New Triterpenes from *Machaerocereus eruca*

Yang Ye,[†] Kaoru Kinoshita,[†] Kiyotaka Koyama,[†] Kunio Takahashi,*[,†] Norio Kondo,[‡] and Hiroshi Yuasa[‡]

Department of Pharmacognosy and Phytochemistry, Meiji College of Pharmacy, 1-22-1, Yato-cho, Tanashi-city, Tokyo 188, Japan, and Research Institute of Evolutionary Biology, 2-4-28, Kamiyoga, Setagaya-ku, Tokyo 142, Japan

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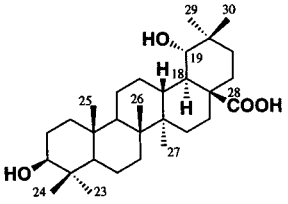
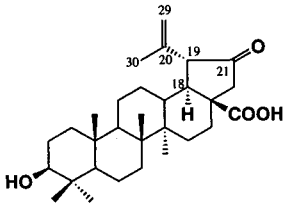
Four triterpenes, three lupanes, and a germanicane were isolated from *Machaerocereus eruca*. The germanicane derivative (**1**) was determined to be 3β,19α-dihydroxygermanican-28-oic acid and named machaeroceric acid. The three new lupane derivatives were identified as 21-ketobetulinic acid (**2**), 16β-hydroxybetulinic acid (**3**), and 22β-hydroxystellatogenin (**4**), respectively, on the basis of their spectroscopic data.

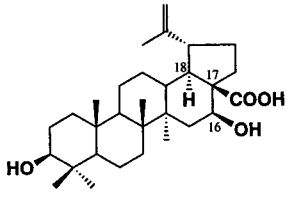
We have been interested in triterpenoids of cacti and previously isolated six known sapogenins, and 10 new ones, containing oleanane-type, lupane-type, and pachanan-type triterpenes, from the acid hydrolysates of methanol extracts of cactaceous plants.[1−4] Pachanols A, B, and C, which were new compounds posessing a new skeleton named pachanan, and bridgesigenin C, a new compound, were isolated from *T. pachanoi*.[2] Four known triterpenes, stellatogenin, betulinic acid, oleanolic acid, and thurberogenin, and a new compound, machaerogenin, were also isolated from *Machaerocereus eruca* Br. & R. (Cactaceae).[4] Djerasii and co-workers[5−7] discovered that *M. eruca* contained stellatogenin and betulinic acid in 1955. We now report four new triterpenes (**1**−**4**) and four known triterpenes, morolic acid, queretaroic acid, 27-desoxyphillyrigenin, and trelesegenic acid (3β-hydroxytaraxastan-28,20β-olide) from the acid hydrolysate of a MeOH extract.



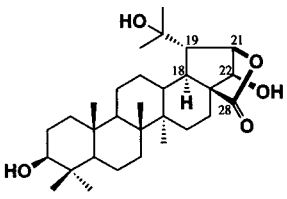
machaeroceric acid (**1**)



21-ketobetulinic acid (**2**)



16β-hydroxybetulinic acid (**3**)



22β-hydroxystellatogenin (**4**)

Results and Discussion

Four new triterpenes **1**−**4** were isolated from *M. eruca*. Compound **1** had molecular formula $C_{30}H_{50}O_4$ as determined by HREIMS and confirmed by ^{13}C NMR and DEPT analysis. The IR spectrum of **1** exhibited hydroxyl (3437 cm^{-1}) and carboxyl (1710 cm^{-1}) absorptions. The ^{13}C NMR spectrum revealed 30 carbon signals, which were assigned by DEPT as seven methyl, 10 methylene, four methine, two alcoholic methine, and seven quaternary (including a carboxyl) carbons. The ^1H NMR revealed seven singlet methyls, a doublet of doublets at δ 3.41, and a doublet at δ 4.65. Unambiguous assignments for the ^1H and ^{13}C NMR signals were made by combination of the 1D difference homo-decoupling experiment, NOE difference spectra, $^1H-^1H$ COSY, HMBC, and HMQC. The ^1H and ^{13}C NMR chemical shifts showed good agreement with similar data for the A/B ring of oleanolic acid, and **1** had one more hydroxyl group on the C/D/E ring. Compound **1** had no sp^2 carbons at positions 12 and 13. In ^2J and ^3J HMBC experiments, the alcoholic methine proton at δ 4.65 showed correlation with the methyl carbons at C-29 (δ 30.8) and C-30 (δ 21.0) and with the methine carbons at C-13 (δ 39.8) and C-18 (δ 46.4), respectively. These findings indicated a hydroxyl group at C-19. The stereochemistry of this alcoholic methine proton was determined by analyzing the NOE difference spectrum (Figure 1) and the value of coupling constant between H-18 and H-19. From the difference decoupling spectrum, irradiation at H-19 (δ 4.65), H-18 was assigned at δ 1.79 (t, J = 10.3 Hz). This indicated that the coupling constants of J_{18-19} and J_{18-13} were equal to 10.3 Hz. NOE enhancement of the H-13 (δ 2.92) proton was observed by irradiation of H-19 (δ 4.65) and CH_3-26 (δ 1.07), respectively. In addition, NOE enhancement was observed for H-18 and H-9, on irradiation of CH_3-27 (δ 1.17). Thus, H-18 was shown to be in the α configuration. Furthermore, the alcoholic methine proton was determined to be in the β configuration from the vicinal coupling constant (J_{18-19} = 10.3 Hz). The ^1H and ^{13}C NMR assignments at the 29 and 30 positions were made by NOE difference spectra. In the NOE difference spectra, enhancement of the methyl protons at δ 1.26 was observed by irradiation of H-19 (δ 4.65), and, in turn, NOE enhancement of this methine proton was observed by irradiation of the methyl protons. Moreover, on irradiation of the methyl protons at δ 1.24, NOE enhancement was observed at H-18 (δ 1.79) (Figure 1). The methyl protons at δ 1.24 and δ 1.26

* To whom all correspondence should be addressed. Tel.: 0424-21-0394. Fax: 0424-21-1489.
[†] Meiji College of Pharmacy.
[‡] Research Institute of Evolutionary Biology.

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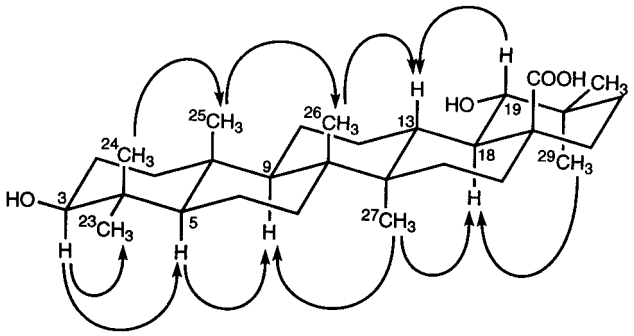

Figure 1. Observed positive NOEs for **1** from NOE-difference spectra (indicated by arrows).

showed a cross peak in the HMQC spectrum at δ 21.0 and δ 30.8, respectively. Thus, the methyl protons and carbon signals at δ 1.24 and δ 30.8 were assigned to CH_3-29 and the methyl protons and carbon signals at δ 1.26 and δ 21.0 were assigned to CH_3-30 (Table 1). Therefore, the new compound **1** was determined to be 3β,19α-dihydroxygermanican-28-oic acid and was named machaeroceric acid.

Compound **2** had molecular formula $C_{30}H_{46}O_4$ as determined by HREIMS and confirmed by ^{13}C NMR and DEPT analysis. The IR spectrum of **2** exhibited hydroxyl (3428 cm^{-1}), carboxyl (1700 cm^{-1}), and carbonyl (1744 cm^{-1}) absorptions. The ^1H NMR spectrum showed five tertiary methyls (δ 0.82−1.23, CH_3-23−27) and one vinylic methyl (δ 1.86, CH_3-30), two protons of an isopropenyl moiety at δ 5.05 and 5.07 (each 1H, s, CH_2-29) and one alcoholic methine proton at δ 3.46 (1H, dd, J = 8.9, 7.4 Hz, CH-3β). The ^{13}C NMR spectra of compound **2** revealed 30 carbon signals, which were assigned by DEPT as six methyl, nine methylene, five methine, five quaternary, one alcoholic methine, one carboxylic acid, and two olefinic (one $=CH_2$ and one quaternary) carbons. The $\Delta^{20,29}$-functionality of a lupane skeleton was inferred for this compound from the resonances of the sp^2 carbons at C-29 (secondary carbon signal deduced by DEPT pulse sequence) at δ 114.4 and C-20 (quaternary carbon) at δ 144.9. The ^1H and ^{13}C NMR (Table 1) confirmed the characteristic features for a betulinic acid parent structure bearing one carbonyl group on ring D or E for the compound. These assignments were performed by $^1H-^{13}C$ COSY and long-range $^1H-^{13}C$ COSY experiments. The signal of CH_3-27 at δ 1.07 had a long-range $^1H-^{13}C$ correlation peak with C-15. Methylene protons at C-15 and C-22 had same correlation peak with C-17, and the methylene protons at C-22 correlated with the carbon of the carbonyl group (δ 215.0). These data indicated that the carbonyl group was at C-21 or C-16. From the 1D homo-decoupling spectrum, however, the methylene protons were assigned to C-16 by irradiation of the methylene protons at C-15. Thus, the carbonyl group was placed at C-21. In comparison with ^{13}C NMR data of betulinic acid, the carbons at C-19 and C-22 of **2** were deshielded (δ 49.7 → 59.0, 37.5 → 52.0), which supported the assignment of the carbonyl group at C-21. Therefore, the new compound was determined to be 21-ketobetulinic acid (**2**).

Compound **3** had the molecular formula $C_{30}H_{48}O_4$ as determined by HREIMS and confirmed by ^{13}C NMR (Table 2) and DEPT analysis. The ^1H NMR spectrum of **3** (Table 2), as in **2**, showed signals attributable to a betulinic acid derivative, except for the signal due to a proton attached to a carbon-bearing oxygen at δ 4.09. In comparison with the data of betulinic acid, the carbon signals for C-14, 15, 16, 17, and 18 appeared slightly or largely shifted downfield (42.8 → 44.2, 31.2 → 40.1, 32.8 → 75.7, 56.6 → 61.5, and 47.7 → 49.4). These assignments were performed by 1D and 2D NMR. From the NOE difference spectrum, the hydroxy group was placed at C-16, and H-16 was shown to be in the α configration. Therefore, the structure of **3** was determined to be 16β-hydroxybetulinic acid.

Compound **4** had molecular formula $C_{30}H_{48}O_5$ as determined by HREIMS and confirmed by ^{13}C NMR and DEPT analysis. The IR spectrum indicated the presence of a hydroxyl (3457 cm^{-1}) and a five-membered lactone (1759 cm^{-1}). ^1H and ^{13}C NMR of **4** (Table 2) confirmed the characteristic feature for the stellatogenin parent structure. In comparison with the NMR data of stellatogenin, the ^{13}C NMR chemical shifts were in good agreement except for the D/E ring. The alcoholic methine proton (δ 5.23) had a long-range $^1H-^{13}C$ correlation with the carbonyl carbon. Thus, this hydroxy group was either at C-16 or C-22. Because the ^{13}C NMR data of **4** (Table 2) was not in agreement with that of 16β-hydroxystellatogenin,[4] the hydroxyl group was assumed to be at C-22. A combination of 1D homodecoupling and 2D NMR allowed assignments of all protons and carbons. The stereochemistry of H-22 was determined to be α by analyzing the NOE difference spectrum. These facts indicated that **4** was 22β-hydroxystellatogenin.

Four known triterpenes were also isolated, and one of the four was identical with morolic acid, which was identified as the monoacetate derivative by comparing with published ^{13}C NMR data and physical characteristics.[8] Unambiguous assignments of ^{13}C NMR signals were made by 2D NMR. The second known compound was identified as queretaroic acid by direct comparison with an authentic sample isolated from *T. bridgesii*.[1] The other two compounds were confirmed to be 27-desoxyphillygenin (3β-hydroxytaraxastan-28,20β-olide)[9] and treleasegenic acid,[10] respectively. This is the first report of the isolation of morolic acid and 27-desoxyphillygenin from a cactus, and the first unambiguous assignments of ^1H and ^{13}C NMR data for 27-desoxyphillygenin and treleasegenic acid are presented in the Experimental Section.

Four new compounds were isolated, and three of the four compounds (**2**, **3**, and **4**) were determined to be 21-ketobetulinic acid, 16β-hydroybetulinic acid, and 22β-hydroxystellatogenin, respectively. Compound **1** was determined to be 3β,19α-dihydroxygermanican-28-oic acid and was named machaeroceric acid. The stereochemistry of 18-H in germanicanes is α in contrast to the β configuration in oleananes. Germanicane-type triterpenes reported earlier are characterized by the $\Delta^{18,19}$ olefinic linkage in their molecules,[13] except for a few compounds having 18α-H.[11,12] Olean-12-ene-type triterpenes are biosynthesized through germanicane-type triterpenes from lupane-type triterpenes, and the stereochemistry of 18-H in lupane-type triterpenes is α. Compound **1**, a germanicane derivative, does not have the $\Delta^{18,19}$ olefinic linkage but has the 18α-H,

Table 1. ^{13}C and ^{1}H NMR Spectral Data of **1** and **2** in C_5D_5N

	1		**2**	
position	δ_C	δ_H	δ_C	δ_H
1	39.1	0.85 (m), 1.53 (m)	39.2	0.99 (m), 1.67 (m)
2	28.3	1.78 (m)	28.3	1.86 (m)
3	78.0	3.41 (dd, J = 10.3, 5.7 Hz)	78.1	3.46 (dd, J = 8.9, 7.4 Hz)
4	39.5		39.5	
5	55.8	0.77 (m)	55.9	0.80 (d, J = 9.1 Hz)
6	18.8	1.54 (m)	18.7	1.47 (m), 1.58 (m)
7	34.9	1.39 (m)	34.5	1.40 (m)
8	41.4		41.2	
9	50.6	1.39 (d, J = 12.6 Hz)[a]	50.6	1.70 (t, J = 8.9 Hz)
10	37.3		37.5	
11	21.9	1.54 (m)	20.9	1.35 (m)
12	28.8	1.78 (m), 2.95 (m)	26.3	1.29 (m), 1.75 (m)
13	39.9	2.92 (m)	38.8	2.53 (dt, J = 12.1, 3.6 Hz)
14	42.9		42.8	
15	29.7	1.27 (m), 1.97 (ddd, J = 14.1, 13.6, 3.8 Hz)	29.5	1.28 (m), 2.27 (dt, J = 13.6, 3.7 Hz)
16	35.5	1.63 (dt, J = 13.1, 3.8 Hz), 2.41 (dt, J = 13.1, 4.0 Hz)	32.1	1.70 (m), 2.63 (ddd, J = 12.9, 3.7, 2.5 Hz)
17	52.3		50.8	
18	46.5	1.79 (t, J = 10.3 Hz)[a]	48.7	2.42 (t, J = 12.1 Hz)
19	75.9	4.65 (d, J = 10.3 Hz)	59.0	3.95 (d, J = 12.1 Hz)
20	37.6		144.9	
21	36.2	1.41 (m), 1.85 (m)	215.0	
22	34.4	1.75 (m), 2.05 (m)	52.0	2.45 (d, J = 16.9 Hz), 2.92 (d, J = 16.9 Hz)
23	28.7	1.23 (s)	28.7	1.23 (s)
24	16.3	1.00 (s)	16.3	1.02 (s)
25	16.4	0.80 (s)	16.3	0.82 (s)
26	16.5	1.07 (s)	16.3	1.07 (s)
27	15.2	1.17 (s)	14.9	1.14 (s)
28	178.8		178.5	
29	21.0	1.24 (s)	114.4	5.04 (s), 5.06 (s)
30	30.8	1.26 (s)	21.5	1.86 (s)

[a] Revealed by ^{1}H difference decoupling spectrum and NOE difference experiment.

supporting this concept of the biosynthesis of triterpenoids. The $\Delta^{18,19}$ germanicanes, such as morolic acid, may be intermediates to the oleananes.

Experimental Section

General Experimental Procedures. Melting points were determined on a Yanagimoto MP micromelting point apparatus. The IR spectra were measured with a JASCO A-102 IR spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded using a JEOL GSX-400 (^{1}H 400 and ^{13}C 100 MHz) spectrometer in pyridine-d_5. Chemical shifts are recorded in parts per million (δ) in pyridine-d_5. The $[\alpha]_D$ values were determined with a JASCO DIP-140 digital polarimeter. Column chromatography was carried out on 70−230 mesh Si gel (Merck). HPLC was performed using an SSC-3100-J pump with an Oyo-Bunko Uvilog 7 UV detector. HRMS and EIMS spectra were obtained using a JEOL JMS-DX 302.

Plant Material. *M. eruca* Br. & R. (Cactaceae) was cultivated originally at the Research Institute of Evolutionary Biology (Setagaya-ku, Tokyo, Japan), Izu National History Park (Itoh, Shizuoka, Japan), and the Japan Cactus Planning Co. (Fukushima City, Fukushima, Japan). These cacti were identified by Drs. N. Kondo and H. Yuasa. A voucher specimen is deposited at the Research Institute of Evolutionary Biology.

Extraction and Isolation. Dry *M. eruca* was extracted with $CHCl_3$ and then repeatedly with MeOH. Extraction of the entire plant of *M. eruca* with MeOH was performed as described previously.[4] The MeOH extract (17.9 g) was hydrolyzed with 3.5% HCl at 110 °C for 2.5 h. The $CHCl_3$-soluble fraction (4.41 g) was subjected to column chromatography on Si gel ($CHCl_3$−MeOH) and purified by HPLC over Si gel (Nucleosil 50−5, 1 × 25 cm), eluted with $CHCl_3$−MeOH, resulting in the isolation of four new and four known triterpenes.

Machaeroceric acid (1): white amorphous powder (3.2 mg); mp 271−274 °C; $[\alpha]^{20}_D$ +5.98° (*c* 0.35, $CHCl_3$−MeOH 1:1); IR ν_{max} (KBr) cm^{-1} 3437, 3125, 2934, 2868 (sh), 1710, 1692, 1642, 1462, 1385, 1261, 1100, 1036, 802; EIMS *m/z* (rel int %) 474 (M^+, 47), 456 (44), 438 (35) 207 (100), 189 (92); HREIMS *m/z* 474.3714, calcd for $C_{30}H_{50}O_4$, 474.3708; ^{1}H and ^{13}C NMR, see Table 1.

21-Ketobetulinic acid (2): white amorphous powder (15 mg); mp 214−217 °C; $[\alpha]^{20}_D$ +26.2° (*c* 0.53, $CHCl_3$−MeOH 1:1); IR ν_{max} (KBr) cm^{-1} 3425, 2950, 2870 (sh), 1732, 1690, 1442, 1260, 1090, 1025, 800; EIMS *m/z* (rel int %) 470 (M^+, 100); 452 (34), 437 (23), 207 (64), 189 (97); HREIMS *m/z* 470.3393, calcd for $C_{30}H_{46}O_4$, 470.3396; ^{1}H and ^{13}C NMR, see Table 1.

16β-Hydroxybetulinic acid (3): white amorphous powder (30 mg); mp 271−274 °C; $[\alpha]^{20}_D$ −14.3° (*c* 0.34, MeOH); IR ν_{max} (KBr) cm^{-1} 3400, 2910, 1680, 1440, 1370, 1250, 1180, 1020, 880, 790; EIMS *m/z* (rel int %) 472 (M^+, 20), 454 (76), 246 (44), 207 (81), 189 (100); HREIMS *m/z* 472.3552, calcd for $C_{30}H_{48}O_4$, 472.3553; ^{1}H and ^{13}C NMR, see Table 2.

22β-Hydroxystellatogenin (4): white amorphous powder (6.3 mg), mp 296−298 °C; $[\alpha]^{20}_D$ −10.0° (*c* 0.31, MeOH); IR ν_{max} (KBr) cm^{-1} 3450, 2855, 1758, 1440, 1370, 1260, 110, 990, 800; EIMS *m/z* (rel int %) 488 (M^+, 1), 470 (100), 427 (68), 205 (34), 189 (86); HREIMS *m/z*

Table 2. ^{13}C and ^{1}H NMR Spectral Data of **3** and **4** in C_5D_5N

	3		**4**	
position	δ_C	δ_H	δ_C	δ_H
1	39.3	0.80 (m), 1.66 (m)	39.2	0.99 (m), 1.60 (m)
2	28.3	1.84 (m)	28.3	1.87 (m)
3	78.0	3.45 (br t, J = 8.1 Hz)	78.1	3.45 (br t, J = 7.9 Hz)
4	39.5		39.5	
5	55.9	0.80 (m)	55.8	0.80 (m)
6	18.7	1.36 (m), 1.54 (m)	18.7	1.40 (m)
7	34.8	1.42 (m)	34.9	1.43 (m)
8	41.2		41.4	
9	50.5	1.28 (t, J = 8.9 Hz)	50.8	1.30 (m)
10	37.5		37.5	
11	21.1	1.18 (m), 1.38 (m)	21.3	1.47 (m)
12	25.6	1.15 (m), 1.91 (m)	28.0	1.31 (m), 1.56 (m)
13	38.0	2.64 (m)	40.8	1.55 (m)
14	44.2		43.4	
15	40.1	1.80 (m), 2.21 (t, J = 12.2 Hz)	26.8	1.78 (m),[a] 2.82 (ddd, J = 13.3, 13.1, 5.2 Hz)
16	75.7	4.09 (dd, J = 11.5, 4.1 Hz)	22.3	1.20 (m),[a] 2.50 (dt, J = 13.9, 5.2 Hz)
17	61.5		56.0	
18	49.4	1.80 (m)	39.7	2.35 (dd, J = 11.9, 6.0 Hz)
19	48.1	3.52 (m)	54.2	2.00 (d, J = 6.0)
20	150.5		69.3	
21	31.4		86.3	5.14 (br s)
22	36.0	1.80 (m), 1.66 (m)	81.8	5.23 (br s)
23	28.6	1.21 (s)	28.6	1.25 (s)
24	16.3 (16.30)	1.01 (s)	16.5	1.15 (s)
25	16.4 (16.36)	0.83 (s)	16.4	0.84 (s)
26	16.4 (16.43)	1.13 (s)	16.4	1.03 (s)
27	16.2	1.12 (s)	14.2	0.95 (s)
28	177.7		179.5	
29	110.2	4.77 (s), 4.92 (s)	31.1	1.53 (s)
30	19.4	1.77 (s)	31.0	1.43 (s)

[a] Assignments may be interchanged.

488.3501; calcd for $C_{30}H_{48}O_5$, 488.3502; ^{1}H and ^{13}C NMR, see Table 2.

Morolic acid: white amorphous powder (5.3 mg); EIMS *m/z* (rel int %) 456 (M^+, 79), 410 (30), 248 (97), 236 (70), 207 (100), 189 (95); HREIMS *m/z* 456.3608, calcd for $C_{30}H_{48}O_3$, 456.3603; ^{13}C NMR (C_5D_5N) δ 39.4 (1-C), 28.3 (2-C), 78.0 (3-C), 39.5 (4-C), 56.0 (5-C), 18.7 (6-C), 34.2 (7-C), 41.0 (8-C), 51.5 (9-C), 37.5 (10-C), 21.3 (11-C), 26.5 (12-C), 41.6 (13-C), 43.0 (14-C), 30.3 (15-C), 34.3 (16-C), 48.6 (17-C), 139.0 (18-C), 132.0 (19-C), 32.4 (20-C), 34.2 (21-C), 34.2 (22-C), 28.6 (23-C), 16.3 (24-C), 16.3 (25-C), 16.9 (26-C), 15.3 (27-C), 179.1 (28-C), 30.8 (29-C), 29.4 (30-C).

Acetylation of Morolic Acid. Morolic acid (2 mg) in 0.5 mL pyridine was treated with 0.5 mL of anhydrous acetic acid. After 24 h at room temperature, the reaction mixture was applied to Si gel column chromatography to obtain the monoacetate.[8]

Queretaroic acid:[1,14,15] white amorphous powder (10 mg); mp >300 °C; IR ν_{max} (KBr) cm^{-1}: 3400, 2950, 1695, 1460, 1030; EIMS *m/z* (rel int %) 472 (M^+, 5), 264 (73), 234 (100), 207 (52), 187 (36); HREIMS *m/z* 472.3550, calcd for $C_{30}H_{48}O_4$, 472.3540; ^{13}C NMR (C_5D_5N) δ 38.9 (1-C), 28.1 (2-C), 78.0 (3-C), 39.7* (4-C), 55.8 (5-C), 18.8 (6-C), 33.2 (7-C), 37.3* (8-C), 48.1 (9-C), 37.9 (10-C), 23.8 (11-C), 122.7 (12-C), 144.7 (13-C), 42.2 (14-C), 28.3 (15-C), 24.0 (16-C), 46.6 (17-C), 41.6 (18-C), 42.0 (19-C), 35.9 (20-C), 29.6 (21-C), 32.9 (22-C), 28.4 (23-C), 16.5 (24-C), 15.3 (25-C), 17.4 (26-C), 26.2 (27-C), 180.2 (28-C), 28.8 (29-C), 65.5 (30-C), (* may be interchanged).

27-Desoxyphillyrigenin:[9] white amorphous powder (65 mg); HREIMS *m/z* 456.3610, calcd for $C_{30}H_{48}O_3$, 456.3603; ^{13}C NMR (C_5D_5N) δ 39.3 (1-C), 28.3 (2-C), 78.1 (3-C), 39.5 (4-C), 55.9 (5-C), 18.6 (6-C), 34.3 (7-C), 40.8 (8-C), 50.9 (9-C), 37.4 (10-C), 21.2 (11-C), 25.4 (12-C), 43.2 (13-C), 41.3 (14-C), 27.7 (15-C), 28.1 (16-C), 42.2 (17-C), 48.3 (18-C), 42.4 (19-C), 83.9 (20-C), 27.3 (21-C), 32.2 (22-C), 28.6 (23-C), 16.3 (24-C), 16.5 (25-C), 15.9 (26-C), 14.3 (27-C), 176.6 (28-C), 18.6 (29-C), 24.1 (30-C); ^{1}H NMR (C_5D_5N) δ 0.96 (m), 1.66 (dt, J = 12.9, 3.4 Hz) (1-CH_2), 1.86 (m) (2-CH_2), 3.45 (br t, J = 8.1 Hz) (3-CH), 0.78 (m) (5-CH), 1.35 (m), 1.52 (m) (6-CH_2), 1.34 (m) (7-CH_2), 1.31 (br s) (9-CH), 1.12 (m), 1.46 (m) (11-CH_2), 0.91 (m), 1.54 (m) (12-CH_2), 1.23 (m) (13-CH), 1.09 (m), 2.28 (dt, J = 13.1, 4.2 Hz) (15-CH_2), 1.19 (m), 2.01 (ddd, J = 13.7, 4.3, 2.5 Hz) (16-CH_2), 1.04 (m) (18-CH), 1.58 (m) (19-CH), 1.50 (m), 1.79 (m) (21-CH_2), 1.49 (m) (22-CH_2), 1.22 (s) (23-CH_3), 1.02 (s) (24-CH_3), 0.82 (s) (25-CH_3), 0.90 (s) (26-CH_3), 0.89 (s) (27-CH_3), 0.87 (d, J = 6.9 Hz) (29-CH_3), 1.26 (s) (30-CH_3).

Treleasegenic acid:[10] white amorphous powder (6 mg); IR ν_{max} (KBr) cm^{-1} 3450, 2950, 1700, 1460, 1260, 1120; EIMS *m/z* (rel int %) 488 (M^+, 1), 470 (2), 442 (39), 424 (100), 393 (21), 234 (44), 216 (52), 190 (46); HREIMS *m/z* 488.3503, calcd for $C_{30}H_{48}O_5$, 488.3502; ^{13}C NMR (C_5D_5N) δ 38.9 (1-C), 28.1 (2-C), 78.1 (3-C), 39.4 (4-C), 55.8 (5-C), 18.8 (6-C), 33.3 (7-C), 39.7 (8-C), 48.1 (9-C), 37.4 (10-C), 23.8 (11-C), 123.2 (12-C), 143.9 (13-C), 42.2 (14-C), 28.4 (15-C), 25.1 (16-C), 48.7 (17-C), 41.4 (18-C), 43.0 (19-C), 40.6 (20-C), 74.0 (21-C), 42.1 (22-C), 28.7 (23-C), 16.5 (24-C), 15.5 (25-C), 17.5 (26-C), 26.1 (27-C), 179.3 (28-C), 25.2 (29-C), 64.3 (30-C); ^{1}H NMR (C_5D_5N) δ: 0.98 (m), 1.53 (m) (1-CH_2), 1.82 (m) (2-CH_2), 3.45 (dd, J = 9.9, 6.4 Hz) (3-CH), 0.89 (m) (5-CH), 1.35 (m), 1.55 (m) (6-CH_2), 1.32 (m), 1.45 (m) (7-CH_2), 1.70 (t, J = 8.9 Hz) (9-CH), 1.85 (m), 1.92 (dd, J = 8.9, 3.1

Hz) (11-CH_2), 5.57 (t-like, $J = 3.1$ Hz) (12-CH), 1.20 (m), 2.20 (m) (15-CH_2), 2.20 (m) (16-CH_2), 3.61 (t, $J = 9.5$ Hz) (18-CH), 1.98 (t, $J = 9.5$ Hz) (19-CH_2), 4.22 (m) (21-CH), 2.46 (dd, $J = 12.3$, 4.7 Hz), 2.57 (dd, $J = 12.7$, 12.3 Hz) (22-CH_2), 1.24 (s) (23-CH_3), 1.02 (s) (24-CH_3), 0.88 (s) (25-CH_3), 1.02 (s) (26-CH_3), 1.32 (s) (27-CH_3), 1.59 (s) (29-CH_3), 4.20 (d, $J = 10.7$ Hz), 4.65 (d, $J = 10.7$ Hz) (30-CH_2).

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