Chemical Evaluation of *Betula* Species in Japan. I. Constituents of *Betula ermanii*

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The constituents of *Betula ermanii* CHAM. in Japan were identified as follows. Fresh leaves: 20(*S*),24(*R*)-epoxydammmaran-3β,11α,25-triol (1), 3-*O*-β-D-glucopyranoside of 1 (2), 2′-acetate of 2 (3), 11,2′-diacetate of 2 (4), dammar-24-en-3β,11α,20(*S*)-triol (5), 3-*O*-β-D-2-*O*-acetylglucopyranoside of 5 (6). Outer bark: betulin (7), betulin 3-caffeate (8), oleanolic acid (9). Inner bark: (+)-lyoniresinol 3α-*O*-α-L-rhamnopyranoside (10), (−)-lyoniresinol 3α-*O*-β-D-xylopyranoside (11), 9,9′-di-*O*-feruloyl-(−)-secoisolariciresinol (12), acerogenin E (13), 3,4,5-trimethoxyphenol β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside (14), 4-(4-hydroxyphenyl)-2-butanol 2-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside (15), (+)-catechine 7-*O*-β-D-xylopyranoside (16), lupeol (17), monogynol A (18). Root outer bark: lupeol caffeate (19), betulin 3-caffeate (8), oleanolic acid caffeate (20), dammarendiol II 3-caffeate (21). Compounds 2, 3, 4, 6, 19 and 21 are new.

Key words *Betula ermanii*; dammarane glucoside; lignan; triterpene; phenolics; caffeoyl ester

The genus *Betula* contains over 35 species found in temperate and boreal zones of the Northern Hemisphere. In Europe, the so-called "white birch," *B. alba* and *B. pendula*, has been used in traditional medicines and as cosmetic ingredients.[1] In North America, birch oil which is obtained from "black birch," *B. lenta*, has been used as an antiinflammatory and antirheumatic agent. On the other hand, *Betula* species in Japan have not been widely used except as pulpwood or material for furniture.

In general, the outer bark of the white birch contains a considerable amount of a lupane-type triterpene, betulin, is a promising starting material for medicines,[2,3] and the leaves contain dammarane-type triterpenes.[4-6] The structures of such dammaranes as betulafolienetriol and betulafolienetriol oxide I resemble those of the sapogenins of ginseng saponin such as ginsenosides and pseudo-ginsenosides.[7]

We because interested in their pharmacological properties and started our study of the use of *Betula* species as medicinal agents. In this paper, we describe the detailed chemistry of *B. ermanii* CHAM.

Constituents of Fresh Leaves From the MeOH extract of fresh leaves collected in June, dammarane-type triterpenes and their glucosides, **1**—**6**, were isolated. Compound **1**, a colorless amorphous powder, $[\alpha]_D$ +22° (c=1.0, MeOH), was given the formula $C_{30}H_{52}O_4$ from the high resolution MS (HR-FAB-MS). The ^{1}H- and ^{13}C-NMR spectra revealed the presence of eight tertiary methyl groups and three secondary and one tertiary oxygenated carbon. The base peak at m/z 143 in electron impact MS (EI-MS) indicated the presence of an ocotillol-type side-chain in the molecule.[4] These results suggested that the structure of **1** is 20(*S*),24(*R*)-epoxydammaran-3β,11α,25-triol which has already been isolated from the same species in Siberia.[8] The ^{13}C-NMR data for **1** in $CDCl_3$ (see Experimental) were identical with those reported, and the ^{1}H–^{1}H, ^{13}C–^{1}H and long range ^{13}C–^{1}H shift correlation spectroscopy (COSY) and nuclear Overhauser effect correlation spectroscopy (NOESY) also confirmed the structure of **1** (Fig. 1).

Compound **2**, a colorless amorphous powder, $[\alpha]_D$ +14° (c=0.5, MeOH), was given the formula $C_{36}H_{62}O_9$ from the HR-FAB-MS. The ^{13}C-NMR data for **2** were in good agreement with those of **1** except for the presence of the additional signals of a hexosyl group and differences in the chemical shifts around C-3, $\Delta_{\delta 2-\delta 1}$: +10.8 for C-3, −1.6 for C-2 (Table 1). On enzymatic hydrolysis with a glycosydase mixture of turbo, **2** gave **1** and D-glucose. Considering the glycosylation shift rule,[9] the structure of **2** was assigned as the 3-*O*-β-D-glucopyranoside of **1**.

Compound **3**, a colorless amorphous powder, $[\alpha]_D$ +21° (c=1.0, MeOH), was given the formula $C_{38}H_{64}O_{10}$ from the HR-FAB-MS. The ^{13}C-NMR data (Table 1) were in good agreement with those of **2** except for the presence of signals of an additional acetyl group and the differences in the chemical shifts around C-2 of the glucosyl group, $\Delta_{\delta 3-\delta 2}$: −3.0 for G-1, +0.4 for G-2, −3.0 for G-3. These

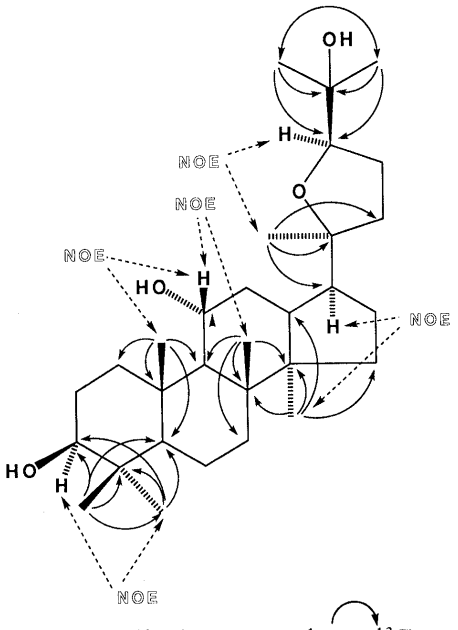

Fig. 1. Long Range ^{13}C–^{1}H COSY (^{1}H ⌒ ^{13}C) and NOESY (←----→) Connections for **1**

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indicated that **3** is a 2′-acetyl derivative of **2**.[10] On alkaline methanolysis with NaOMe in MeOH, **3** gave **2**. Thus, the structure of **3** was determined to be the 2′-*O*-acetyl derivative of **2**.

Compound **4**, a colorless amorphous powder, $[\alpha]_D$ +25° (c=1.0, MeOH), was given the formula $C_{40}H_{66}O_{11}$ from the HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectra showed the presence of one more acetyl group than **3**. Considering the differences in the chemical shifts between **3** and **4**, $\Delta_{\delta 4-\delta 3}$: −2.9 for C-9, +2.7 for C-11, −4.3 for C-12, and the fact that **4** gave **2** on alkaline methanolysis, the structure of **4** was determined as the 12-*O*-acetyl derivative of **3**.

Table 1. ^{13}C-NMR Data in C_5D_5N

C	1	2	3	4	5	6	6a
1	41.8	41.6	41.4	40.5	41.7	41.4	41.6
2	28.8	27.2	26.9	26.8	28.7	26.9	27.2
3	78.0	88.8	89.0	88.6	78.0	89.0	88.8
4	40.3	40.3	40.0	39.9	40.3	40.0	40.3
5	56.9	56.9	56.8	56.1	56.9	56.8	57.0
6	18.7	18.4	18.4	18.3	18.7	18.4	18.4
7	36.7	36.5	36.5	36.1	36.6	36.6	36.6
8	41.0	40.9	40.9	41.3	41.1	41.0	41.0
9	56.2	56.0	56.0	53.1	56.1	56.0	56.0
10	39.7	39.3	38.2	38.8	39.6	39.2	39.2
11	70.4	70.3	70.3	73.0	70.5	70.4	70.4
12	40.1	40.0	40.0	35.7	40.8	40.7	40.7
13	41.8	41.8	41.8	40.9	41.1	41.1	41.1
14	50.2	50.2	50.2	50.0	50.6	50.6	50.6
15	31.5	31.4	31.4	31.4	31.3	31.3	31.3
16	26.1	26.0	26.1	26.6	25.5	25.5	25.5
17	50.1	50.1	50.1	49.8	50.3	50.3	50.3
18	17.0	17.0	16.9	16.8	17.0	17.0	17.0
19	17.1	17.0	16.9	17.0	17.0	16.9	17.0
20	86.0	86.0	86.0	85.9	73.9	73.9	73.9
21	23.0	23.0	23.0	23.5	25.8	25.8	25.8
22	36.5	36.5	36.5	36.1	41.8	41.8	41.8
23	26.8	26.8	26.8	26.8	23.3	23.3	23.3
24	84.2	84.2	84.2	84.2	126.0	126.0	126.0
25	71.1	71.1	71.1	71.2	130.7	130.7	130.7
26	26.1	26.1	26.1	26.1	26.1	26.1	26.1
27	27.0	27.0	27.0	27.1	17.7	17.7	17.7
28	29.0	28.4	28.1	28.1	29.0	28.2	28.4
29	16.6	16.9	16.8	16.6	16.6	16.7	16.7
30	16.5	16.5	16.5	16.3	16.8	16.8	16.9
G-1		106.9	103.9	103.9		103.9	106.8
G-2		75.8	76.2	76.2		76.2	75.8
G-3		78.8	75.8	75.8		75.8	78.7
G-4		71.8	71.8	71.8		71.8	71.8
G-5		78.2	78.4	78.5		78.4	78.2
G-6		62.9	62.6	62.6		62.6	62.9
Ac			170.0	170.0		169.9	
			21.3	169.9		21.3	
				21.9			
				21.2			

Compound **5**, a crystalline powder, mp 157—159 °C, $[\alpha]_D$ +23.0° (c=1.0, $CHCl_3$), was given the formula $C_{30}H_{52}O_3$ from the HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectra showed the presence of two secondary and one tertiary hydroxyl group, an isopropylidene-type side-chain and six more methyl groups. From these results, the structure of **5** was assigned as dammar-24-en-3β,11α,20(*S*)-triol which has already been isolated from the same species in Siberia. The ^{13}C-NMR data of its diacetate, **5a**, were the same as those previously reported.[11]

Compound **6**, a colorless amorphous powder, $[\alpha]_D$ +20° (c=1.0, MeOH), was given the formula $C_{38}H_{64}O_9$ from HR-FAB-MS. The ^{1}H- and ^{13}C-NMR data showed the presence a dammar-24-en-3β,11α,20(*S*)-triol moiety and an acetylated hexosyl moiety in the molecule (Table I). The data of the latter resemble those of the sugar moiety of **3**. On alkaline methanolysis with NaOMe in MeOH, **6** gave a deacety compound, **6a**, a colorless amorphous powder, $[\alpha]_D$ +15° (c=1.0, MeOH) which was then hydrolyzed with a glycosydase mixture of turbo to obtain **5** and D-glucose. Considering the glucosylation shifts observed between **6a** and **5**, $\Delta_{\delta 6a-\delta 5}$: +10.8 for C-3, −1.5 for C-2, and acetylation shifts between **6** and **6a**, $\Delta_{\delta 6-\delta 6a}$: −2.9 for G-1, +0.4 for G-2, −2.9 for G-3, the positions of the glucosylation and acetylation were deduced as the C-3 of the aglycone and the C-2 of the glucosyl, respectively. Thus, the structure of **6** was determined as dammar-24-en-3β,11α,20(*S*)-triol 3-*O*-β-D-2-*O*-acetylglucopyranoside. Compounds **2**, **3**, **4** and **6** are new and the first examples of dammarane-type glycosides isolated from the leaves of *Betula* species.

Constituents of Outer Bark From the air-dried outer bark collected in June, betulin (**7**), betulin 3-caffeate (**8**) and oleanolic acid (**9**) were isolated. Their structures were identified by comparison of their physical properties and spectral data with those previously reported (see Experi-

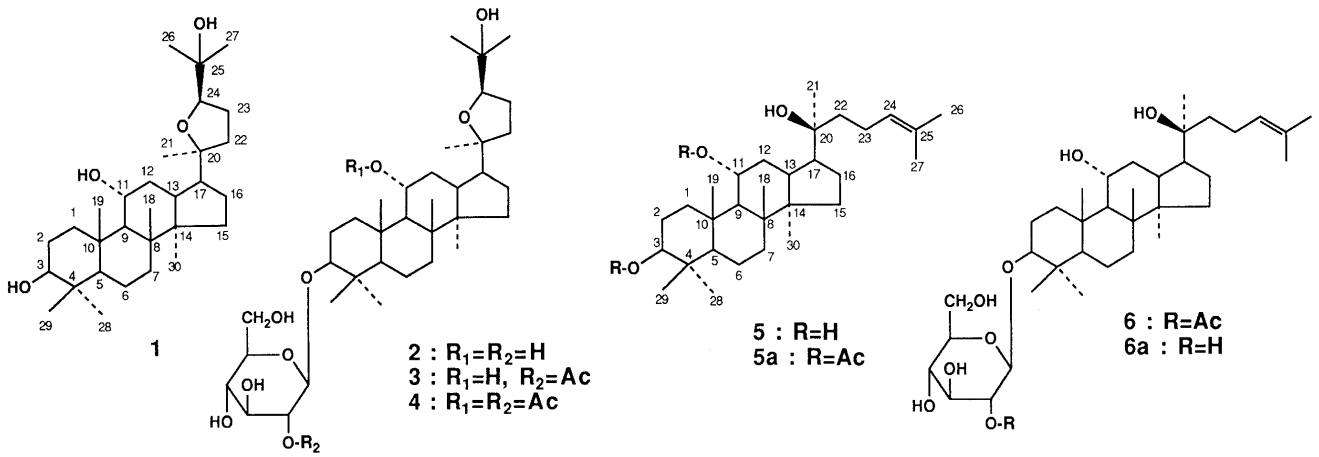
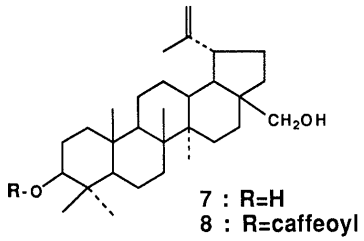


Chart 1. Constituents of Leaves

mental). The content of betulin is below 5%, while that of *B. platyphylla* Sukat. var. *japonica* is about 10%.[12] The difference seems to affect the degree of whiteness of both barks.

Constituents of Inner Bark From the air-dried inner bark collected in June, (+)-lyoniresinol 3α-*O*-α-L-rhamnopyranoside (**10**), (−)-lyoniresinol 3α-*O*-β-D-xylopyranoside (**11**) and 9,9′-di-*O*-feruloyl-(−)-secoisolariciresinol (**12**), acerogenin E (**13**), 3,4,5-trimethoxyphenol β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside (**14**), 4-(4-hydroxyphenyl)-2-butanol 2-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside (**15**), (+)-catechine 7-*O*-β-D-xylopyranoside (**16**), lupeol (**17**) and monogynol A (**18**) were isolated. Their structures were identified by comparison of the in physical properties and spectral data with those previously reported (see Experimental). It is noteworthy that both enantiomers of lyoniresinol form glycosides, **10** and **11**, with different sugars.

Constituents of Root Bark From the air-dried root bark collected in June, four triterpene caffeates, lupeol caffeate (**19**), betulin 3-caffeate (**8**), oleanolic acid caffeate (**20**) and dammarendiol II 3-caffeate (**21**), were isolated. The structures for compound **8** and **20** were determined by comparison of their physical properties and spectral data with those previously reported.[13,14] Compound **19** and **21** have not been previously reported. On alkaline methanolysis, they gave methyl caffeate and corresponding triterpenes (see Experimental). These caffeates were identified as the main components of the outer root bark by TLC. In the inner root bark, no important constituents were identified except for much polar substances which were left untouched.



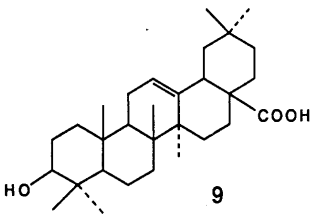
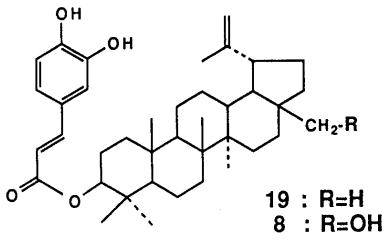
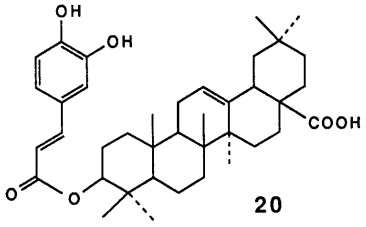


Chart 2. Constituents of Outer Bark





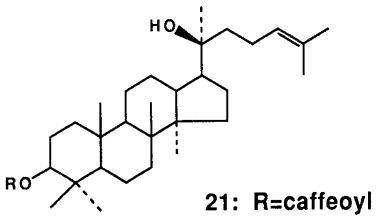
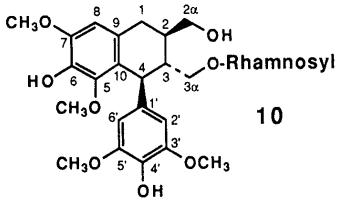
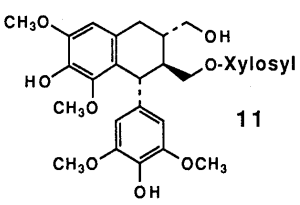
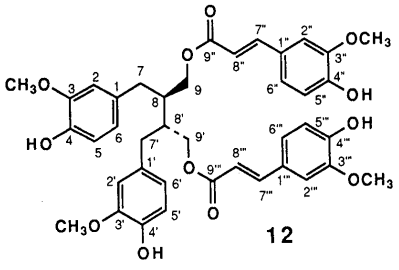
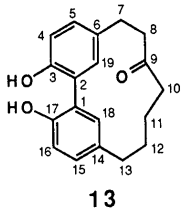


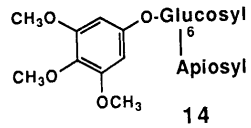
Chart 4. Constituents of Root Bark

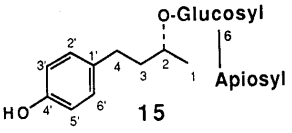


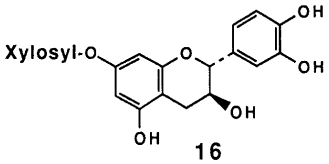












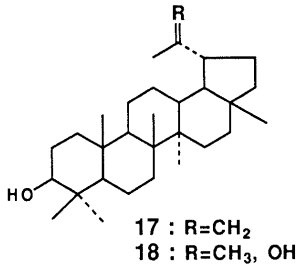


Chart 3. Constituents of Inner Bark

Experimental

Melting points were determined with a Yanagimoto micromelting-point apparatus and are uncorrected. Optical rotations were recorded on a JASCO DIP-360 automatic polarimeter. The ^{13}C-NMR spectra were measured with a JEOL GSX-500 spectrometer. The ^{1}H-NMR spectra were measured using a JEOL GSX-500 (500 MHz) and an FX-100 (100 MHz) spectrometer (multiplicity, s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, NC: coupling patterns were not confirmed because of overlapping signals). UV spectra were recorded on a Hitachi 323 spectrometer and IR spectra on a Shimadzu IR-460 spectrometer. Mass spectra were measured with a JEOL SX-102 spectrometer (FAB-MS) or a Hitachi M-80A spectrometer (EI-MS). Gas-liquid chromatography (GLC) and HPLC were run on a Shimadzu GC-8A apparatus using an HR-1701 capillary column (0.3 mm i.d. × 30 m) and a Shimadzu LC-9A apparatus with a UV detector (Shimadzu SPD-6AV), respectively.

Isolation Materials of *B. ermanii* were collected in Kuzumaki, Iwate Prefecture, in June.

Fresh Leaves: Fresh leaves (2 kg) were extracted with 30 l MeOH at room temperature for 2 weeks. The extract and 10 l MeOH were passed over a column of activated charcoal (130 g). The resulting solution was concentrated to a syrup under reduced pressure. The syrup was chromatographed on silica-gel using $CHCl_3$ and MeOH. The fractions containing **1** and **5** was rechromatographed on silica-gel using *n*-hexane and EtOAc to obtain **1** (25 mg) and **5** (23 mg). The fractions containing **4** were rechromatographed on Sephadex LH-20 using 90% MeOH to obtain **4** (56 mg). The fractions containing **2**, **3** and **6** were rechromatographed on Chromatorex ODS (Fuji Silysia Chemical Ltd.) using 90% MeOH and on silica-gel using $CHCl_3$ and MeOH to obtain **2** (30 mg), **3** (36 mg) and **6** (38 mg).

Outer Bark: Air-dried outer bark (330 g) was extracted with 1 l of $CHCl_3$ under reflux for 6 h. The extract was concentrated to a syrup and chromatographed on silica-gel using $CHCl_3$ and EtOAc, and then *n*-hexane and EtOAc to obtain **7** (11.6 g), **8** (98 mg) and **9** (230 mg).

Inner Bark: Air-dried inner bark (700 g) was extracted with 5 l MeOH under reflux for 6 h. The extract was concentrated and partitioned between water (2 l) and ether (2 l). The water layer was concentrated and chromatographed on silica-gel using $CHCl_3$ and MeOH. The fractions containing **10** and **11** were rechromatographed on Sephadex LH-20 using 50% MeOH and subjected to HPLC (Shim-pack octadecyl silica (ODS) with 50% MeOH and Carbon 500 with 80% MeCN) to obtain **10** (34 mg) and **11** (31 mg). The fractions containing **14**, **15** and **16** were rechromatographed on Sephadex LH-20 or Chromatorex ODS using 80% MeOH and subjected to HPLC (Shim-pack ODS with 40—80% MeOH) to obtain **14** (136 mg), **15** (164 mg) and **16** (509 mg). The ether layer was concentrated and chromatographed on silica-gel using *n*-hexane and EtOAc, and then, on Lichroprep Si-60 (E. Merck) using benzene–EtOAc or on Chromatorex ODS using 80% MeOH to obtain **12** (17 mg), **13** (15 mg), **17** (98 mg) and **18** (78 mg).

Root Bark: Air-dried root bark (660 g) was extracted with 5 l MeOH under reflux for 6 h. The extract was concentrated and partitioned between $CHCl_3$ (1 l), MeOH (1 l) and water (0.75 l). The lower layer was chromatographed on silica-gel using $CHCl_3$ and MeOH, and on Sephadex LH-20 using MeOH or benzene–MeOH to obtain **8** (245 mg), **19** (48 mg), **20** (180 mg) and **21** (101 mg).

Compound 1 (20(S),24(*R*)-Epoxydammaran-3β,11α,25-triol) A colorless amorphous powder, $[\alpha]_D$ +22° (c=1.0, MeOH). ^{1}H-NMR (C_5D_5N) δ: 0.98 (3H, s), 1.07 (3H, s), 1.14 (3H, s), 1.21 (3H, s), 1.28 (3H, s), 1.30 (3H, s), 1.39 (3H, s), 1.41 (3H, s), 3.55 (1H, d, J=10.4 Hz), 3.98 (1H, t, J=7.3 Hz), 4.26 (1H, m). ^{13}C-NMR ($CDCl_3$) δ: 40.9 (C-1), 27.5 (C-2), 78.4 (C-3), 39.0 (C-4), 55.7 (C-5), 18.1 (C-6), 36.2 (C-7), 40.7 (C-8), 56.0 (C-9), 39.4 (C-10), 71.1 (C-11), 39.7 (C-12), 41.3 (C-13), 49.8 (C-14), 31.0 (C-15), 25.6 (C-16), 49.3 (C-17), 16.7 (C-18), 16.6 (C-19), 85.9 (C-20), 23.2 (C-21), 36.0 (C-22), 26.2 (C-23), 83.3 (C-24), 71.4 (C-25), 24.2 (C-26), 27.4 (C-27), 28.2 (C-28), 15.4 (C-29), 16.3 (C-30). HR-EI-MS m/z: 461.363 $[M-CH_3]^+$, Calcd for $C_{29}H_{49}O_4$: 460.763. The ^{13}C-NMR data were identical with those reported.[8]

Compound 2 (20(*S*),24(*R*)-Epoxydammaran-3β,11α,25-triol 3-*O*-β-D-Glucopyranoside) A colorless amorphous powder, $[\alpha]_D$ +14° (c=0.5, MeOH). ^{1}H-NMR (C_5D_5N) δ: 1.00 (3H, s), 1.03 (3H, s), 1.10 (3H, s), 1.19 (3H, s), 1.20 (3H, s), 1.37 (3H, s), 1.39 (3H, s), 1.41 (3H, s), 3.98 (1H, t, J=8.2 Hz), 4.97 (1H, d, J=7.6 Hz). HR-FAB-MS (negative mode) m/z: 637.433 $[M-H]^-$, Calcd for $C_{36}H_{61}O_9$: 636.533.

Enzymatic Hydrolysis of 2 A solution of **2** (28 mg) and a glycosidase mixture of turbo (100 mg, Seikagaku Kogyo Co., Ltd.) in 0.05 M citrate buffer (pH 4.0, 20 ml) was stirred at 40 °C for 17 h. The reaction mixture was extracted with ether (100 ml). The ether solution was washed with water, dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica-gel using $CHCl_3$ and ether to obtain **1** (11 mg). The buffer solution was neutralized with 5% Na_2CO_3 solution and evaporated. The residue was chromatographed on silica-gel using 20% MeOH in $CHCl_3$ to obtain D-glucose (2.4 mg), $[\alpha]_D$ +40° (c=0.1, MeOH). Its trimethylsilyl ether was identified by comparison with an authentic sample on GLC.

Compound 3 (20(*S*),24(*R*)-Epoxydammaran-3β,11α,25-triol 3-*O*-β-D-2-*O*-Acetylglucopyranoside) A colorless amorphous powder, $[\alpha]_D$ +21° (c=1.0, MeOH). ^{1}H-NMR (C_5D_5N) δ: 1.00 (6H, s), 1.02 (3H, s), 1.13 (3H, s), 1.15 (3H, s), 1.20 (3H, s), 1.38 (3H, s), 1.40 (3H, s), 2.15 (3H, s), 3.33 (1H, dd, J=12.5, 3.8 Hz), 4.92 (1H, d, J=8.2 Hz). HR-FAB-MS (negative mode) m/z: 679.441 $[M-H]^-$, Calcd for $C_{38}H_{63}O_{10}$: 681.041.

Alkaline Methanolysis of 3 A mixture of **3** (30 mg) and 3% NaOMe in MeOH (10 ml) was refluxed for 1 h. The mixture was diluted with water (100 ml) and extracted with *n*-BuOH (100 ml). The *n*-BuOH solution was washed with water, evaporated and the residue was chromatographed on silica-gel using 10% MeOH in $CHCl_3$ to obtain **2** (20 mg).

Compound 4 (11α-Acetoxy-20(*S*),24(*R*)-Epoxydammaran-3β,25-diol 3-*O*-β-D-2-*O*-Acetylglucopyranoside) A colorless amorphous powder, $[\alpha]_D$ +25° (c=1.0, MeOH). ^{1}H-NMR (C_5D_5N) δ: 0.94 (6H, s), 0.95 (6H, s), 0.96 (3H, s), 1.15 (3H, s), 1.17 (3H, s), 1.40 (3H, s), 1.44 (3H, s), 1.92 (3H, s), 2.16 (3H, s), 3.32 (1H, dd, J=11.9, 4.6 Hz), 3.96 (1H, t, J=7.0 Hz), 5.00 (1H, d, J=7.9 Hz). HR-FAB-MS (negative mode) m/z: 721.452 $[M-H]^-$, Calcd for $C_{40}H_{65}O_{11}$: 721.852.

Alkaline Methanolysis of 4 Compound **4** (40 mg) was subjected to alkaline methanolysis in the same manner as **3** to obtain **2** (28 mg).

Compound 5 (Dammar-24-en-3β,11α,20(*S*)-triol) A crystalline powder from MeOH, mp 157—159 °C, $[\alpha]_D$ +23° (c=1.0, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.07 (3H, s), 1.08 (3H, s), 1.26 (3H, s), 1.29 (3H, s), 1.43 (3H, s), 1.63 (3H, s), 1.68 (3H, s), 3.54 (1H, dd, J=11.2, 4.6 Hz), 4.27 (1H, m), 5.29 (1H, t, J=6.9 Hz). IR ν_{max}^{KBr} nm: 3395, 2965, 1450, 1374, 1110, 1036, 1007. HR-FAB-MS (negative mode) m/z: 459.383 $[M-H]^-$, Calcd for $C_{30}H_{51}O_3$: 460.183.

Acetylation of 5 A mixture of **5** (8 mg), pyridine (2 ml) and Ac_2O (2 ml) was allowed to stand at room temperature overnight. The reaction mixture was poured into ice-water and extracted with ether. The extract was washed with 5% HCl solution, 5% Na_2CO_3 solution and water, then dried over anhydrous Na_2SO_4 and concentrated to yield **5a** (7.5 mg).

Compound 5a (3β,11α-Diacetoxydammar-24-en-20(*S*)-ol) A colorless amorphous powder, $[\alpha]_D$ +14° (c=0.5, $CHCl_3$). ^{13}C-NMR ($CDCl_3$) δ: 39.8 (C-1), 23.8 (C-2), 80.3 (C-3), 38.2 (C-4), 55.7 (C-5), 18.0 (C-6), 35.5 (C-7), 40.8 (C-8), 52.6 (C-9), 38.6 (C-10), 72.5 (C-11), 34.7 (C-12), 39.8 (C-13), 50.0 (C-14), 30.6 (C-15), 24.9 (C-16), 49.8 (C-17), 16.9 (C-18), 16.0 (C-19), 75.0 (C-20), 25.6 (C-21), 40.2 (C-22), 22.6 (C-23), 124.5 (C-24), 131.7 (C-25), 25.7 (C-26), 17.7 (C-27), 28.1 (C-28), 16.4 (C-29), 16.8 (C-30). The ^{13}C-NMR data were identical with those previously reported.[11]

Compound 6 (Dammar-24-en-3β,11α,20(*S*)-triol 3-*O*-β-D-2-*O*-Acetylglucopyranoside) A colorless amorphous powder, $[\alpha]_D$ +20° (c=1.0, MeOH). ^{1}H-NMR (C_5D_5N) δ: 1.01 (3H, s), 1.02 (3H, s), 1.10 (3H, s), 1.13 (3H, s), 1.15 (3H, s), 1.43 (3H, s), 1.63 (3H, s), 1.68 (3H, s), 2.16 (3H, s), 5.29 (1H, t, J=7.0 Hz). HR-FAB-MS (negative mode) m/z: 663.448 $[M-H]^-$, Calcd for $C_{38}H_{63}O_9$: 662.948.

Alkaline Methanolysis of 6 Compound **6** (61 mg) was subjected an alkaline methanolysis in the same manner as **3** to yield **6a** (55 mg).

Compound 6a (Dammar-24-en-3β,11α,20(*S*)-triol 3-*O*-β-D-Glucopyranoside) A colorless amorphous powder, $[\alpha]_D$ +15° (c=1.0, MeOH). ^{1}H-NMR (C_5D_5N) δ: 1.02 (3H, s), 1.09 (6H, br s), 1.17 (3H, s), 1.36 (3H, s), 1.42 (3H, s), 1.63 (3H, s), 1.67 (3H, s), 2.66 (1H, m), 3.23 (1H, br d, J=13.9 Hz), 3.48 (1H, dd, J=11.2, 4.6 Hz), 4.93 (1H, d, J=8.6 Hz), 5.28 (1H, t, J=6.9 Hz).

Enzymatic Hydrolysis of 6a Compound **6a** (55 mg) was hydrolyzed in the same manner as **2** to yield **5** (33 mg) and D-glucose (1.4 mg), $[\alpha]_D$ +40° (c=0.1, MeOH).

Compound 7 (Betulin) Colorless needles from EtOH, mp 248—250 °C, $[\alpha]_D$ +20° (c=0.5, Pyridine). ^{13}C-NMR ($CDCl_3$) δ: 38.7 (C-1), 27.3 (C-2), 78.9 (C-3), 38.8 (C-4), 55.2 (C-5), 18.2 (C-6), 34.2 (C-7), 40.9 (C-8), 50.4 (C-9), 37.1 (C-10), 20.8 (C-11), 25.2 (C-12), 37.3 (C-13), 42.7 (C-14), 27.0 (C-15), 29.1 (C-16), 47.8 (C-17), 48.7 (C-18), 47.8 (C-19), 150.5 (C-20), 29.7 (C-21), 33.9 (C-22), 28.0 (C-23), 15.3 (C-24), 16.1 (C-25), 16.0 (C-26), 14.7 (C-27), 60.4 (C-28), 109.7 (C-29), 19.1 (C-30). It was identical with an authentic sample following direct comparison.

Compound 8 (Betulin 3-Caffeate) A pale yellow amorphous powder, $[\alpha]_D$ +38° (c=1.8, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.33), 244 (4.12), 299 (4.20), 327 (4.28). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (6H, s), 0.90 (3H, s), 0.98 (3H, s), 1.01 (3H, s), 1.69 (3H, s), 3.83 (1H, d, J=10.6 Hz), 4.59 (1H, t, J=7.6 Hz), 6.24 (1H, d, J=16.2 Hz), 6.86 (1H, d, J=8.3 Hz), 6.97 (1H, d, J=8.3 Hz), 7.09 (1H, s), 7.56 (1H, d, J=16.2 Hz). ^{13}C-NMR ($CDCl_3$) δ: 38.4 (C-1), 23.8 (C-2), 81.3 (C-3), 38.1 (C-4), 55.4 (C-5), 18.2 (C-6), 34.1 (C-7), 40.9 (C-8), 50.3 (C-9), 37.1 (C-10), 20.8 (C-11), 25.1 (C-12), 37.3 (C-13), 42.7 (C-14), 27.0 (C-15), 29.2 (C-16), 48.2 (C-17), 48.8 (C-18), 47.7 (C-19), 150.4 (C-20), 29.7 (C-21), 34.0 (C-22), 28.0 (C-23), 16.7 (C-24), 16.2 (C-25), 16.0 (C-26), 14.8 (C-27), 60.6 (C-28), 109.8 (C-29), 19.1 (C-30), 127.3 (C-1′), 115.3 (C-2′), 144.2 (C-3′), 146.8 (C-4′), 114.2 (C-5′), 122.3 (C-6′), 144.9 (C-7′), 115.8 (C-8′), 168.0 (C-9′). The ^{13}C-NMR data were identical with those previously reported.[13] EI-MS m/z: 604 (M^+), 588, 424, 393, 299, 248, 191, 163, 69. On alkaline methanolysis with 5% NaOMe, **8** gave betulin (**7**) and methyl caffeate.

Compound 9 (Oleanolic Acid) Colorless needles from MeOH, mp >300 °C, $[\alpha]_D$ +80° (c=0.5, $CHCl_3$). ^{13}C-NMR (C_5D_5N) δ: 39.0 (C-1), 28.1 (C-2), 78.1 (C-3), 39.4 (C-4), 55.8 (C-5), 18.8 (C-6), 33.2 (C-7), 39.7 (C-8), 48.1 (C-9), 37.4 (C-10), 23.8 (C-11), 122.5 (C-12), 144.8 (C-13), 42.2 (C-14), 28.3 (C-15), 23.7 (C-16), 46.6 (C-17), 42.0 (C-18), 46.5 (C-19), 31.0 (C-20), 34.2 (C-21), 33.3 (C-22), 28.8 (C-23), 16.5 (C-24), 15.6 (C-25), 17.4 (C-26), 26.2 (C-27), 180.1 (C-28), 33.3 (C-29), 23.8 (C-30). It was identical with an authentic sample following direct comparison.

Compound 10 ((+)-Lyoniresinol 3α-*O*-α-L-Rhamnopyranoside) A colorless amorphous powder, $[\alpha]_D$ +13° (c=1.0, EtOH). UV λ_{max}^{EtOH} nm (log ε): 278 (3.67). ^{1}H-NMR (C_5D_5N) δ: 1.64 (3H, d, J=6.1 Hz), 2.08 (1H, m), 2.75 (1H, m), 3.12 (1H, dd, J=14.7, 4.3 Hz), 3.20 (1H, dd, J=14.7, 11.6 Hz), 3.67 (6H, s), 3.79 (6H, s), 3.83 (1H, dd, J=9.5, 3.7 Hz), 4.06 (1H, dd, J=10.7, 6.4 Hz), 4.12 (1H, dd, J=10.7, 4.0 Hz), 4.20 (1H, dd, J=9.5, 6.4 Hz), 4.30 (1H, t, J=9.2 Hz), 4.38 (1H, dq, J=9.2, 6.1 Hz), 4.60 (1H, dd, J=9.2, 3.4 Hz), 4.68 (1H, d, J=3.4 Hz), 5.03 (1H, d, J=5.2 Hz), 5.45 (1H, s), 6.80 (1H, s), 6.91 (2H, s). ^{13}C-NMR (C_5D_5N) δ: 33.6 (C-1), 41.3 (C-2), 65.6 (C-2a), 46.0 (C-3), 69.7 (C-3a), 42.4 (C-4), 147.9 (C-5), 139.4 (C-6), 148.4 (C-7), 107.5 (C-8), 129.7 (C-9), 126.1 (C-10), 138.6 (C-1′), 107.1 (C-2′), 149.0 (C-3′), 135.7 (C-4′), 149.0 (C-5′), 107.1 (C-6′), 102.1 (Rha-1), 72.5 (Rha-2), 73.1 (Rha-3), 74.1 (Rha-4), 70.2 (Rha-5), 18.6 (Rha-6), 59.8 (5-OCH_3), 56.1 (7-OCH_3), 56.5 (3′-OCH_3), 56.5 (5′-OCH_3). IR ν_{max}^{KBr} cm^{-1}: 3410, 2920, 1608, 1505, 1495, 1450, 1312, 1220, 1110, 1050, 750. EI-MS m/z: 566 (M^+), 420, 419, 401, 371, 249, 217, 183, 167. HR-EI-MS m/z: 566.236 (M^+), Calcd for $C_{28}H_{38}O_{12}$: 566.236. CD (c=0.01, MeOH) $[\theta]_{286}$ −2841°, $[\theta]_{271}$ +8870°, $[\theta]_{242}$ +36000°. The physical properties and spectral data were identical with those reported.[15] On acid hydrolysis with 3% HCl, **10** gave (+)-lyoniresinol and L-rhamnose, $[\alpha]_D$ +3.2° (c=0.3, H_2O). (+)-Lyoniresinol[16]: a colorless amorphous powder, $[\alpha]_D$ +31.9° (c=0.4, MeOH). ^{1}H-NMR (C_5D_5N) δ: 6.94 (2H, s), 6.79 (1H, s), 5.07 (1H, d, J=5.9 Hz), 4.05—4.21 (4H, NC), 3.78 (3H, s), 3.76 (3H, s), 3.65 (6H, s), 3.05—3.16 (2H, NC), 2.67 (1H,m), 2.23 (1H, m). ^{13}C-NMR (C_5D_5N) δ: 149.0 (C-3′ and C-5′), 148.3 (C-5), 148.0 (C-7), 139.5 (C-6), 139.0 (C-1′), 135.9 (C-4′), 129.6 (C-9), 126.7 (C-10), 107.4 (C-8), 107.3 (C-2′ and C-6′), 66.4 (C-2α), 64.1 (C-3α), 59.7 (5-OMe), 56.4 (3′-OMe and 5′-OMe), 56.1 (7-OMe), 49.4 (C-3), 42.4 (C-4), 41.7 (C-2), 33.9 (C-1).

Compound 11 ((−)-Lyoniresinol 3α-*O*-β-D-Xylopyranoside (=nudiposide)) A colorless amorphous powder, $[\alpha]_D$ −56° (c=1.0, EtOH). UV λ_{max}^{EtOH} nm (log ε): 277 (3.67). ^{1}H-NMR (C_5D_5N) δ: 2.20 (1H, m), 2.73 (1H, m), 3.03 (1H, dd, J=15.0, 4.3 Hz), 3.21 (1H, dd, J=15.0, 11.6 Hz), 3.68 (6H, s), 3.77 (6H, s), 3.62—3.63 (1H, NC), 4.03—4.08 (3H, NC), 4.08—4.18 (2H, NC), 4.25 (1H, m), 4.36 (1H, dd, J=11.3, 5.5 Hz), 4.40 (1H, dd, J=9.8, 4.3 Hz), 4.75 (1H, d, J=7.6 Hz), 5.01 (1H, d, J=6.4 Hz), 6.74 (1H, s), 6.97 (2H, s). ^{13}C-NMR (C_5D_5N) δ: 33.8 (C-1), 40.8 (C-2), 65.6 (C-2a), 46.2 (C-3), 70.9 (C-3a), 42.6 (C-4), 148.0 (C-5), 139.4 (C-6), 148.3 (C-7), 107.5 (C-8), 129.5 (C-9), 126.4 (C-10), 138.7 (C-1′), 107.4 (C-2′), 148.9 (C-3′), 135.7 (C-4′), 148.9 (C-5′), 107.4 (C-6′), 105.4 (Xyl-1), 74.9 (Xyl-2), 78.5 (Xyl-3), 71.2 (Xyl-4), 67.3 (Xyl-5), 59.7 (5-OCH_3), 56.2 (7-OCH_3), 56.5 (3′-OCH_3), 56.5 (5′-OCH_3). IR ν_{max}^{KBr} cm^{-1}: 3400, 2920, 1605, 1492, 1450, 1312, 1210, 1110, 1040, 750. EI-MS m/z: 552 (M^+), 431, 420, 419, 401, 371, 249, 217, 183, 167. HR-EI-MS m/z: 552.220 (M^+), Calcd for $C_{27}H_{36}O_{12}$: 552.220. CD (c=0.01, MeOH): $[\theta]_{285}$ +5060°, $[\theta]_{270}$ −18300°, $[\theta]_{242}$ −49800°. The physical properties and spectral data were identical with those previously reported.[17] On acid hydrolysis with 3% HCl, **10** gave (−)-lyoniresinol and D-xylose, $[\alpha]_D$ +4.2° (c=0.2, H_2O). (−)-Lyoniresinol: a colorless amorphous powder, $[\alpha]_D$ −37.3° (c=0.3, MeOH).

Compound 12 (9,9′-*O*-Diferuloyl-(−)-secoisolariciresinol) A pale yellow amorphous powder, $[\alpha]_D$ −41.2° (c=0.68, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.53), 230 (4.46), 289 (4.33), 300 (4.31), 326 (4.44). ^{1}H-NMR ($CDCl_3$) δ: 2.22 (2H, m), 2.70 (2H, dd, J=14.1, 7.5 Hz), 2.75 (2H, dd, J=14.1, 7.5 Hz), 3.77, 3.92 (each 6H, s), 4.22 (2H, dd, J=11.4, 5.5 Hz), 4.39 (2H, dd, J=11.4, 5.7 Hz), 6.28 (2H, d, J=15.9 Hz), 6.53 (2H, d, J=1.8 Hz), 6.61 (2H, dd, J=8.1, 1.8 Hz), 6.81 (2H, d, J=8.1 Hz), 6.91 (2H, d, J=8.2 Hz), 7.01 (2H, d, J=1.8 Hz), 7.06 (2H, dd, J=8.2, 1.8 Hz), 7.59 (2H, d, J=15.9 Hz). ^{13}C-NMR ($CDCl_3$) δ: 131.7 (C-1, 1′), 111.3 (C-2, 2′), 146.5 (C-3, 3′), 144.0 (C-4, 4′), 114.2 (C-5, 5′), 121.8 (C-6, 6′), 35.3 (C-7, 7′), 40.2 (C-8, 8′), 64.5 (C-9, 9′), 55.8 (3, 3′-OCH_3), 126.9 (C-1″, 1‴), 109.5 (C-2″, 2‴), 148.1 (C-3″, 3‴), 146.8 (C-4″, 4‴), 115.2 (C-5″, 5‴), 123.1 (C-6″, 6‴), 145.2(C-7″, 7‴), 114.8 (C-8″, 8‴), 167.3 (C-9″, 9‴), 56.0 (3″, 3‴-OCH_3). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530, 3010, 2920, 1700, 1625, 1592, 1512, 1460, 1420, 1362, 1268. FAB-MS (negative mode) m/z: 713 $[M-H]^-$. The ^{13}C-NMR data were identical with those reported.[18] On alkaline methanolysis with 5% NaOMe, **12** gave (−)-secoisolariciresinol and methyl ferulate. (−)-Secoisolariciresinol[17b,19]: a colorless amorphous powder, $[\alpha]_D$ −24.6° (c=0.4, EtOH). ^{1}H-NMR (acetone-d_6) δ: 1.90 (2H, m), 2.65 (2H, dd, J=13.7, 6.7 Hz), 2.70 (2H, dd, J=13.7, 7.6 Hz), 3.57 (2H, m), 3.67 (2H, m), 3.77 (6H, s), 6.61 (2H, dd, J=7.9, 1.8 Hz), 6.70 (2H, d, J=7.9 Hz), 6.72 (2H, d, J=1.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 146.2 (C-3, 3′), 143.8 (C-4, 4′), 132.5 (C-1, 1′), 121.7 (C-6, 6′), 114.1 (C-5, 5′), 111.4 (C-2, 2′), 61.0 (C-9, 9′), 55.9 (3, 3′-OCH_3), 43.9 (C-8, 8′), 36.0 (C-7, 7′).

Compound 13 (Acerogenin E) Cololess prisms from AcOEt–*n*-hexane. mp 236—237.5 °C, $[\alpha]_D$ *ca.* 0° (c=0.5, $CHCl_3$). UV λ_{max}^{MeOH} nm (log ε): 246 (4.02), 299 (3.89). ^{1}H-NMR (C_5D_5N) δ: 1.83 (2H, m), 1.87 (2H, m), 2.62—2.71 (4H, m), 2.79 (2H, m), 3.04 (2H, m), 7.06—7.24 (6H, NC). ^{13}C-NMR (C_5D_5N) δ: 212.6 (C-9), 152.94, 152.97 (C-3 and C-17), 134.24, 134.16 (C-18 and C-19), 131.5, 132.4 (C-6 and C-14), 129.0, 130.0 (C-5 and C-15), 127.2, 127.8 (C-1 and C-2), 116.9, 117.1 (C-4 and C-16), 45.1 (C-10), 42.2 (C-8), 31.7 (C-13), 28.5 (C-7), 26.1 (C-11), 22.4 (C-12). IR ν_{max}^{KBr} cm^{-1}: 3250, 2920, 1685, 1505, 1435, 1395, 1360, 1230, 1110, 812. EI-MS m/z: 296 (M^+), 268, 250, 225, 211, 197, 165, 113, 77, 27. The physical properties and spectral data were identical with those previously reported.[20]

Compound 14 (3,4,5-Trimethoxyphenol β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside) A colorless amorphous powder, $[\alpha]_D$ −88.9° (c=2.0, MeOH). UV λ_{max}^{MeOH} nm (log ε): 205 (4.63), 225 (4.09), 275 (3.58). ^{1}H-NMR (CD_3OD) δ: 3.70 (3H, s), 3.81 (6H, s), 4.79 (1H, d, J=7.6 Hz), 4.96 (1H, d, J=2.6 Hz), 6.45 (2H, s). ^{13}C-NMR (CD_3OD) δ: 155.4 (C-1), 154.8 (C-3, 5), 134.6 (C-4), 110.8 (Api-1), 103.1 (Glc-1), 96.3 (C-2, 6), 80.4 (Api-3), 77.9 (Glc-3 or Api-2), 77.8 (Api-2 or Glc-3), 77.0 (Glc-5), 74.9 (Glc-2 or Api-4), 74.8 (Api-4 or Glc-2), 71.5 (Glc-4), 68.7 (Glc-6), 65.3 (Api-5), 61.2 (4-OCH_3), 56.7 (3, 5-OCH_3). IR ν_{max}^{KBr} cm^{-1}: 3420, 2920, 1592, 1500, 1455, 1418, 1225, 1125, 1055, 820. FAB-MS (negative mode) m/z: 477 $[M-H]^-$. The physical properties and spectral data were identical with those previously reported.[21]

Compound 15 ((2*R*)-4-(4-Hydroxyphenyl)-2-butanol 2-*O*-β-D-Apiofuranosyl-(1→6)-β-D-glucopyranoside) A colorless amorphous powder, $[\alpha]_D$ −83.1° (c=3.2, MeOH). UV λ_{max}^{MeOH} nm (log ε): 223 (4.88), 279 (4.28). ^{1}H-NMR (CD_3OD) δ: 1.18 (3H, d, J=6.3 Hz), 1.68 (1H, m), 1.82 (1H, m), 2.50—2.70 (2H, NC), 4.29 (1H, d, J=7.6 Hz), 5.02 (1H, d, J=2.3 Hz), 6.68 (2H, d, J=8.6 Hz), 7.04 (2H, d, J=8.6 Hz). ^{13}C-NMR (CD_3OD) δ: 156.1 (C-4′), 134.7 (C-1′), 130.5 (C-2′, 6′), 116.0 (C-3′, 5′) C110.9 (Api-1), 102.3 (Glc-1), 80.5 (Api-3), 78.1 (Glc-3), 78.0 (Api-2), 76.7 (Glc-5), 75.2 (Glc-2), 75.0 (C-2 and Api-4), 71.5 (Glc-4), 68.4 (Glc-6), 65.7 (Api-5), 40.6 (C-3), 31.8 (C-4), 20.1 (C-1). IR ν_{max}^{KBr} cm^{-1}: 3400, 2910, 1608, 1510, 1426, 1368, 1230, 1050, 1009, 825. FAB-MS (negative mode) m/z: 459 $[M-H]^-$. The physical properties and spectral data were identical with those previously reported.[22,23]

Compound 16 ((+)-Catechin 7-*O*-β-D-Xylopyranoside) A pale yellow amorphous powder, $[\alpha]_D$ −37.9°(c=1.6, MeOH). UV λ_{max}^{MeOH} nm (log ε): 279 (4.88). ^{1}H-NMR (CD_3OD) δ: 2.54 (1H, dd, J=16.2, 7.9 Hz), 2.86 (1H, dd, J=16.5, 5.5 Hz), 3.89 (1H, dd, J=11.3, 5.5 Hz), 4.00 (1H, ddd, J=7.9, 7.5, 5.5 Hz), 4.60 (1H, d, J=7.5 Hz), 4.76 (1H, d, J=7.6 Hz), 6.11 (1H, d, J=2.4 Hz), 6.17 (1H, d, J=2.4 Hz), 6.71 (1H, dd, J=8.2, 2.1 Hz), 6.76 (1H, d, J=8.2 Hz), 6.83 (1H, d, J=2.1 Hz). ^{13}C-NMR (CD_3OD) δ: 158.5 (C-9), 157.6 (C-5), 156.9 (C-7), 146.3 (C-3′ and C-4′), 132.1 (C-1′), 120.0 (C-6′), 116.2 (C-5′), 115.3 (C-2′), 103.8 (C-10), 102.9 (Xyl-1), 97.6 (C-6), 97.1 (C-8), 83.0 (C-2), 77.8 (Xyl-3), 74.7 (Xyl-2), 71.1 (Xyl-4), 68.6 (C-3), 66.9 (Xyl-5), 28.5 (C-4). IR ν_{max}^{KBr} cm^{-1}: 3370, 2900, 1625, 1595, 1515, 1440, 1272, 1160, 1110, 1040, 815. FAB-MS (negative mode) m/z: 421 $[M-H]^-$. The physical properties and spectral data were identical with those previously reported.[23]

Compound 17 (Lupeol) Colorless needles from MeOH, mp 202—205 °C, $[\alpha]_D$ +17° (c=0.3, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.76 (3H, s), 0.79 (3H, s), 0.73 (3H, s), 0.94 (3H, d, J=0.6 Hz),0.97 (3H, s), 1.03 (3H, s), 1.68 (3H, d, J=0.6 Hz), 2.38 (1H, td, J=11.0, 5.8 Hz), 3.19 (1H, dd, J=11.0, 3.7 Hz), 4.57 (1H, q, J=1.2 Hz), 4.69 (1H, d, J=2.4 Hz). ^{13}C-NMR ($CDCl_3$) δ: 151.0 (C-20), 109.3 (C-29), 79.0 (C-3), 55.3 (C-5), 50.5 (C-9), 48.4 (C-18), 48.0 (C-19), 43.0 (C-17), 42.9 (C-14), 40.9 (C-8), 40.0 (C-22), 38.9 (C-4), 38.7 (C-1), 38.1 (C-13), 37.2 (C-10), 35.6 (C-16), 34.3 (C-7), 29.9 (C-21), 28.0 (C-23), 27.5 (C-2 and C-15), 25.2 (C-12), 21.0 (C-11), 19.3 (C-30), 18.4 (C-6), 18.0 (C-28), 16.1 (C-25), 16.0 (C-26), 15.4 (C-24), 14.6 (C-27). The ^{13}C-NMR data were identical with those previously reported.[24] IR ν_{max}^{KBr} cm^{-1}: 3320, 2930, 1632, 1445, 1372, 1040, 880. EI-MS m/z: 426 (M^+), 411, 315, 207, 189, 135, 95, 81.

Compound 18 (Monogynol A) Colorless needles from MeOH, mp 232—240 °C , $[\alpha]_D$ +6.0° (c=1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.76 (3H, s), 0.81 (3H, s), 0.84 (3H, s), 0.96 (3H, d, J=0.6 Hz), 0.97 (3H, s), 1.06 (3H, s), 1.12 (3H, s), 1.23 (3H, s), 3.20 (1H, dd, J=11.3, 4.9 Hz). ^{13}C-NMR ($CDCl_3$) δ: 79.0 (C-3), 73.5 (C-20), 55.2 (C-5), 50.3 (C-4), 50.0 (C-19), 48.3 (C-18), 44.6 (C-17), 43.5 (C-14), 41.4 (C-8), 40.2 (C-22), 38.8 (C-4), 38.7 (C-1), 37.5 (C-13), 37.1 (C-10), 35.6 (C-16), 34.6 (C-7), 31.6 (C-30), 29.1 (C-12), 28.7 (C-21), 28.0 (C-23), 27.6 (C-15), 27.4 (C-2), 24.8 (C-29), 21.4 (C-11), 19.2 (C-28), 18.3 (C-6), 16.2 (C-25 and C-26), 15.4 (C-24), 14.8 (C-27). IR ν_{max}^{KBr} cm^{-1}: 3420, 2940, 2960, 1455, 1370, 1060, 955, 798. EI-MS m/z: 444 (M^+), 411, 386, 234, 218, 207, 189, 149, 135. The physical properties and spectral data were identical with those previously reported.[25]

Compound 19 (Lupeol Caffeate) A pale yellow amorphous powder, $[\alpha]_D$ +34.2° (c=1.0, MeOH). UV λ_{max}^{MeOH} nm (log ε): 221 (4.22), 245 (3.98), 300 (4.05), 328 (4.16). ^{1}H-NMR ($CDCl_3$) δ: 0.79 (3H, s), 0.88 (6H, s), 0.90 (3H, s), 0.95 (3H, s), 1.04 (3H, s), 1.69 (3H, s), 6.86 (1H, d, J=7.6 Hz), 6.96 (1H, d, J=7.6 Hz), 7.09 (1H, s), 7.54 (1H, d, J=15.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 167.7 (C-9′), 151.0 (C-20), 147.3 (C-4′), 144.9 (C-3′ and C-7′), 127.1 (C-1′), 122.0 (C-6′), 115.7 (C-8′), 115.1 (C-2′), 113.9 (C-5′), 109.4 (C-30), 81.0 (C-3), 55.4 (C-5), 50.3 (C-9), 48.3 (C-18), 48.0 (C-15), 43.0 (C-14 or C-17), 42.8 (C-17 or C-14), 40.9 (C-8), 40.0 (C-22), 38.4 (C-1), 38.1 (C-4 and C-13), 37.1 (C-10), 35.6 (C-16), 34.2 (C-7), 29.9 (C-21), 28.0 (C-23), 27.4 (C-15), 25.1 (C-12), 23.9 (C-2), 21.0 (C-11), 19.3 (C-29), 18.2 (C-6), 18.0 (C-28), 16.7 (C-24), 16.2 (C-25 or C-26), 16.0 (C-26 or C-25), 14.5 (C-27). IR ν_{max}^{KBr} cm^{-1}: 3350, 2930, 1670, 1625, 1592, 1510, 1440, 1370, 1262, 1160, 1105, 1000, 972, 880, 810, 755. EI-MS m/z: 588 (M^+), 497, 440, 408, 371, 257, 163, 121, 57. HR-EI-MS m/z: 588.416 (M^+), Calcd for $C_{39}H_{56}O_4$, 588.418. On alkaline methanolysis with 5% NaOMe, **19** gave lupeol (**17**) and methyl caffeate.

Compound 20 (Oleanolic Acid Caffeate) A crystalline powder from AcOEt, mp 300 °C <, $[\alpha]_D$ +75.0° (c=0.2, MeOH). UV λ_{max}^{MeOH} nm (log ε): 216 (4.31), 243 (4.08), 300 (4.11), 328 (4.18). ^{1}H-NMR (acetone-d_6) δ: 0.83 (3H, s), 0.91 (3H, s), 0.93 (3H, s), 0.95 (3H, s), 0.96 (3H, s), 1.00 (3H, s), 1.21 (3H, s), 1.92 (2H, dd, J=9.2, 3.4 Hz), 2.90 (1H, dd, J=13.7, 4.3 Hz), 4.58 (1H, dd, J=11.3, 4.9 Hz), 5.26 (1H, t, J=3.4 Hz), 6.29 (1H, d, J=15.9 Hz), 6.86 (1H, d, J=8.2 Hz), 7.04 (1H, dd, J=8.2, 2.1 Hz), 7.16 (1H, d, J=2.1 Hz), 7.54 (1H, d, J=15.9 Hz). ^{13}C-NMR (acetone-d_6) δ: 178.9 (C-28), 167.2 (C-9′), 148.7 (C-4′), 146.3 (C-3′), 145.3 (C-7′), 144.9 (C-13), 127.7 (C-1′), 122.9 (C-12), 122.4 (C-6′), 116.4 (C-5′), 116.2 (C-8′), 115.2 (C-2′), 80.9 (C-3), 56.1 (C-5), 48.4 (C-9), 46.9 (C-17), 46.8 (C-19), 42.5 (C-14), 42.2 (C-18), 40.2 (C-8), 38.8 (C-1), 38.6 (C-4), 37.7 (C-10), 34.5 (C-21), 33.5 (C-7), 33.4 (C-29), 33.4 (C-22). IR ν_{max}^{KBr} cm^{-1}: 3350, 2920, 1695, 1595, 1510, 1440, 1360, 1270, 1180, 1110, 1105, 970, 810, 755. EI-MS m/z: 618 (M^+), 438, 395, 248, 203, 163, 121, 95, 81, 69. The ^{13}C-NMR data were identical with those previously reported.[14] On alkaline methanolysis with 5% NaOMe, **20** gave oleanolic acid (**9**) and methyl caffeate.

Compound 21 (Dammarenediol II 3-Caffeate) A crystalline powder from AcOEt, mp 205—207 °C, $[\alpha]_D$ +47.0° (c=0.2, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.27), 244 (4.08), 300 (4.19), 328 (4.29). ^{1}H-NMR (C_5D_5N) δ: 0.84 (3H, s), 0.96 (3H, s), 0.97 (3H, s), 0.98 (3H, s), 0.99 (3H, s), 1.43 (3H, s), 1.66 (3H, s), 1.71 (3H, s), 4.86 (1H, dd, J=11.2, 5.3 Hz), 5.34 (1H, t, J=7.3 Hz), 6.70 (1H, d, J=15.8 Hz), 7.24 (2H, s), 7.67 (1H, s), 8.04 (1H, d, J=15.8 Hz). ^{13}C-NMR (C_5D_5N) δ: 167.4 (C-9′), 150.4 (C-4′), 147.8 (C-3′), 145.6 (C-7′), 130.8 (C-25), 127.0 (C-1′), 126.1 (C-24), 122.1 (C-6′), 116.7 (C-8′), 115.9 (C-2′), 115.7 (C-5′), 80.5 (C-3), 74.1 (C-20), 56.2 (C-5), 50.9 (C-9), 50.7 (C-14), 50.4 (C-17), 42.5 (C-13), 41.9 (C-22), 40.7 (C-8), 38.8 (C-1), 38.3 (C-4), 37.2 (C-10), 35.5 (C-7), 31.7 (C-15), 28.1 (C-16 and C-28), 26.2 (C-26), 25.8 (C-21), 25.4 (C-12), 24.3 (C-2), 23.3 (C-23), 21.9 (C-11), 18.5 (C-6), 17.7 (C-27), 16.9 (C-30), 16.8 (C-18), 16.4 (C-19), 15.7 (C-29). IR ν_{max}^{KBr} cm^{-1}: 3440, 2910, 1680, 1600, 1508, 1440, 1270, 1180, 1108, 970, 810. EI-MS m/z: 588 ($M^+ - H_2O$), 497, 440, 408, 371, 339, 299, 236, 189, 163, 109. HR-EI-MS m/z: 588.420 (M^+), Calcd for $C_{39}H_{56}O_4$, 588.418. On alkaline methanolysis with 5% NaOMe, **21** gave dammarenediol II (**22**) and methyl caffeate. Dammarenediol II (**22**): $[\alpha]_D$ +15° (c=0.2, $CHCl_3$), ^{1}H-NMR ($CDCl_3$) δ: 0.77 (3H, s), 0.85 (3H, s), 0.88 (3H, s), 0.96 (3H, s), 0.97 (3H, s), 1.14 (3H, s), 1.61 (3H, s), 1.69 (3H, s), 3.20 (2H, dd, J=10.6, 5.3 Hz), 5.12 (1H, t, J=6.9 Hz). ^{13}C-NMR ($CDCl_3$): 131.6 (C-25), 124.7 (C-24), 79.0 (C-3), 75.4 (C-20), 55.8 (C-5), 50.6 (C-9), 50.3 (C-14), 49.8 (C-17), 42.3 (C-13), 40.5 (C-22), 40.3 (C-8), 39.0 (C-4), 39.0 (C-1), 37.1 (C-10), 35.2 (C-7), 31.2 (C-15), 28.0 (C-28), 27.5 (C-12), 27.4 (C-2), 25.7 (C-26), 25.4 (C-21), 24.8 (C-16), 22.5 (C-23), 21.5 (C-11), 18.3 (C-6), 17.7 (C-27), 16.4 (C-30), 16.2 (C-19), 15.5 (C-18), 15.3 (C-29). The ^{13}C-NMR data were identical with those previously reported.[26]

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