# Chemical Evaluation of *Betula* Species in Japan. II.[1] Constituents of *Betula platyphylla* var. *japonica*

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**The constituents of *Betula platyphylla* var. *japonica* were identified as follows: Fresh leaves: 12-*O*-acetyl-3-*O*-malonylbetulafolienetriol, 12-*O*-acetyl-3-*O*-malonylbetulafolienetriol oxide I (=papyriferic acid), 12-*O*-acetylbetulafolienediolone, hydroxyhopanone, caryophyllene oxide, kaempferol 3-*O*-(4-*O*-acetyl)-α-L-rhamnopyranoside*, quercetin 3-*O*-(4-*O*-acetyl)-α-L-rhamnopyranoside. Outer bark: betulin, lupeol, betulinic acid, betulone, betulin 3-*O*-caffeate, oleanolic acid, oleanolic acid 3-*O*-acetate. Inner bark: (−)-catechin, (−)-catechin 7-*O*-β-D-xylopyranoside, rhododendrin (=betuloside), aceroside VII, aceroside VIII, 1,7-bis[4-hydroxyphenyl]-3-hepten-5-one, 2-hydroxy-1,7-bis[4-hydroxyphenyl]-3-hepten-5-one*, acerogenin E, (3*R*)-3,5′-dihydroxy-4′-methoxy-3′,4″-oxo-1,7-diphenyl-1-heptene*, 7α-hydroxy-β-sitosterol, 7β-hydroxy-β-sitosterol. Root bark: dammarenediol II 3-*O*-*p*-coumarate*, dammarenediol II 3-*O*-caffeate, ocotillol II 3-*O*-caffeate*, stigmast-4-ene-3-one. Spikes: caryophyllene oxide, (−)-rhododendrol (=betuligenol), 12-*O*-acetylbetulafolienetriol. The compounds with an asterisk are new.**

**Key words** *Betula platyphylla* var. *japonica*; dammarane; lupane; diarylheptanoid; caryophyllene oxide; flavonoid

In the previous paper, we reported the constituents of *Betula ermanii* CHAM.[1] For comparison, a detailed chemical examination of *B. platyphylla* SUKATCHEV var. *Japonica* (MIQ.) HARA, Shirakanba in Japanese, was made. Several reports had already revealed the presence of the following compounds: betulafolientriol (**1a**), betulafolientriol oxide I (**2a**), dammar-24-ene-12β,20(*S*)-diol-3-one (**3a**), hydroxyhopanone (**4**),[2] 3α,12β,20(*S*),24-tetrahydroxydammar-25-ene and 3α,12β,20(*S*),25-tetrahydroxydammar-23-ene[3] from the nonsaponifiable fraction of the ether extracts of the leaves; betulin (**8**), lupeol (**9**), betulin 3-*O*-caffeate (**12**), betulinic acid 3-*O*-caffeate, oleanolic acid (**13**), oleanolic acid 3-*O*-acetate (**14**), β-sitosterol, several long-chain hydrocarbons[4] and several antifungal phenolics[5] from the outer bark; salidoroside, rhododendrin (=betuloside) (**17**) and platyphylloside[6] from the inner bark; ocotillol II, 3-epiocotillol II, sinapic acid, apigenin, hydroxyhopanone and betulafolienetriol oxide I (**2a**) from the pollen grains.[7] The examination was carried out referring to these reports, and herein the result is described.

**Constituents of Fresh Leaves** From the MeOH extract of fresh leaves collected in June, acylated dammarane-type triterpenes, 12-*O*-acetyl-3-*O*-malonylbetulafolienetriol

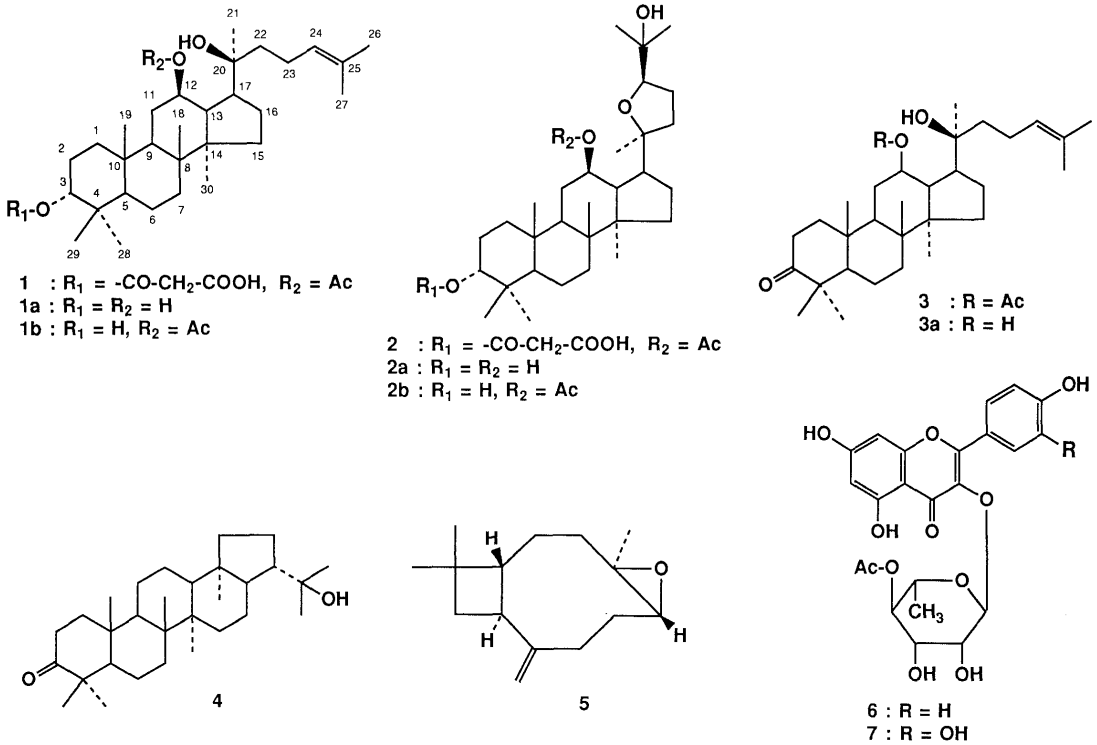


Chart 1. Constituents of Leaves

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(**1**),[8] 12-*O*-acetyl-3-*O*-malonylbetulafolienetriol oxide I (**2**)[9] and 12-*O*-acetylbetulafolienediolone (**3**)[10] were isolated together with hydroxyhopanone (**4**),[2] caryophyllene oxide (**5**),[11] quercetin 3-*O*-(4-*O*-acetyl)-α-L-rhamnopyranoside (**7**)[12] and a new flavonol glycoside **6**. Their structures were confirmed by comparison of the physical properties and spectral data with those previously reported (see Experimental).

The new flavonol glycoside **6**, a pale yellow amorphous powder, $[\alpha]_D$ −138° ($c$=1.0, MeOH), was formulated as $C_{23}H_{22}O_{11}$ by high resolution fast atom bombardment mass spectrum (HR-FAB-MS). Its $^1$H- and $^{13}$C-NMR data were similar to those of **7** except for the B-ring signals which were characteristic of a *p*-hydroxyphenyl group (see Experimental). On alkaline methanolysis, **6** gave afzelin; thus, the structure was determined to be kaempferol 3-*O*-(4-*O*-acetyl)-α-L-rhamnopyranoside.

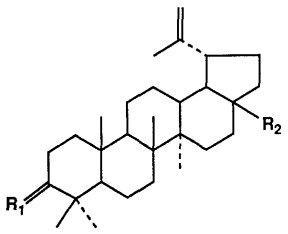
Compounds **1**, **2** and **3** are the original forms of the previously reported compounds, **1a**, **2a** and **3a**, respectively.[2] Compound **2** has been isolated from *B. papyrifera* subsp. *humilis*,[9a] *B. nana* subsp. *exilis*[9b] and *B. pendula*[9c] and named papyriferic acid. This compound is known as a herbivore-deterent of the juvenile twigs of these birches. Confirming the role of this compound, the leaves collected in August contained neither **2**, **1** nor **3**.

Caryophyllene oxide (**5**) is responsible for a noticeable and pleasant odor of the leaves.

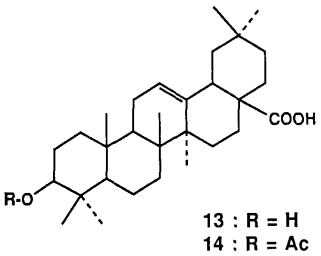
**Constituents of Outer Bark** From the dried outer bark, 12% of betulin (**8**) was obtained together with lupeol (**9**),[4] betulinic acid (**10**),[13] betulone (**11**),[14] betulin 3-*O*-caffeate (**12**),[4] oleanolic acid (**13**),[4] oleanolic acid 3-*O*-acetate (**14**).[4] All the compounds have already been reported. A large amount of betulin causes the characteristic white color of the outer bark.[15]

**Constituents of Inner Bark** From the dried inner bark collected in June, (−)-catechin (**15**),[1] (−)-catechin 7-*O*-β-D-xylopyranoside (**16**),[1] rhododendrin (=betuloside) (**17**),[6] aceroside VII (**18**),[16] aceroside VIII (**19**),[16] 1,7-bis[4-hydroxyphenyl]-3-hepten-5-one (**20**),[17] acerogenin E (**22**),[18] 7β-hydroxy-β-sitosterol (**24**),[19] 7α-hydroxy-β-sitosterol (**25**)[19] and two new diarylheptanoids, **21** and **23**, were isolated.

Compound **21** was found to have a molecular formula with one more oxygen atom than **20**, $C_{19}H_{20}O_4$, from the HR-EI-MS. The $^1$H- and $^{13}$C-NMR data of **21** are similar to those of **20** and revealed its structure as 1,7-bis[4-hydroxyphenyl]-3-hepten-5-one with one more hydroxyl group. The position of the hydroxyl group was easily determined to be at C-2 based on the coupling of the carbinyl proton (δ 4.39, ddt, $J$=5.2, 1.5, 6.7 Hz) with the

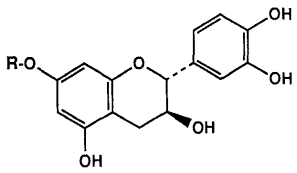


**8** : $R_1$ = β-OH, α-H ; $R_2$ = $CH_2OH$
**9** : $R_1$ = β-OH, α-H ; $R_2$ = $CH_3$
**10** : $R_1$ = β-OH, α-H ; $R_2$ = COOH
**11** : $R_1$ = O ; $R_2$ = $CH_2OH$
**12** : $R_1$ = β-caffeoyloxy, α-H ; $R_2$ = $CH_2OH$

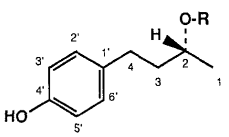


**13** : R = H
**14** : R = Ac

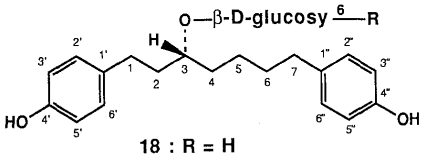
Chart 2. Constituents of Outer Bark



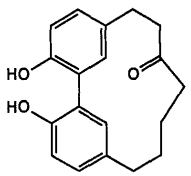
**15** : R = H
**16** : R = β-D-xylosyl



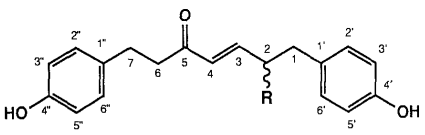
**17** : R = β-D-glucosyl
**17a** : R = H



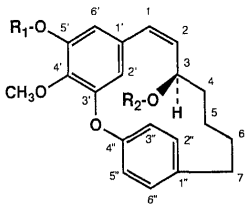
**18** : R = H
**19** : R = β-D-apiosyl



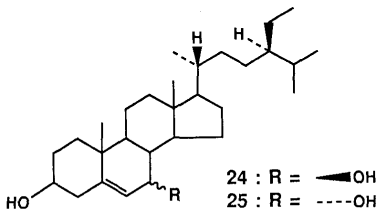
**22**



**20** : R = H
**21** : R = OH



**23** : $R_1$ = $R_2$ = H
**23a** : $R_1$ = $CH_3$, $R_2$ = H
**23b** : $R_1$ = $CH_3$, $R_2$ = (*S*)-MTPA
**23c** : $R_1$ = $CH_3$, $R_2$ = (*R*)-MTPA



**24** : R = ◀OH
**25** : R = ----OH

Chart 3. Constituents of Inner Bark

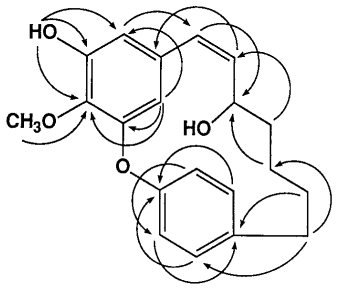



Fig. 1. Diagnostic Correlations Observed in the Long-Range $^{13}C$–$^{1}H$ COSY of **23**

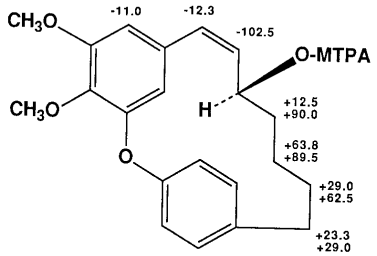
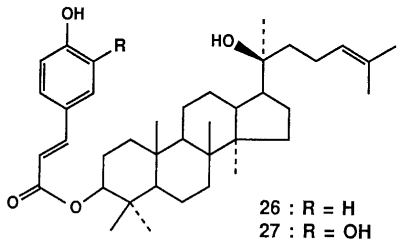


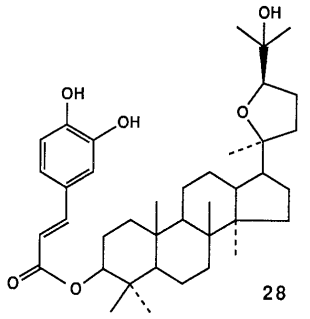

Fig. 2. Chemical Shift Differences, $\Delta\delta(\delta S-\delta R)$, for the (*R*)-MTPA Ester (**23b**) and (*S*)-MTPA Ester (**23c**) in Hertz at 500 MHz

olefinic proton at C-3 ($\delta$ 6.81, dd, $J=15.9$, 5.2 Hz) in the $^{1}H$-NMR. The $^{1}H$–$^{1}H$ and long range $^{13}C$–$^{1}H$ COSY which indicated a correlation between H-2 and C-1′ also confirmed the structure. As **21** showed no optical rotation, it may be a racemate resulting from enolization.

Compound **23**, a colorless crystalline powder, mp 186—187 °C from a mixture of EtOAc and *n*-hexane, $[\alpha]_D$ +79° ($c=1.0$, $CHCl_3$), was formulated as $C_{20}H_{22}O_4$ from the HR-EI-MS. The $^{1}H$-NMR spectrum showed the presence of a 3,4,5-trisubstituted phenyl group [6.38 (1H, d, $J=2.1$ Hz), 5.17 (1H, d, $J=2.1$ Hz)], a 4-substituted phenyl group which is restricted free rotation [7.33 (1H, dd, $J=8.2$, 2.1 Hz), 7.30 (1H, dd, $J=8.2$, 2.1 Hz), 7.12 (1H, dd, $J=8.2$, 2.4 Hz), 7.01 (1H, dd, $J=8.2$, 2.4 Hz)], an aromatic methoxy group [4.11 (3H, s)], a *cis*-substituted double bond [6.11 (1H, d, $J=11.3$ Hz), 5.30 (1H, dd, $J=11.3$, 8.6 Hz)] and a secondary hydroxy group [3.95 (1H, ddd, $J=11.3$, 8.6, 3.1 Hz)]. By the $^{1}H$–$^{1}H$ and long-range $^{13}C$–$^{1}H$ COSY and the nuclear Overhauser effect correlation spectroscopy (NOESY), the structure of **23** was determined as 3,5′-dihydroxy-4′-methoxy-3′,4″-oxo-1,7-diphenyl-1-heptene (Fig. 1). The absolute configuration at C-3 was confirmed by application of the modified Mosher method.[20] After methylation of the phenolic hydroxy group at C-5′ (**23a**), (−)-(*S*)-α-methoxy-α-(trifluoromethyl)phenylacetic (MTPA) ester (**23b**) and (+)-(*R*)-MTPA ester (**23c**) were prepared. As shown in Fig. 2 , the signals due to the protons at C-1, C-2, C-2′ and C-6′ in the (−)-(*S*)-MTPA ester (**23b**) were observed at higher field in the $^{1}H$-NMR spectrum than those in the (+)-(*R*)-MTPA ester (**23c**), while the signals due to the protons at C-4, C-5, C-6 and C-7 in **23b** were observed at lower field than those in **23c**. Thus, the absolute configuration at C-3 was determined as *R*.

**Constituents of Root Bark** From the dried root bark collected in June, two new acylated triterpenes, **26** and **28**, were isolated together with dammarendiol II 3-*O*-caffeate (**27**)[1] and stigmast-4-ene-3-one (**29**).[19]



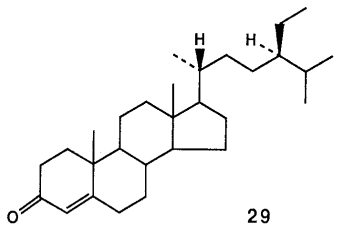




Chart 4. Constituents of Root Bark

Compound **26**, a colorless amorphous powder, $[\alpha]_D$ −16° ($c=0.5$, MeOH), gave the molecular formula, $C_{39}H_{58}O_4$, which is one oxygen atom less than that of **27**, in the HR-FAB-MS. The $^{1}H$- and $^{13}C$-NMR spectra of **26** were similar to those of **27** except that the signals of the caffeoyl group of **27** were substituted by those of a *p*-coumaroyl group in **26**. On alkaline methanolysis, **26** gave dammarenediol II and methyl *p*-coumarate. Thus, the structure of **26** was determined as dammarenediol II 3-*O*-*p*-coumarate.

Compound **28**, a colorless crystalline powder from EtOAc, mp 222—224 °C, $[\alpha]_D$ −10° ($c=0.5$, MeOH), gave the molecular formula, $C_{39}H_{58}O_6$, which was one oxygen atom more than that of **27**, in the HR-FAB-MS. In the $^{1}H$- and $^{13}C$-NMR spectra, **28** showed the presence of a caffeoyl group and a dammarane-type triterpene having the side chain as that of betulafolienetriol oxide I. On alkaline methanolysis, **28** gave methyl caffeate and a triterpene which was identified as ocotillol II by comparison of its physical properties and spectral data. Thus, the structure of **28** was determined as ocotillol II 3-*O*-caffeate.

It is remarkable that the dammarane-type triterpenes are present in both leaves and root bark, but not in stem bark. Those in leaves have 3α- and 12β-hydroxyl groups and those in root bark have 3β-hydroxyl group and lack 12-hydroxyl group.

**Constituents of Spikes** From the fresh spikes collected in August, 12-*O*-acetylbetulafolienetriol (**1b**),[8,21] caryophyllene oxide (**5**) and (−)-rhododendrol (=betuligenol) (**17a**)[11] were isolated. Their structures were determined by comparison of their physical properties and spectral data with those of authentic samples or those reported.

Concerning the stereochemistry of (−)-rhododendrol (**17a**), two groups have reported opposite conclusions. Inoue *et al.* concluded (*S*) for (+)-rhododendrol by comparison of the optical rotation with those of the related compounds and application of Brewster's rule,[22] while Klischies & Zenk as (*S*) for (−)-rhododendrol as a result of a tritium labelled experiment.[23]

In this study, we applied the glucosylation shift rule in $^{13}$C-NMR spectroscopy.[24] In case of the β-D-glucopyranoside of a secondary alcohol, rotation around the glucosidic bond is rather restricted and a conformation where an anomeric proton and a *sec*-carbinol proton are *syn* to each other is predominant.[25] This causes unequal β-D-glucosylation shifts of the β-carbons. Thus, the β-carbons of aglycones situated on the same side as the C-2-hydroxyl group of the glucosyl are more shielded (−3.6—−4.4 ppm) than those on the opposite side (−1.8—−2.7 ppm) in the $^{13}$C-NMR spectra in $C_5D_5N$. When compared with rhododendrin (**17**), (−)-rhododendrol (**17a**) showed β-D-glucosylation shifts of −3.7 ppm for C-1 and −1.5 ppm for C-3 in $CD_3OD$ solution. Furthermore, β-D-glucosylation shifts of −1.4 ppm for C-1 and −2.4 ppm for C-3 in $CD_3OD$ solution can be estimated for (+)-rhododendrol from the reported $^{13}$C-NMR data for (+)-rhododendrin (=epirhododendrin).[26] The results indicated (*R*)-configuration at C-2 for (−)-rhododendrol (**17a**) and (*S*) for (+)-rhododendrol.

Spikes contain a dammarane-type triterpene (**1b**) even in August when leaves lose this type of compounds. It seems that the compound plays a role of antifeedant in spikes which are very important organs for the plant.

In this study, thirty-one compounds including five which were new, **6**, **21**, **23**, **26** and **28**, were isolated, and, the following remarkable distinction between *B. platyphylla* var. *japonica* and *B. ermanii* was revealed.

1) The dammarane-type triterpenes in leaves of *B. platyphylla* var. *japonica* have 3α- and 12β-hydroxyl groups and form malonates, while those of *B. ermanii* have 3β- and 11α-hydroxyl groups and form glucosides.

2) The lignans in inner bark of *B. ermanii* are replaced by diarylheptanoids in that of *B. platyphylla* var. *japonica*.

3) The content of betulin in outer bark of *B. ermanii* is less than half of that in *B. platyphylla* var. *japonica*.

A more detailed report of the comparative studies among *Betula* species will be presented in the near future.

## Experimental

The instruments, materials and experimental conditions were the same as described in Part 1 of this series.[1]

**Isolation. Leaves** Fresh leaves (1.8 kg) collected in June at Iizuna Highland, Nagano Prefecture, were extracted with MeOH (20 l) at room temperature for 2 weeks. The extract and then MeOH (10 l) were passed over activated charcoal (130 g) packed in a column of 7 cm diameter. The resulting solution was concentrated to a syrup under reduced pressure. The syrup was chromatographed on silica gel using $CHCl_3$ and MeOH. Each fraction was rechromatographed on silica gel using *n*-hexane and EtOAc and/or on Sephadex LH-20 using 90% MeOH to yield **1** (141 mg), **2** (35 mg), **3** (66 mg), **4** (12 mg), **5** (52 mg), **6** (33 mg) and **7** (22 mg).

**Outer Bark** Outer bark (460 g) of a tree aged 32 years and collected in June at Iizuna Highland was extracted twice with $CHCl_3$ (3 l) under reflux for 3 h. The extracts were concentrated to 700 ml and EtOH (1 l) was added. Crystallized crude betulin was filtered off and recrystallized from EtOH to obtain 56 g of betulin (**8**). The filtrates were combined and chromatographed on silica gel using *n*-hexane–$CHCl_3$, *n*-hexane–EtOAc and $CHCl_3$–EtOAc as eluents to obtain **9** (1.4 g), **10** (210 mg), **11** (140 mg), **12** (255 mg), **13** (470 mg) and **14** (80 mg). All the compounds were identified by direct comparison with their authentic samples.

**Inner Bark** Air-dried inner bark (2 kg) was extracted twice with MeOH (4 l) under reflux for 6 h. The extracts were concentrated to a syrup under reduced pressure. The syrup was extracted with $Et_2O$ (2 l). The $Et_2O$ soluble compounds were chromatographed on silica gel using $CHCl_3$–MeOH and *n*-hexane–EtOAc, and on Sephadex LH-20 using MeOH to obtain **20** (220 mg), **21** (7 mg), **22** (33 mg), **23** (36 mg) and a mixture of **24** and **25**. The mixture was chromatographed on silica gel impregnated with 20% $AgNO_3$ using $CHCl_3$ to obtain **24** (7 mg) and **25** (6 mg). The $Et_2O$ insoluble compounds were chromatographed on silica gel using $CHCl_3$–MeOH and on Sephadex LH-20 using 80% MeOH to obtain **15** (210 mg), **16** (70 mg), **19** (65 mg) and a mixture of **17** and **18**. The mixture was subjected to droplet counter current chromatography using $CHCl_3$–MeOH–$H_2O$ (4 : 4 : 3) to obtain **17** (35 mg) and **18** (15 mg).

**Root Bark** Air-dried root bark (360 g) was extracted three times with MeOH (1.5 l) under reflux for 6 h. The extracts were concentrated and partitioned with $CHCl_3$ (1 l), MeOH (1 l) and $H_2O$ (750 ml). The upper layer was concentrated to a syrup and chromatographed on silica gel using $CHCl_3$–MeOH and *n*-hexane–EtOAc to obtain **26** (10 mg), **27** (42 mg) and **28** (108 mg). The lower layer was concentrated to a syrup and chromatographed on silica gel using *n*-hexane–EtOAc to obtain **29** (6 mg).

**Spikes** Fresh spikes (1.3 kg) collected in August at Iizuna highland were extracted with MeOH (10 l) at room temperature for 4 weeks. The extract and MeOH (5 l) were passed over activated charcoal (80 g). The resulting solution was concentrated to a syrup, and partitioned with $CHCl_3$ (500 ml), MeOH (500 ml) and $H_2O$ (350 ml). The upper layer was chromatographed on silica gel using $CHCl_3$–MeOH and on Sephadex LH-20 using 90% MeOH to yield **17a** (56 mg). The lower layer was chromatographed on silica gel using *n*-hexane–EtOAc and benzene, and on ODS using MeOH to obtain **1b** (12 mg) and **5** (8 mg).

**12-*O*-Acetyl-3-*O*-malonylbetulafolienetriol (1)** A colorless amorphous powder, $[\alpha]_D$ +2° (*c*=1.0, $CHCl_3$). $^1$H-NMR ($C_5D_5N$) δ: 0.77 (3H, s), 0.80 (3H, s), 0.85 (3H, s), 0.96 (3H, s), 1.03 (3H, s), 1.37 (3H, s), 1.69 (3H, s), 1.72 (3H, s), 2.22 (3H, s), 3.84 (2H, s), 4.93 (1H, br s), 5.19 (1H, dt, *J*=5.5, 10.7 Hz), 5.39 (1H, t, *J*=7.3 Hz). $^{13}$C-NMR ($CDCl_3$) δ: 34.4 (C-1), 22.6 (C-2), 80.2 (C-3), 37.1 (C-4), 50.6 (C-5), 18.0 (C-6), 34.0 (C-7), 40.0 (C-8), 49.8 (C-9), 36.8 (C-10), 28.1 (C-11), 76.9 (C-12), 44.8 (C-13), 52.9 (C-14), 31.5 (C-15), 27.2 (C-16), 52.8 (C-17), 16.1 (C-18), 15.6 (C-19), 73.9 (C-20), 26.1 (C-21), 36.1 (C-22), 22.2 (C-23), 125.1 (C-24), 131.4 (C-25), 25.8 (C-26), 17.7 (C-27), 27.9 (C-28), 21.6 (C-29), 17.5 (C-30), 21.6 ($\underline{C}H_3$–CO), 169.9 ($CH_3$–$\underline{C}O$), 41.8 (CO–$\underline{C}H_2$–CO), 166.0 ($\underline{C}O$–$CH_2$–CO), 167.2 (CO–$CH_2$–$\underline{C}O$). FAB-MS (positive mode) *m/z*: 571 $[M+H-H_2O]^+$, 511 $[M+H-H_2O-AcOH]^+$.

**12-*O*-Acetylbetulafolienetriol (1b)** A colorless amorphous powder, $[\alpha]_D$ +2° (*c*=1.0, MeOH). $^1$H-NMR ($CDCl_3$) δ: 0.77 (3H, s), 0.80 (3H, s), 0.87 (3H, s), 0.89 (3H, s), 0.94 (3H, s), 1.07 (3H, s), 1.57 (3H, s), 1.64 (3H, s), 1.98 (3H, s), 3.33 (1H, t, *J*=2.8 Hz), 4.67 (1H, dt, *J*=5.1, 11.4 Hz), 5.09 (1H, t, *J*=6.9 Hz). $^{13}$C-NMR ($CDCl_3$) δ: 33.9 (C-1), 25.8 (C-2), 76.5 (C-3), 38.0 (C-4), 49.9 (C-5), 18.6 (C-6), 35.0 (C-7), 40.4 (C-8), 50.3 (C-9), 37.7 (C-10), 31.6 (C-11), 77.6 (C-12), 45.3 (C-13), 53.3 (C-14), 28.8 (C-15), 27.6 (C-16), 53.3 (C-17), 16.5 (C-18), 16.0 (C-19), 74.2 (C-20), 26.6 (C-21), 36.5 (C-22), 22.7 (C-23), 125.6 (C-24), 131.8 (C-25), 26.2 (C-26), 18.1 (C-27), 28.6 (C-28), 22.5 (C-29), 17.8 (C-30), 170.1 ($CH_3\underline{C}O$), 22.0 ($\underline{C}H_3CO$). EI-MS *m/z*: 502 ($M^+$), 484.

**12-*O*-Acetyl-3-*O*-malonylbetulafolienetriol Oxide I (=Papyriferic Acid, 2)** A colorless amorphous powder, $[\alpha]_D$ −12° (*c*=0.38, $CHCl_3$). $^1$H-NMR ($CDCl_3$) δ: 0.85, 0.86, 0.88, 0.96, 0.98, 1.10, 1.17, 1.19, 2.01 (each 3H, s), 3.45 (2H, s), 3.65 (1H, dd, *J*=8.2, 6.4 Hz), 4.70 (1H, br s), 4.82 (1H, td, *J*=10.7, 5.2 Hz). $^{13}$C-NMR ($CDCl_3$) δ: 33.9 (C-1), 22.6 (C-2), 80.3 (C-3), 36.8 (C-4), 50.6 (C-5), 18.0 (C-6), 34.3 (C-7), 39.8 (C-8), 49.6 (C-9), 37.0 (C-10), 28.2 (C-11), 75.7 (C-12), 46.2 (C-13), 52.3 (C-14), 31.3 (C-15), 26.8 (C-16), 50.4 (C-17), 15.5 (C-18), 15.9 (C-19), 85.8 (C-20), 22.3 (C-21), 38.7 (C-22), 26.1 (C-23), 83.3 (C-24), 71.2 (C-25), 27.4 (C-26),

24.1 (C-27), 27.9 (C-28), 21.8 (C-29), 17.7 (C-30), 169.2 (HOOC$\underline{C}$H$_2$CO), 40.9 (HOOC$\underline{C}$H$_2$CO), 167.1 (HOOCCH$_2\underline{C}$O), 21.5 ($\underline{C}$H$_3$C=O), 170.8 (CH$_3\underline{C}$=O). FAB-MS (negative mode) *m/z*: 603 $[M-H]^-$.

**12-*O*-Acetylbetulafolienediolone (3)** A colorless amorphous powder, $[\alpha]_D$ +25° (*c*=1.0, $CHCl_3$). $^1$H-NMR ($CDCl_3$) $\delta$: 0.94 (3H, s), 0.97 (3H, s), 1.04 (3H, s), 1.05 (3H, s), 1.09 (3H, s), 1.14 (3H, s), 1.64 (3H, br s), 1.71 (3H, br s), 2.05 (3H, s), 4.74 (1H, dt, *J*=10.7, 6.1 Hz), 5.16 (1H, t, *J*=7.0 Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$: 39.5 (C-1), 33.8 (C-2), 217.5 (C-3), 47.2 (C-4), 55.0 (C-5), 19.6 (C-6), 33.8 (C-7), 39.6 (C-8), 49.3 (C-9), 36.8 (C-10), 28.6 (C-11), 76.3 (C-12), 45.0 (C-13), 52.7 (C-14), 31.4 (C-15), 27.1 (C-16), 52.9 (C-17), 16.0 (C-18), 15.2 (C-19), 73.6 (C-20), 26.2 (C-21), 36.1 (C-22), 22.2 (C-23), 125.2 (C-24), 131.3 (C-25), 25.7 (C-26), 17.7 (C-27), 26.8 (C-28), 20.9 (C-29), 17.2 (C-30), 21.5 ($\underline{C}$H$_3$CO), 169.6 (CH$_3\underline{C}$O). EI-MS *m/z*: 500 ($M^+$), 482, 440.

**Hydroxyhopanone (4)** Colorless needles from MeOH, mp 247—252 °C, $[\alpha]_D$ +54° (*c*=0.5, $CHCl_3$). $^1$H-NMR ($CDCl_3$) $\delta$: 0.76 (3H, s), 0.92 (3H, s), 0.96 (3H, s), 1.00 (3H, s), 1.02 (3H, s), 1.07 (3H, s), 1.18 (3H, s), 1.20 (3H, s). $^{13}$C-NMR ($CDCl_3$) $\delta$: 39.6 (C-1), 34.2 (C-2), 218.8 (C-3), 47.4 (C-4), 54.9 (C-5), 19.8 (C-6), 32.6 (C-7), 41.7 (C-8), 49.7 (C-9), 36.9 (C-10), 21.6 (C-11), 24.1 (C-12), 50.0 (C-13), 41.9 (C-14), 34.4 (C-15), 21.9 (C-16), 53.9 (C-17), 44.1 (C-18), 41.3 (C-19), 26.6 (C-20), 51.1 (C-21), 74.1 (C-22), 26.6 (C-23), 21.1 (C-24), 15.7 (C-25), 16.5 (C-26), 16.9 (C-27), 16.2 (C-28), 28.7 (C-29), 30.7 (C-30). EI-MS *m/z*: 442 ($M^+$), 424, 409, 384, 236, 189, 149.

**Caryophyllene Oxide (5)** Colorless oil, $[\alpha]_D$ −40° (*c*=1.0, $CHCl_3$). $^1$H-NMR ($CDCl_3$) $\delta$: 0.99 (3H, s), 1.01 (3H, s), 1.20 (3H, s), 2.88 (1H, dd, *J*=10.4, 4.0 Hz), 4.86 (1H, br s), 4.97 (1H, br s). $^{13}$C-NMR ($CDCl_3$) $\delta$: 50.7 (C-1), 27.2 (C-2), 39.1 (C-3), 59.8 (C-4), 63.7 (C-5), 30.2 (C-6), 29.8 (C-7), 151.8 (C-8), 48.7 (C-9), 39.7 (C-10), 34.0 (C-11), 29.9 (C-12), 21.6 (C-13), 112.7 (C-14), 17.0 (C-15). EI-MS *m/z*: 220 ($M^+$), 205, 187, 177.

**Kaempferol 3-*O*-(4-*O*-Acetyl)-α-L-rhamnopyranoside (6)** A yellow amorphous powder, $[\alpha]_D$ −138° (*c*=1.0, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log ε): 342 (4.04), 262 (4.30). $^1$H-NMR (DMSO-$d_6$) $\delta$: 0.70 (3H, d, *J*=6.3 Hz), 2.00 (3H, s), 3.26 (1H, dq, *J*=9.9, 5.9 Hz), 3.70 (1H, dd, *J*=9.9, 3.0 Hz), 4.03 (1H, dd, *J*=3.0, 1.0 Hz), 4.70 (1H, t, *J*=9.9 Hz), 5.29 (1H, d, *J*=1.0 Hz), 6.23 (1H, d, *J*=1.0 Hz), 6.43 (1H, d, *J*=1.0 Hz), 6.95 (2H, d, *J*=8.6 Hz), 7.74 (2H, d, *J*=8.6 Hz), 12.58 (1H, s). $^{13}$C-NMR (DMSO-$d_6$) $\delta$: 156.6 (C-2), 134.0 (C-3), 177.6 (C-4), 160.2 (C-5), 98.8 (C-6), 164.4 (C-7), 93.8 (C-8), 157.4 (C-9), 104.1 (C-10), 120.3 (C-1′), 130.6 (C-2′,6′), 115.3 (C-3′,5′), 161.3 (C-4′), 101.4 (C-1″), 69.9 (C-2″), 67.9 (C-3″), 73.1 (C-4″), 67.8 (C-5″), 17.1 (C-6″), 169.9 and 20.9 (Ac). HR-FAB-MS (negative mode) *m/z*: 473.106 $[M-H]^-$, Calcd for $C_{23}H_{21}O_{11}$: 473.108. On alkaline methanolysis, **6** gave afzelin which was identified by direct comparison with an authentic sample.

**Quercetin 3-*O*-(4-*O*-Acetyl)-α-L-rhamnopyranoside (7)** A yellow crystalline powder, mp 171—176 °C, $[\alpha]_D$ −158° (*c*=1.0, MeOH). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3400, 1719, 1644, 1559, 1495, 1437, 1349, 1293, 1255, 1194, 1160, 950. UV $\lambda_{max}^{MeOH}$ nm (log ε): 348 (4.21), 256 (4.35). $^1$H-NMR (DMSO-$d_6$) $\delta$: 0.73 (3H, d, *J*=6.3 Hz), 2.01 (3H, s), 3.40 (1H, dq, *J*=9.9, 6.3 Hz), 3.75 (1H, dd, *J*=9.9, 3.0 Hz), 4.04 (1H, dd, *J*=3.0, 1.0 Hz), 4.72 (1H, t, *J*=9.9 Hz), 5.24 (1H, d, *J*=1.0 Hz), 6.22 (1H, d, *J*=2.0 Hz), 6.40 (1H, d, *J*=2.0 Hz), 6.91 (1H, d, *J*=8.3 Hz), 7.24 (1H, dd, *J*=8.3, 2.0 Hz), 7.30 (1H, d, *J*=2.0 Hz), 12.61 (1H, s). $^{13}$C-NMR (DMSO-$d_6$) $\delta$: 156.5 (C-2), 134.0 (C-3), 177.6 (C-4), 161.3 (C-5), 98.9 (C-6), 164.6 (C-7), 93.7 (C-8), 157.5 (C-9), 104.0 (C-10), 121.0 (C-1′), 115.5 (C-2′), 145.3 (C-3′), 148.6 (C-4′), 115.8 (C-5′), 120.6 (C-6′), 101.5 (C-1″), 70.0 (C-2″), 67.9 (C-3″), 73.2 (C-4″), 67.9 (C-5″), 17.1 (C-6″), 170.0 and 20.9 (Ac). HR-FAB-MS (negative mode) *m/z*: 489.105 $[M-H]^-$, Calcd for $C_{23}H_{21}O_{12}$: 489.103.

**Rhododendrin (=Betuloside) (17)** Colorless needles from MeOH–$H_2O$, mp 191—193 °C, $[\alpha]_D$ −48° (*c*=1.0, MeOH). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3350, 2915, 1611, 1507, 1444, 1377, 1248, 1166, 1103, 1057, 1026, 826, 612. UV $\lambda_{max}^{MeOH}$ nm (log ε): 278 (3.43). $^1$H-NMR ($CD_3OD$) $\delta$: 1.19 (3H, d, *J*=6.1 Hz), 4.32 (1H, d, *J*=7.9 Hz), 6.67 (2H, d, *J*=10.2 Hz), 7.02 (2H, d, *J*=10.2 Hz). $^{13}$C-NMR ($CD_3OD$) $\delta$: 19.9 (C-1), 74.9 (C-2), 40.9 (C-3), 31.7 (C-4), 134.4 (C-1′), 130.2 (C-2′, 6′), 115.9 (C-3′, 5′), 156.0 (C-4′), 102.0 (Glc-1), 75.0 (Glc-2), 78.0 (Glc-3), 71.6 (Glc-4), 77.6 (Glc-5), 62.7 (Glc-6). HR-FAB-MS *m/z*: 328.151 $[M^+]$, Calcd for $C_{16}H_{24}O_7$: 328.152. On acid hydrosis with 3% HCl, **17** gave (−)-rhododendrol and D-glucose, $[\alpha]_D$ +50° (*c*=1.0, $H_2O$).

**(−)-Rhododendrol (=Betuligenol) (17a)** A colorless amorphous powder, $[\alpha]_D$ −16° (*c*=1.0, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log ε): 276(3.76). $^1$H-NMR ($CD_3OD$) $\delta$: 1.17 (3H, d, *J*=6.3 Hz), 1.65 (2H, m), 2.58 (2H, m), 3.76 (1H, m), 6.68 (2H, d, *J*=8.4 Hz), 7.00 (2H, d, *J*=8.4 Hz). $^{13}$C-NMR ($CD_3OD$) $\delta$: 23.6 (C-1), 67.9 (C-2), 42.4 (C-3), 32.3 (C-4), 134.4 (C-1′), 130.3 (C-2′, 6′), 116.1 (C-3′, 5′), 156.3 (C-4′). EI-MS *m/z*: 166 ($M^+$), 148, 133, 107, 77.

**Aceroside VII (18)** A colorless amorphous powder, $[\alpha]_D$ −30° (*c*=1.0, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log ε): 279 (3.56). $^1$H-NMR ($C_5D_5N$) $\delta$: 1.5—2.9 (12H), 3.98 (1H, ddd, *J*=9.2, 5.2, 2.4 Hz), 4.96 (1H, d, *J*=7.6 Hz), 7.17 (4H, d, *J*=8.5 Hz), 7.19 (2H, d, *J*=8.5 Hz), 7.32 (2H, d, *J*=8.5 Hz). $^{13}$C-NMR ($C_5D_5N$) $\delta$: 31.1 (C-1), 37.7 (C-2), 78.5 (C-3), 34.4 (C-4), 25.0 (C-5), 32.5 (C-6), 35.3 (C-7), 133.6 (C-1′ or 1″), 133.4 (C-1′ or 1″), 130.1 (C-2′, 6′ or 2″, 6″), 129.8 (C-2′, 6′ or 2″, 6″), 116.1 (C-4′, 4″), 103.6 (Glc-1), 75.4 (Glc-2), 78.6 (Glc-3), 71.8 (Glc-4), 78.2 (Glc-5), 63.0 (Glc-6). FAB-MS *m/z*: 463 $[M+H]^+$, 375, 301, 283, 185, 145, 137, 107.

**Aceroside VIII (19)** A colorless amorphous powder, $[\alpha]_D$ −48° (*c*=1.0, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log ε): 279 (3.81). $^1$H-NMR ($C_5D_5N$) $\delta$: 1.4—3.1 (12H), 4.90 (1H, d, *J*=7.6 Hz), 5.81 (1H, d, *J*=2.4 Hz), 7.17 (4H, d, *J*=8.5 Hz), 7.23 (2H, d, *J*=8.5 Hz), 7.32 (2H, d, *J*=8.5 Hz). $^{13}$C-NMR ($C_5D_5N$) $\delta$: 31.2 (C-1), 37.8 (C-2), 78.5 (C-3), 34.6 (C-4), 25.0 (C-5), 32.5 (C-6), 35.2 (C-7), 133.8 (C-1′ or 1″), 133.4 (C-1′ or 1″), 130.1 (C-2′, 6′ or 2″, 6″), 129.8 (C-2′, 6′ or 2″, 6″), 116.1 (C-3′, 5′ or 3″, 5″), 116.0 (C-3′, 5′ or 3″, 5″), 156.8 (C-4′ or 4″), 156.7 (C-4′ or 4″), 103.5 (Glc-1), 75.2 (Glc-2), 78.6 (Glc-3), 71.6 (Glc-4), 76.8 (Glc-5), 68.6 (Glc-6), 111.0 (Api-1), 77.8 (Api-2), 80.4 (Api-3), 74.9 (Api-4), 65.6 (Api-5). FAB-MS *m/z*: 595 $[M+H]^+$, 300, 283, 185, 133, 107.

**1,7-Bis[4-hydroxyphenyl]-3-hepten-5-one (20)** A colorless oil. UV $\lambda_{max}^{MeOH}$ nm (log ε): 225 (4.20), 278 (3.67). $^1$H-NMR ($CDCl_3$–$CD_3OD$, 1 : 1) $\delta$: 2.49 (2H, t, *J*=7.3 Hz), 2.67 (2H, t, *J*=7.3 Hz), 2.80 (4H, s), 6.07 (1H, br d, *J*=16.2 Hz), 6.74 (4H, d, *J*=7.3 Hz), 6.85 (1H, dt, *J*=16.2, 7.3 Hz), 6.99 (4H, d, *J*=7.3 Hz). $^{13}$C-NMR ($C_5D_5N$) $\delta$: 34.7 (C-1), 33.8 (C-2), 146.5 (C-3), 131.1 (C-4), 199.2 (C-5), 42.2 (C-6), 29.7 (C-7), 131.7 and 132.2 (C-1′ and 1″), 129.9 and 130.0 (C-2′, 6′ and 2″, 6″), 116.3 (C-3′, 5′, 3″, 5″), 157.3 and 157.2 (C-4′ and 4″). HR-EI-MS *m/z*: 296.142, Calcd for $C_{19}H_{20}O_3$: 296.141.

**2-Hydroxy-1,7-bis[4-hydroxyphenyl]-3-hepten-5-one (21)** A colorless oil. UV $\lambda_{max}^{MeOH}$ nm (log ε): 224 (4.16), 278 (3.64). $^1$H-NMR ($CD_3OD$) $\delta$: 2.7—2.8 (6H), 4.39 (1H, tdd, *J*=6.7, 5.2, 1.5 Hz), 6.18 (1H, dd, *J*=15.9, 1.5 Hz), 6.68 (2H, d, *J*=8.6 Hz), 6.70 (2H, d, *J*=8.6 Hz), 6.81 (1H, dd, *J*=15.9, 5.2 Hz), 6.84 (2H, d, *J*=8.6 Hz), 7.02 (2H, d, *J*=8.6 Hz). $^{13}$C-NMR ($CD_3OD$) $\delta$: 40.1 (C-1), 73.3 (C-2), 150.5 (C-3), 131.6 (C-4), 202.7 (C-5), 43.5 (C-6), 30.6 (C-7), 129.7 and 133.2 (C-1′ and 1″), 129.3 and 130.3 (C-2′, 6′ and 2″, 6″), 116.1 and 116.2 (C-3′, 5′ and 3″, 5″), 156.1 and 156.7 (C-4′ and 4″). HR-EI-MS *m/z*: 312.137, Calcd for $C_{19}H_{20}O_4$: 312.136.

**(3*R*)-3,5′-Dihydroxy-4′-methoxy-3′,4″-oxo-1,7-diphenyl-1-heptene (23)** A colorless crystalline powder from *n*-hexane–EtOAc, mp 186—187 °C, $[\alpha]_D$ +79° (*c*=1.0, $CHCl_3$). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3300, 3010, 2940, 2860, 1574, 1500, 1425, 1400, 1350, 1250, 1208, 1170, 1130, 1100, 1035, 1012, 995, 920, 865, 830, 770. UV $\lambda_{max}^{MeOH}$ nm (log ε): 223 (4.39), 258 (3.95). $^1$H-NMR ($CDCl_3$) $\delta$: 2.43 (1H, td, *J*=12.8, 5.5 Hz, H-7), 3.02 (1H, ddd, *J*=12.8, 4.9, 2.8 Hz, H-7), 3.95 (1H, ddd, *J*=11.3, 8.6, 3.1 Hz, H-3), 4.11 (3H, s, C$\underline{H}_3$O–), 5.17 (1H, d, *J*=2.1 Hz, H-2′), 5.30 (1H, dd, *J*=11.3, 8.6 Hz, H-2), 6.11 (1H, d, *J*=11.3 Hz, H-1), 6.38 (1H, d, *J*=2.1 Hz, H-6′), 7.01 (1H, dd, *J*=8.2, 2.4 Hz, H-3″ or 5″), 7.12 (1H, dd, *J*=8.2, 2.4 Hz, H-3″ or 5″), 7.30 (1H, dd, *J*=8.2, 2.1 Hz, H-2″ or 6″), 7.33 (1H, dd, *J*=8.2, 2.1 Hz, H-2″ or 6″). $^{13}$C-NMR ($CDCl_3$) $\delta$: 127.8 (C-1), 135.3 (C-2), 69.1 (C-3), 37.5 (C-4), 22.0 (C-5), 28.8 (C-6), 35.6 (C-7), 132.1 (C-1′), 109.0 (C-2′), 153.5 (C-3′), 134.5 (C-4′), 149.3 (C-5′), 108.8 (C-6′), 139.2 (C-1″), 130.1 (C-2″ or 6″), 123.9 (C-3″ or 5″), 154.1 (C-4″), 122.3 (C-3″ or 5″), 132.7 (C-2″ or 6″), 61.4 (C$\underline{H}_3$O–). HR-EI-MS *m/z*: 326.152, Calcd for $C_{20}H_{22}O_4$: 326.152.

**Methylation of 23** A solution of $CH_2N_2$ in ether (9 ml) was added to a solution of **23** (22 mg) in MeOH and the mixture was allowed to stand at room temperature for 12 h. Then the reaction mixture was concentrated *in vacuo* and the residue was crystallized (AcOEt–*n*-hexane) to afford **23a** (15 mg) as a colorless crystalline powder.

**Compound 23a** A colorless crystalline powder, mp 132—135 °C, $[\alpha]_D$ +141° (*c*=1.0, $CHCl_3$). UV $\lambda_{max}^{MeOH}$ nm (log ε): 222 (4.40), 261 (4.07). $^1$H-NMR ($CDCl_3$) $\delta$: 2.43 (1H, td, *J*=12.8, 5.2 Hz, H-7), 3.02 (1H, ddd, *J*=12.8, 4.6, 2.8 Hz, H-7), 3.85 (3H, s, C$\underline{H}_3$O–), 4.03 (3H, s, C$\underline{H}_3$O–), 5.27 (1H, d, *J*=2.1 Hz, H-2′), 5.32 (1H, dd, *J*=11.9, 8.3 Hz, H-2), 6.16 (1H, d, *J*=11.9 Hz, H-1), 6.33 (1H, d, *J*=2.1 Hz, H-6′), 7.01 (1H, dd, *J*=8.2, 2.4 Hz, H-3″ or 5″), 7.13 (1H, dd, *J*=8.2, 2.4 Hz, H-2″ or 6″), 7.29 (1H, dd, *J*=8.2, 2.1 Hz, H-2″ or 6″), 7.33 (1H, dd, *J*=8.2, 2.1 Hz,

H-3″ or 5″). $^{13}$C-NMR ($CDCl_3$) $\delta$: 127.8 (C-1), 135.4 (C-2), 69.1 (C-3), 37.5 (C-4), 22.0 (C-5), 28.8 (C-6), 35.6 (C-7), 131.6 (C-1′), 109.8 (C-2′ or 6′), 153.5 (C-3′), 137.0 (C-4′), 154.6 (C-5′), 106.0 (C-2′ or 6′), 139.0 (C-1″), 130.1 (C-2″ or 6″), 124.0 (C-3″ or 5″), 154.5 (C-4″), 122.4 (C-3″ or 5″), 132.6 (C-2″ or 6″), 61.3 (C$H_3$O–), 56.2 (C$H_3$O–). HR-EI-MS *m/z*: 340.166 [$M^+$], Calcd for $C_{21}H_{24}O_4$: 340.167.

**MTPA Ester of 23a** (*S*) or (*R*)-MTPA chloride (6 mg) was added to a solution of **23a** (7 mg) in dry pyridine (1 ml) and the mixture was stirred at room temperature for 15 h. The reaction mixture was then poured into water and extracted with $CHCl_3$ and the extract was concentrated *in vacuo*. The residue was purified by preparative thin-layer chromatography (TLC) to give **23b** or **23c** as a colorless oil.

**(*S*)-MTPA Ester (23b)** A colorless oil, $[\alpha]_D$ −21° (*c*=2.3, $CHCl_3$). IR $\nu_{max}^{CHCl_3\ soln.}$ $cm^{-1}$: 3010, 2920, 1740, 1572, 1495, 1445, 1090, 992. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 222 (4.40), 263 (4.02). $^1$H-NMR ($CDCl_3$) $\delta$: 0.31—0.38 (1H, m, H-4), 0.88—0.98 (1H, m, H-5), 1.13—1.23 (1H, m, H-6), 1.50—1.60 (1H, m, H-4), 1.62—1.73 (1H, m, H-5), 2.00—2.08 (1H, m, H-6), 2.41 (1H, td, *J*=12.8, 5.2 Hz, H-7), 3.02 (1H, ddd, *J*=12.8, 4.9, 2.1 Hz, H-7), 3.52 (3H, s, MTPA-OC$H_3$), 3.87 (3H, s, 5′-OC$H_3$), 4.05 (3H, s, 4′-OC$H_3$), 5.05 (1H, dd, *J*=11.9, 8.6 Hz, H-2), 5.18 (1H, ddd, *J*=11.6, 8.6, 3.1 Hz, H-3), 5.27 (1H, d, *J*=2.1 Hz, H-2′), 6.25 (1H, d, *J*=11.9 Hz, H-1), 6.38 (1H, d, *J*=2.1 Hz, H-6′), 7.12 (1H, dd, *J*=8.2, 2.1 Hz), 7.15 (1H, dd, *J*=8.2, 2.1 Hz), 7.28—7.34 (2H), 7.37—7.41 (3H), 7.44—7.47 (2H). HR-EI-MS *m/z*: 556.207 [$M^+$], Calcd for $C_{31}F_3H_{31}O_6$: 556.207.

**(*R*)-MTPA Ester (23c)** A colorless oil, $[\alpha]_D$ +93° (*c*=0.3, $CHCl_3$). IR $\nu_{max}^{CHCl_3\ soln.}$ $cm^{-1}$: 3010, 2920, 2850, 1740, 1572, 1495, 1445, 1415, 1390, 1322, 1232, 1090, 992, 855. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 222 (4.48), 263 (4.04). $^1$H-NMR ($CDCl_3$) $\delta$: 0.38—0.46 (1H, m, H-4), 0.77—0.85 (1H, m, H-5), 1.08—1.17 (1H, m, H-6), 1.32—1.42 (1H, m, H-4), 1.46—1.55 (1H, m, H-5), 1.87—1.95 (1H, m, H-6), 2.37 (1H, td, *J*=12.8, 5.2 Hz, H-7), 2.96 (1H, ddd, *J*=12.8, 4.9, 2.7 Hz, H-7), 3.49 (3H, s, MTPA-OC$H_3$), 3.86 (3H, s, 5′-OC$H_3$), 4.05 (3H, s, 4′-OC$H_3$), 5.26 (1H, dd, *J*=11.9, 8.5 Hz, H-2), 5.26—5.32 (1H, m, H-3), 5.29 (1H, d, *J*=2.1 Hz, H-2′), 6.28 (1H, d, *J*=11.9 Hz, H-1), 6.36 (1H, d, *J*=2.1 Hz, H-6′), 7.11 (1H, dd, *J*=8.0, 2.1 Hz), 7.14 (1H, dd, *J*=8.0, 2.1 Hz), 7.27—7.31 (2H), 7.37—7.42 (3H), 7.48—7.52 (2H). HR-EI-MS *m/z*: 556.206, Calcd for $C_{31}F_3H_{31}O_6$: 556.207.

**Dammarenediol II 3-*O*-*p*-Coumarate (26)** A colorless amorphous powder, $[\alpha]_D$ −16° (*c*=0.5, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 329 (4.23). $^1$H-NMR ($CDCl_3$) $\delta$: 0.889, 0.893, 0.90, 0.93, 0.97, 1.15, 1.63, 1.69 (each 3H, s), 4.62 (1H, dd, *J*=10.7, 4.9 Hz), 5.12 (1H, br t, *J*=7.0 Hz), 6.30 (1H, d, *J*=15.9 Hz), 6.84 (2H, d, *J*=8.9 Hz), 7.43 (2H, d, *J*=8.9 Hz), 7.61 (1H, d, *J*=15.9 Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$: 38.8 (C-1), 23.8 (C-2), 80.9 (C-3), 38.2 (C-4), 56.0 (C-5), 18.2 (C-6), 35.2 (C-7), 40.4 (C-8), 50.6 (C-9), 37.1 (C-10), 21.6 (C-11), 27.5 (C-12), 42.3 (C-13), 50.3 (C-14), 31.2 (C-15), 24.8 (C-16), 49.8 (C-17), 15.5 (C-18), 16.3 (C-19), 75.6 (C-20), 25.4 (C-21), 40.5 (C-22), 22.6 (C-23), 124.7 (C-24), 131.7 (C-25), 25.7 (C-26), 17.7 (C-27), 28.0 (C-28), 16.7 (C-29), 16.5 (C-30), 127.3 (C-1′), 129.9 (C-2′, 6′), 115.9 (C-3′, 5′), 157.7 (C-4′), 144.0 (C-7′), 116.3(C-8′), 167.3 (C-9′). HR-EI-MS *m/z*: 590.435, Calcd for $C_{39}H_{58}O_4$: 590.433. On alkaline methanolysis, **26** gave dammarenediol II and methyl *p*-coumarate. Dammarenediol II: $[\alpha]_D$ +15° (*c*=0.2, $CHCl_3$). $^{13}$C-NMR ($CDCl_3$) $\delta$: 39.0 (C-1), 27.4 (C-2), 79.0 (C-3), 39.0 (C-4), 55.8 (C-5), 18.3 (C-6), 35.2 (C-7), 40.3 (C-8), 50.6 (C-9), 37.1 (C-10), 21.5 (C-11), 27.5 (C-12), 42.3 (C-13), 50.3 (C-14), 31.2 (C-15), 24.8 (C-16), 49.8 (C-17), 15.5 (C-18), 16.2 (C-19), 75.4 (C-20), 25.4 (C-21), 40.5 (C-22), 22.5 (C-23), 124.7 (C-24), 131.6 (C-25), 25.7 (C-26), 17.7 (C-27), 28.0 (C-28), 15.3 (C-29), 16.4 (C-30). The $^{13}$C-NMR data were identical with those reported.[27]

**Ocotillol II 3-*O*-Caffeate (28)** A colorless crystalline powder from EtOAc, mp 222—224 °C, $[\alpha]_D$ −10° (*c*=0.5, MeOH). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3450, 1705, 1178. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 329 (4.31). $^1$H-NMR ($CDCl_3$) $\delta$: 0.85, 0.87, 0.88, 0.91, 0.95, 1.14, 1.15, 1.24 (each 3H, s), 4.59 (1H, dd, *J*=9.0, 7.0 Hz), 6.25 (1H, d, *J*=16 Hz), 6.87 (1H, d, *J*=8 Hz), 6.99 (1H, dd, *J*=8.5, 1.5 Hz), 7.10 (1H, d, *J*=1.5 Hz), 7.56 (1H, d, *J*=16 Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$: 38.7 (C-1), 23.8 (C-2), 81.1 (C-3), 38.1 (C-4), 56.0 (C-5), 18.2 (C-6), 35.2 (C-7), 40.4 (C-8), 50.7 (C-9), 37.1 (C-10), 21.6 (C-11), 25.8 (C-12), 43.0 (C-13), 50.1 (C-14), 31.5 (C-15), 27.5 (C-16), 49.4 (C-17), 15.4 (C-18), 16.3 (C-19), 86.7 (C-20), 23.8 (C-21), 35.4 (C-22), 26.2 (C-23), 83.2 (C-24), 72.1 (C-25), 24.1 (C-26), 27.5 (C-27), 28.0 (C-28), 16.7 (C-29), 16.5 (C-30), 127.3 (C-1′), 129.9 (C-2′, 6′), 115.9 (C-3′, 5′), 157.7 (C-4′), 144.0 (C-7′), 116.3 (C-8′), 167.3 (C-9′). HR-EI-MS *m/z*: 622.423, Calcd for $C_{39}H_{58}O_6$: 622.423. On alkaline methanolysis, **28** gave ocotillol II and methyl caffeate. Ocotillol II: $[\alpha]_D$ +28° (*c*=0.5, $CHCl_3$). $^{13}$C-NMR ($CDCl_3$) $\delta$: 39.1 (C-1), 27.4 (C-2), 79.0 (C-3), 39.0 (C-4), 55.9 (C-5), 18.3 (C-6), 35.3 (C-7), 40.4 (C-8), 50.8 (C-9), 37.2 (C-10), 21.6 (C-11), 25.7 (C-12), 43.0 (C-13), 50.0 (C-14), 31.5 (C-15), 27.4 (C-16), 49.5 (C-17), 15.4 (C-18), 16.2 (C-19), 86.4 (C-20), 23.5 (C-21), 35.7 (C-22), 26.1 (C-23), 83.3 (C-24), 71.5 (C-25), 24.3 (C-26), 27.5 (C-27), 28.0 (C-28), 15.3 (C-29), 16.5 (C-30). The $^{13}$C-NMR data were identical with those previously reported.[28]

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