on a Hyperprep ODS column with MeCN−H_2O (60:40) as eluent to give subfractions 1 and 2. Subsequently, HPLC of subfraction 1 on a silica column with CH_2Cl_2−EtOAc (3:7) as eluent afforded **3** (6 mg), **4** (4 mg), **5** (10.8 mg), **6** (12 mg), and **9** (3.5 mg). Subfraction 2 was purified by using the same column with *n*-hexane−EtOAc (2:1) as eluent to yield **7** (12 mg) and **8** (14 mg).

(3*S*)-*O*-α-L-rhamnopyranosyl-(1→3)-[4-*O*-(*E*)-coumaroyl]-α-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranosyllinalool (1): amorphous white powder; mp 144−146 °C; $[\alpha]^{25}_D$ −31.8° (*c* 0.67, MeOH); IR (KBr) ν_{max} 3413, 1605, 1169, 1046 cm^{-1}; UV λ_{max} (MeOH) (log ϵ) 203 (4.0), 227 (3.9), 313 (4.2) nm; ^{1}H and ^{13}C NMR data, see Table 1; FABMS *m*/*z* [M + Na]$^+$ 777 (20), 639 (4), 585 (3), 439 (17), 293 (47), 154 (48), 147 (100), 136 (37), 82 (35), 69 (56); HRFABMS *m*/*z* [M + H]$^+$ 755.3472 (calcd for $C_{37}H_{55}O_{16}$ 755.3490); R_f 0.32 [EtOAc−HCO_2H−H_2O (85:10:15)].

(3*S*)-*O*-α-L-rhamnopyranosyl-(1→3)-[4-*O*-(*Z*)-coumaroyl]-α-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranosyllinalool (2): amorphous white powder; mp 136−137 °C; $[\alpha]^{25}_D$ −87.4° (*c* 0.39, MeOH); IR (KBr) ν_{max} 3401, 1605, 1163, 1046 cm^{-1}; UV λ_{max} (MeOH) (log ϵ) 203 (4.1), 312 (4.1) nm; ^{1}H NMR (CD_3OD) δ 7.69 (2H, d, J = 8.7 Hz, H-5′′′′, -9′′′′), 6.92 (1H, d, J = 12.9 Hz, H-3′′′′), 6.76 (2H, d, J = 8.7 Hz, H-6′′′′, -8′′′′), 6.04 (1H, dd, J = 10.7, 18.0 Hz, H-2), 5.77 (1H, d, J = 12.9

Hz, H-2′′′′), 5.20 (2H, m, H_2-1), 5.12 (1H, t, *J* = 9.8 Hz, H-4′′), 5.09 (1H, t, *J* = 7.3 Hz, H-6), 4.79 (1H, brs, H-1′′′), 4.75 (1H, brs, H-1′′), 4.32 (1H, d, *J* = 7.8 Hz, H-1′), 3.95 (1H, H-2′′), 3.92 (1H, dd, *J* = 3.3, 10.5 Hz, H-6′b), 3.90 (1H, H-3′′), 3.86 (1H, dq, *J* = 9.8, 6.2 Hz, H-5′′), 3.77 (1H, dq, *J* = 9.4, 6.3 Hz, H-5′′′), 3.71 (1H, H-2′′′), 3.70 (1H, H-3′′′), 3.54 (1H, dd, *J* = 6.2, 10.5 Hz, H-6′a), 3.32 (1H, H-4′′′), 3.31 (1H, H-2′), 3.26 (1H, H-5′), 3.23 (1H, H-4′), 3.17 (1H, dd, *J* = 7.9, 9.0 Hz, H-2′), 2.04 (2H, m, H_2-5), 1.65 (3H, s, H_3-10), 1.61 (2H, m, H_2-4), 1.58 (3H, s, H_3-8), 1.33 (3H, s, H_3-9), 1.24 (3H, d, *J* = 6.2 Hz, H_3-6′′′), 1.16 (3H, d, *J* = 6.2 Hz, H_3-6′′); ^{13}C NMR (CD_3OD) δ 167.2 (s, C-1′′′′), 160.3 (s, C-7′′′′), 146.8 (d, C-3′′′′), 144.3 (d, 134.0 (d, C-5′′′′, -9′′′′), 132.1 (s, C-7), 127.5 (s, C-4′′′′), 125.8 (d, C-6, 115.9 (d, C-6′′′′, -8′′′′), 115.8 (d, C-2′′′′), 115.3 (t, C-1), 104.1 (d, C-1′′), 101.9 (d, C-1′′), 99.2 (d, C-1′), 81.4 (s, C-3), 78.6 (d, C-3′′), 78.3 (d, C-3′), 76.5 (d, C-5′), 75.1 (d, C-2′), 73.9 (d, C-4′′′), 73.8 (d, C-4′′), 72.5 (d, C-2′′′), 72.1 (d, C-3′′′), 72.0 (d, C-2′′), 71.9 (d, C-4′), 70.2 (d, C-5′′′) 68.2 (t, C-6′), 68.0 (d, C-5′′), 41.8 (t, C-4), 25.9 (q, C-10), 23.7 (t, C-5), 23.6 (q, C-9), 18.1 (q, C-6′′′), 18.0 (q, C-6′′), 17.8 (q, C-8); FABMS *m*/*z* $[M + Na]^+$ 777 (23), 639 (3), 439 (10), 293 (25), 176 (14), 154 (52), 147 (80), 136 (40), 82 (48), 69 (100); HRFABMS *m*/*z* $[M + H]^+$ 755.3478 (calcd for $C_{37}H_{55}O_{16}$ 755.3490); R_f 0.38 [EtOAc−HCO_2H−H_2O (85:10:15)].

1*β*,2α,19α-Trihydroxy-3-oxo-12-ursen-28-oic acid (3): amorphous white powder; mp 218−220 °C; $[\alpha]^{25}_{D}$ +29.7° (*c* 0.59, MeOH); IR (KBr) ν_{max} 2934, 1716, 1688, 1653, 1558, 1541, 1456 cm^{-1}; ^{1}H and ^{13}C NMR data, see Table 2; FABMS *m*/*z* $[M + Na]^+$ 525 (100), 439 (18), 307 (12), 233 (8), 187 (18), 154 (42), 119 (40), 91 (50), 56 (52); HREIMS *m*/*z* $[M]^+$ 502.3256 (calcd for $C_{30}H_{46}O_6$ 502.3294); R_f 0.5 [EtOAc−CH_2Cl_2 (7:3)].

2α,3α,19α-Trihydroxy-12-oleanen-28-oic acid (4): amorphous white powder; mp 215−217 °C; $[\alpha]^{25}_{D}$ +19.6°(*c* 0.1, MeOH); IR (KBr) ν_{max} 2932, 1693, 1682, 1454 cm^{-1}; ^{1}H and ^{13}C NMR data, see Table 2; FABMS *m*/*z* $[M + Na]^+$ 511 (100), 407 (10), 246 (12), 201 (37), 187 (35), 145 (37), 119 (88), 91 (88), 56 (98); HREIMS *m*/*z* $[M]^+$ 488.3470 (calcd for $C_{30}H_{48}O_5$ 488.3502); R_f 0.46 [EtOAc−CH_2Cl_2 (7:3)].

Acid Hydrolysis of 1. Compound **1** (80 mg) was hydrolyzed by 2 N HCl (10 mL) at room temperature overnight. The reaction mixture was then extracted with *n*-hexane (10 mL × 3). The *n*-hexane layer was evaporated to give a residue, which was chromatographed by semipreparative HPLC (Hyperprep HS Silica, 250 × 10 mm) using *n*-hexane−EtOAc (2:1) as the eluent to give *S*-(+)-linalool (4.6 mg): $[\alpha]^{25}_{D}$ +2.7° (*c* 0.23, $CHCl_3$) (lit.[18] $[\alpha]^{20}_{D}$ +19.2°); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.04 (1H, dd, *J* = 1.2, 10.8 Hz, H-1a), 5.19 (1H, dd, *J* = 1.2, 17.3 Hz, H-1b), 5.89 (1H, dd, *J* = 10.8, 17.3 Hz, H-2), 1.55 (2H, m, H_2-4), 2.00 (2H, m, H_2-5), 5.10 (1H, t, *J* = 6.5 Hz, H-6), 1.58 (3H, s, H_3-8), 1.26 (3H, s, H_3-9), 1.66 (3H, s, H_3-10); GC−MS *m*/*z* 154 $[M]^+$; R_f 0.47 [*n*-hexane−EtOAc (2:1)].

Monosaccharide Composition Analysis of 1. Compound **1** (1 mg) was methanolyzed with 0.5 M methanolic HCl at 80 °C for 16 h. Evaporation of the reaction mixture gave a residue, which was treated with the Sylon HTP trimethylsilylation reagent (Supelco, Bellefonte, PA) for 20 min at room temperature. After removal of the excess reagent and organic solvent by condensation, the persilylated products were dissolved in *n*-hexane, and this solution was used for GC−MS analysis. GC−MS analysis of the trimethylsilylated derivatives was performed on a fused silica capillary column using a temperature gradient of 60 to 140 °C at 25 °C/min, increased to 250 °C at 5 °C/min, and then increased to 300 °C at 10 °C/min. When compared with the authentic standards, the retention time of persilylated glucose and rhamnose was found to be 15.54 (15.89) and 10.08 (10.30) min, respectively.

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