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Constituents of *Myrica rubra*. III.[1] Structures of Two Glycosides of Myricanol

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Two new diarylheptanoid glycosides (**1** and **2**) were isolated together with vanillic acid and six known triterpenoids, maslinic acid, alphitolic acid, arjunolic acid, myricolal, oleanolic acid and oleanolic acid acetate, from the stem bark of *Myrica rubra* SIEB. *et* ZUCC. (Myricaceae). On the basis of spectral and chemical evidence, the structures of **1** and **2** were established as myricanol 5-*O*-*β*-D-(6′-*O*-galloyl)-glucopyranoside and myricanol 5-*O*-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranoside, respectively.

Keywords——*Myrica rubra*; Myricaceae; diarylheptanoid glycoside; myricanol galloylglucoside; myricanol gentiobioside; maslinic acid; alphitolic acid; arjunolic acid; myricolal; vanillic acid

Previously we have reported the isolation and characterization of triterpenoids, taraxerol, taraxerone and 28-hydroxy-D-friedoolean-14-en-3-one,[1] and diarylheptanoids, myricanol, myricanone, and myricanol glucoside,[2] from the stem bark of *Myrica rubra* SIEB. *et* ZUCC. (Myricaceae). Myricanol, myricanone and 13-oxomyricanol have been isolated from *M. nagi*[3] and porson,[4a] galeon and hydroxygaleon[4b] from *M. gale*. Recently, myricanol, myricanone, porson and 5-deoxymyricanone were obtained from the bacterial gall of *M. rubra*.[5]

In a continuation of our chemical studies on the bark of *M. rubra*, we isolated two new diarylheptanoid glycosides, named myricanol galloylglucoside (**1**) and myricanol gentiobioside (**2**), together with six known triterpenoids and a phenol carboxylic acid, oleanolic acid (**3**), oleanolic acid acetate (**4**), maslinic acid (**5**), alphitolic acid (**6**), arjunolic acid (**7**) and myricolal (**8**), and vanillic acid (**9**). The present paper deals with the isolation and structure elucidation of these compounds on the basis of spectral and chemical evidence. The extraction and separation were carried out as described in the experimental section.

Compound **1**, a white crystalline powder mp 267—269 °C, $[\alpha]_D$ −78.4°, $C_{34}H_{40}O_{14}$, showed an intense blue coloration with the ferric chloride reagent. The infrared (IR) spectrum showed strong hydroxyl (3450 cm^{-1}), carbonyl (1720 cm^{-1}) and aromatic ring (1595 and 1510 cm^{-1}) absorptions. The ultraviolet (UV) spectrum of **1** showed absorption maxima at 256 and 285 nm. The ^1H- nuclear magnetic resonance (^1H-NMR) spectrum exhibited two three-proton singlets due to methoxyl groups at δ 4.03 and 4.10 ppm, and a two-proton singlet due to galloyl protons at δ 7.15 ppm. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum showed signals indicating the presence of three benzene rings, six methylenes, two methoxyls, a methine bearing a hydroxy group, a sugar moiety and an ester carbonyl. The anomeric signal in the sugar was observed at δ 105.8 ppm. The spectral data were very similar to those of myricanol glucoside (**12**), except for the galloyl group (Table. I). On acid hydrolysis, **1** afforded an aglycone (**10**), gallic acid (**11**) and glucose. Compound **10** was identified as myricanol (**10**) by direct comparison with an authentic sample. Enzymatic hydrolysis of **1** with tannase from *Aspergillus niger*[6] yielded colorless crystals (**12**), mp 220—

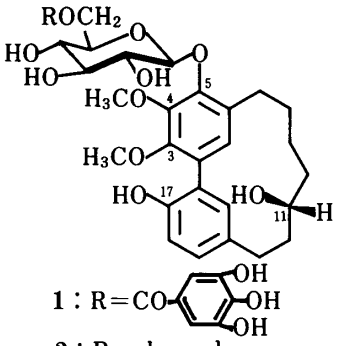
23 °C, and gallic acid (**11**). By direct comparison with an authentic sample, **12** was identified as myricanol glucoside.[2] Therefore, **1** is a gallate of myricanol glucoside. The location of the galloyl group in **1** was determined as follows. The electron impact-mass spectrum (MS) of **1** showed a peak at *m/z* 358 due to elimination of the galloylated glycosyl moiety. The ^{1}H-NMR spectrum of **1** showed a doublet (J=2.9 Hz) at a lower field (δ 4.98 ppm) due to methylene protons adjacent to the galloyl group. Comparison of the ^{13}C-NMR spectrum of **1** with that of **12** revealed that the signals assignable to C-5 and C-6 of the glucose moiety were shifted by *ca.* −2.7 and +1.3 ppm by the acylation,[7] respectively, while other signals remained almost unchanged. Consequently, the galloyl group of **1** is located at C-6 in the glucose moiety: Thus, the structure of **1** was established as myricanol 5-*O*-β-D-(6′-*O*-galloyl)-glucopyranoside.

Compound **2**, an off-white powder, $[\alpha]_D$ −64.6°, $C_{33}H_{46}O_{15}\cdot 2.5H_2O$, showed a strong hydroxyl absorption at 3360 cm^{-1} in its IR spectrum. The MS of **2** showed the same peak at *m/z* 358 arising from the elimination of the sugar moiety as compound **1**. The ^{1}H-NMR spectrum of **2** showed two methoxyl signals at δ 4.03 and 4.11 ppm. The ^{13}C-NMR spectrum of **2** showed signals indicating the presence of two benzene rings, six methylene carbons, a methine bearing a hydroxyl group, and two hexoses. The anomeric carbons appeared at δ 105.3 and 105.8 ppm (Table I). On acid hydrolysis, **2** gave glucose as the sugar moiety and myricanol (**10**) as the aglycone moiety. Therefore, **2** was suggested to be a diglucoside of myricanol. Methylation of **2** with dimethyl sulfate followed by hydrolysis with 35% HCl yielded a monomethylated genin (**13**) and a dimethylated genin (**14**). In the IR spectrum of a diluted solution in carbon tetrachloride, **13** showed absorptions due to hydroxyl groups at 3630 and 3530 cm^{-1} (11-OH and 5-OH, respectively). Compound **13** was found to be identical (thin layer chromatography (TLC) and ^{1}H-NMR spectrum) with an authentic sample of myricanol 17-methyl ether. The ^{1}H-NMR spectrum of **14** exhibited a three-proton singlet due to a methyl group linked to an alcoholic hydroxyl group at δ 3.21 ppm, together with three three-proton singlets due to anisole methoxyl protons at δ 3.88, 3.89 and 3.98 ppm. Compound **14** was concluded to be myricanol 11, 17-dimethyl ether. The binding position of the sugar moiety in **2** was thus confirmed to be at C-5 in myricanol. Comparison of the ^{13}C-NMR chemical shifts of **2** with those of myricanol glucoside (**12**) revealed that the signals assignable to C-5 and C-6 of the glucose moiety of **12** were shifted by −1.0 and +7.7 ppm by glucosylation,[8] respectively, while other signals were almost unchanged. Thus **2** was confirmed to be myricanol 5-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside or myricanol

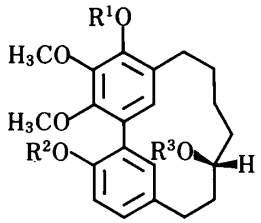
TABLE I. ^{13}C-NMR Spectral Data[a] (Sugar and Galloyl Moieties)

Carbon No.		**1**	**2**	**12**
Glucose	1′	105.78	105.80	105.40
	2′	75.65[b]	75.12	75.71
	3′	78.20	78.37	78.32
	4′	71.08	71.51	71.52
	5′	75.73[b]	77.37	78.40
	6′	63.90	70.23	62.57
Galloyl or glucose	1″	121.22	105.30	
	2″	110.23	75.71	
	3″	147.42	78.37	
	4″	140.79	71.60	
	5″	147.42	78.37	
	6″	110.23	62.72	
	COO	167.14		

a) Measurements in pyridine-d_5 at 100 MHz with TMS as an internal standard. *b*) Assignments may be interchanged.



1 : R=CO-(OH, OH, OH)
2 : R=glucosyl
12 : R=H



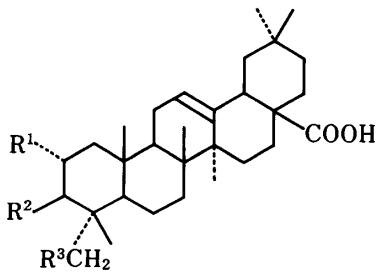
10 : $R^1=R^2=R^3=H$
13 : $R^1=R^3=H$, $R^2=CH_3$
14 : $R^1=H$, $R^2=R^3=CH_3$

Chart 1

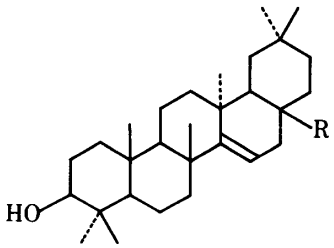
5-*O*-*β*-gentiobioside.

Compounds **3** and **4** were identified as oleanolic acid and its acetate. Compound **5**, mp 259—264 °C, $C_{30}H_{48}O_4$, was isolated as colorless needles. The ^{1}H-NMR spectrum of **5** showed the presence of the diequatorial 2*α*,3*β*-hydroxyl groups: the H-2 and H-3 signals appeared at δ 3.70 and 3.04 ppm, respectively ($J_{2a,1a}=J_{2a,3a}=10$ Hz; $J_{2a,1e}=4$ Hz). Methylation of **5** with diazomethane gave a methyl ester (**5a**). Compound **5a** was identified as maslinic acid methyl ester[9] by comparison with an authentic sample. Compound **6**, mp 294—298 °C, $C_{30}H_{48}O_4$ was isolated as colorless needles. The ^{1}H-NMR spectrum of **6** showed signals due to five methyl groups and an isopropenyl group and the signals due to H-2 and H-3 at δ 4.08 and 3.38 ppm, respectively. Methylation of **6** gave a methyl ester (**6a**). Compounds **6** and **6a** were identified as alphitolic acid and its methyl ester,[10] respectively, by comparisons with authentic samples. Compound **7**, mp 295—297 °C, $C_{30}H_{48}O_5 \cdot 0.5\ H_2O$, was isolated as colorless needles. Acetylation of **7** yielded a triacetate (**7a**). The ^{1}H-NMR of **7a** showed an AB quartet ($J=12$ Hz) due to H_2-23 at δ 3.58 and 3.86 ppm and a two-proton multiplet due to H-2 and H-3 at δ 5.10 ppm. Compound **7** was identified as arjunolic acid[11] by comparison with an authentic sample. Compound **8**, mp 269—271 °C, $C_{30}H_{48}O_2$, was isolated as colorless needles. From the ^{13}C-NMR and MS data, **8** was considered to be a Δ^{14}-friedooleane type triterpene having an aldehyde group. Reduction of **8** with sodium borohydride yielded compound **15**, which was identified as myricadiol by comparison with an authentic sample. Compound **8** was established to be myricolal[12] by comparison of the ^{1}H- and ^{13}C-NMR data with those of myricadiol.

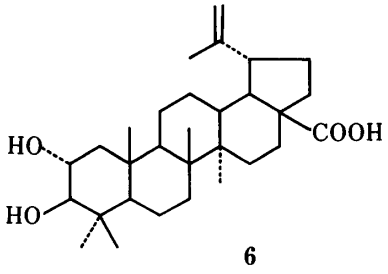
Compound **9** was isolated as an off-white powder. On methylation **9** gave a methyl ester (**9a**). Compounds **9** and **9a** were identified as vanillic acid and its methyl ester by comparison with authentic samples.



3 : $R^1=R^3=H$, $R^2=OH$
4 : $R^1=R^3=H$, $R^2=OCOCH_3$
5 : $R^1=R^2=OH$, $R^3=H$
7 : $R^1=R^2=R^3=OH$



8 : R=CHO
15 : $R=CH_2OH$



6

Chart 2

Various diarylheptanoids of linear and cyclic types have so far been isolated from several families, but they have rarely been obtained as glycosides. Compounds **1** and **2** are the first examples of a galloylglucoside and a diglucoside of diarylheptanoid as natural products.

Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-181 automatic polarimeter in a 1 dm tube. ^{1}H- and ^{13}C-NMR spectra were recorded with a JEOL JNM FX-100 or a FX-400 spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts are given on the δ scale (ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants (J values) are given in Hz. Mass spectra were recorded with a JEOL JMS-D300 at 70 eV. Precoated TLC plates (Kieselgel 60F_{254}, Merck) were used and detection was carried out by ultraviolet irradiation and by spraying 10% H_2SO_4 followed by heating.

Extraction and Isolation of Constituents——The air dried stem bark of *M. rubra* (4 kg) was extracted with benzene (A), EtOAc (B) and MeOH (C) (3.5 l × 3 each solvent) successively. The benzene solution (A) was concentrated *in vacuo* to 2 l. The concentrated benzene solution was extracted with 2 N NaOH. The emulsion layer was collected, acidified and dissolved in EtOAc. The EtOAc solution was concentrated *in vacuo* to dryness. The residue (17.4 g) was chromatographed repeatedly on silica gel using solvent systems of benzene–EtOAc (10 : 1—1 : 2) and $CHCl_3$–MeOH (100 : 1—5 : 1) to give **3** (1.6 g) and **4** (30 mg). The EtOAc solution (B) was extracted with 2 N NaOH. The 2 N NaOH layer was acidified and extracted with EtOAc. Hot H_2O was added to the acidic fraction (24 g) after evaporation of the solvent, and the insoluble precipitates (18 g) were collected and chromatographed repeatedly on silica gel and Sephadex LH-20 using solvent systems of $CHCl_3$–MeOH–H_2O (65 : 35 : 7) (solvent 1) to give **1** (150 mg), **5** (150 mg), **6** (230 mg), **7** (150 mg), **8** (38 mg) and **9** (60 mg). The MeOH solution (C) was concentrated *in vacuo*. Hot H_2O was added to the MeOH extract (1020 g), and the aqueous solution was passed through a column of Amberlite XAD-4 (1.5 l). After being washed with H_2O, the resin was eluted with MeOH. The MeOH solution was concentrated *in vacuo*, and the residue (160 g) was chromatographed repeatedly on silica gel and Sephadex LH-20 (20 g) using solvent 1, and on polyamide (200 g) using H_2O containing increasing concentrations of MeOH to afford **1** (170 mg) and **2** (150 mg).

Compound 1——A white crystalline powder, mp 267—269 °C (from MeOH–H_2O (1 : 1)), $[\alpha]_D^{24}$ −78.4° (c = 1.0, EtOH). $FeCl_3$: dark blue. *Anal.* Calcd for $C_{34}H_{40}O_{14}$: C, 60.71; H, 5.99. Found: C, 60.43; H, 6.01. UV λ_{max}^{EtOH} nm (log ε): 256 (4.20), 285 (4.11). IR ν_{max}^{KBr} cm^{-1}: 3450, 3225, 1720, 1640, 1595, 1510, 1460, 1230, 1060. ^{1}H-NMR (C_5D_5N): 4.03, 4.10 (each 3H, s, $OCH_3 \times 2$), 4.98 (2H, d, J = 2.9 Hz, H-6′), 5.61 (1H, d, J = 7.3 Hz, anomeric H), 7.15 (2H, s, galloyl H). ^{13}C-NMR (C_5D_5N): 23.51, 26.32, 27.11, 27.99, 35.72, 40.45 (each t, $6 \times CH_2$), 61.10, 61.57 (each q, $2 \times OCH_3$), 67.99 (d, C-11), 116.96, 130.16, 130.31, 131.04, 135.08 (each, d, $4 \times$ ArCH), 126.55, 128.98, 130.42, 131.04 (each s, $4 \times$ ArC-C), 145.89, 148.91, 149.66, 153.05 (each s, $4 \times$ ArC-O) (aglycone moiety). Table I (sugar and galloyl moieties). The triplet at δ 63.9 ppm changed to a singlet on irradiation of a doublet at δ 4.98 ppm in a proton selective decoupling experiment. MS m/z: 358 (100), 340, 273, 271, 170, 153, 136, 125.

Acid Hydrolysis of 1——Compound **1** (24 mg) was refluxed with 5% H_2SO_4–50% MeOH (5 ml) for 1 h. After usual work-up, the crude product was purified by column chromatography on Sephadex LH-20 using solvent 1, to give myricanol (**10**) (5 mg) and gallic acid (**11**) (2 mg). Compounds **10** and **11** were identified by comparison with authentic samples (TLC and IR spectra).

Enzymatic Hydrolysis of 1——A mixture of **1** (20 mg) and tannase (from *Aspergillus niger*) (20 mg) in water (100 ml) was incubated at 37 °C for 4 h. After usual work-up, the crude product was purified by column chromatography on Sephadex LH-20 using solvent 1 to give myricanol (**10**) (2 mg), gallic acid (**11**) (0.5 mg) and myricanol glucoside (**12**) (5 mg), mp 220—223 °C. Compound **12** was identified by comparison with an authentic sample (mixed melting point, TLC and IR spectrum).

Compound 2——An off-white powder, $[\alpha]_D^{20}$ −64.6° (c = 1.1, pyridine). *Anal.* Calcd for $C_{33}H_{46}O_{15} \cdot 2.5\,H_2O$: C, 54.46; H, 7.06. Found: C, 54.71; H, 6.92. IR ν_{max}^{KBr} cm^{-1}: 3360, 1595, 1505, 1070. ^{1}H-NMR (C_5D_5N): 4.03, 4.11 (each 3H, s, $OCH_3 \times 2$). ^{13}C-NMR (C_5D_5N): 23.56, 26.53, 27.26, 28.00, 35.85, 40.51 (each t, $6 \times CH_2$), 61.04, 61.66 (each q, $2 \times OCH_3$), 67.94 (d, C-11), 116.99, 130.22, 130.28, 135.36 (each d, $4 \times$ ArCH), 126.74, 128.98, 130.16, 131.05 (each s, $4 \times$ ArC-C), 145.91, 149.20, 149.57, 150.17 (each s, $4 \times$ ArC-O) (aglycone moiety). Table I (sugar moiety). MS m/z: 358 (100), 340, 273, 271.

Acid Hydrolysis of 2——Compound **2** (19 mg) in 35% HCl–50% MeOH (1 : 3) (4 ml) was refluxed for 0.5 h. After usual work-up, the crude product was purified by column chromatography on silica gel using benzene–EtOAc (4 : 1) to give myricanol (**10**) (5 mg), which was shown to be identical with an authentic sample (TLC, mixed melting point and IR spectrum). The aqueous layer was passed through Amberlite MB-3 and the eluate was concentrated to detect glucose (Rf 0.5) on TLC (cellulose F_{254}) using EtOAc–pyridine–AcOH–H_2O (5 : 5 : 1 : 3).

Methylation of 2 Followed by Hydrolysis——Dimethyl sulfate (1 ml) was added to a stirred solution of **2** (15 mg) in 30% NaOH (3 ml). The mixture was stirred for 1.5 h. The reaction mixture was diluted with H_2O, and extracted

with EtOAc. The extracts were washed with H_2O and dried over Na_2SO_4. Removal of the solvent *in vacuo* gave a residue, which was dissolved in a mixture of 50% MeOH (3 ml) and 35% HCl (1 ml). This mixture was refluxed for 40 min. Removal of the solvent *in vacuo* gave a residue, which was diluted with H_2O and extracted with EtOAc. The extract was washed with H_2O, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, 3 g) with benzene–EtOAc (5 : 1) to give the dimethylated genin (**14**) (1 mg) and the monomethylated genin (**13**) (2 mg). Compound **13**: mp 143—145 °C. High MS *m/z*: 372.1938 (Calcd for $C_{22}H_{28}O_5$, 372.1937). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630, 3530. ^{1}H-NMR ($CDCl_3$): 3.87, 3.89, 3.97. Compound **13** was identical with an authentic sample (TLC, mixed melting point, IR and ^{1}H-NMR spectra). Compound **14**: an amorphous powder. High MS *m/z*: 386.2092. (Calcd for $C_{23}H_{30}O_5$, 386.2092). ^{1}H-NMR ($CDCl_3$): 3.21, 3.88, 3.89, 3.98 (each 3H, s, $OCH_3 \times 4$).

Oleanolic Acid (3)——Compound **3** (50 mg) was methylated with CH_2N_2, followed by acetylation to give oleanolic acid methyl ester acetate (**3a**) (40 mg), mp 222—223 °C (from EtOH). This product was identical with an authentic sample (TLC, mixed melting point and IR spectrum).

Oleanolic Acid Acetate (4)——Colorless needles. mp 268—270 °C [from $CHCl_3$–MeOH (1 : 1)]. Methylation of **4** gave oleanolic acid methyl ester acetate (**3a**) as colorless needles, mp 222—223 °C (from EtOH). This product was identical with an authentic sample (TLC, mixed melting point and IR spectrum).

Maslinic Acid (5)——Colorless crystals, mp 259—264 °C [from $CHCl_3$–MeOH (1 : 1)], $[\alpha]_D^{22}$ +38.1° (*c*=0.7, pyridine). High MS *m/z*: 472.3565 (M^+) (Calcd for $C_{30}H_{48}O_4$, 472.3551). IR ν_{max}^{KBr} cm^{-1}: 3400, 1690. ^{1}H-NMR [$CDCl_3$–C_5D_5N (10 : 1)]: 0.81, 0.85, 0.92 (each 3H, s), 0.97 (6H, s), 1.05, 1.16 (each 3H, s), 2.95 (1H, dd, *J*=14.5, 4.0 Hz, H-18), 3.04 (1H, d, *J*=10.0 Hz, H-3), 3.70 (1H, sextet, *J*=10.0, 10.0, 4.0 Hz, H-2), 5.34 (1H, t, *J*=4.0 Hz, H-12). MS *m/z*: 472, 457, 436, 248 (100), 203. ^{13}C-NMR (C_5D_5N): 68.5 (C-2), 83.7 (C-3), 122.5 (C-12), 144.7 (C-13), 180.0 (C-28). Methylation of **5** gave a methyl ester (**5a**), mp 227—229 °C, which was identical with an authentic sample (TLC, mixed melting point and IR spectrum).

Alphitolic Acid (6)——Colorless crystals, mp 294—298 °C (from MeOH), $[\alpha]_D^{22}$ +0.43° [*c*=0.7, $CHCl_3$–MeOH (1 : 1)]. High MS *m/z*: 472.3535 (M^+) (Calcd for $C_{30}H_{48}O_4$, 472.3551). IR ν_{max}^{KBr} cm^{-1}: 3425, 1700, 1650, 890. ^{1}H-NMR (C_5D_5N): 0.92 (3H, s), 1.06 (12H, s), 1.79 (3H, s), 3.38 (1H, d, *J*=10.0 Hz, H-3), 4.08 (1H, sextet, *J*=10.0, 10.0, 4.0 Hz, H-2), 4.77, 4.92 (each 1H, d like, H_2-30). ^{13}C-NMR (C_5D_5N): 68.8 (C-2), 83.7 (C-3), 109.9 (C-30), 151.2 (C-20), 178.7 (C-28). MS *m/z*: 472, 454, 436, 248, 205, 189 (100). Methyl ester (**6a**): mp 243—245 °C (from benzene). Compounds **6** and **6a** were identical with the respective authentic samples (TLC, mixed melting point and IR spectrum).

Arjunolic Acid (7)——Colorless crystals, mp 295—297 °C [from MeOH–H_2O (1 : 1)], $[\alpha]_D^{24}$ +60.6° (*c*=1.0, MeOH). *Anal.* Calcd for $C_{30}H_{48}O_5 \cdot 0.5\ H_2O$: C, 72.42; H, 9.93. Found: C, 72.24; H, 10.02. IR ν_{max}^{KBr} cm^{-1}: 3370, 1690. ^{13}C-NMR (C_5D_5N): 66.6 (C-23), 68.5 (C-2), 78.2 (C-3), 122.3 (C-12), 144.6 (C-13), 179.8 (C-28). MS *m/z*: 488, 470, 452, 248 (100), 203. Triacetate (**7a**): MS *m/z*: 614 (M^+), 248, 203 (100). ^{1}H-NMR ($CDCl_3$): 1.99, 2.03, 2.09 (each 3H, s, $OCOCH_3 \times 3$), 2.83 (1H, dd, *J*=13.9, 4.0 Hz, H-18), 3.58, 3.86 (each 1H, d, *J*=12.0 Hz, H_2-23), 5.10 (2H, m, H-2, 3), 5.28 (1H, m, H-12). Compound **7** was identical with an authentic sample (TLC, mixed melting point and IR spectrum).

Myricolal (8)——Colorless needles, mp 269—271 °C [from EtOH–$CHCl_3$ (4 : 1)], $[\alpha]_D^{21}$ −9.0° (*c*=0.7, $CHCl_3$). High MS: 440.3644 (Calcd for $C_{30}H_{48}O_2$, 440.3652). IR ν_{max}^{KBr} cm^{-1}: 3350, 1725. ^{1}H-NMR ($CDCl_3$): 0.79, 0.89, 0.91 (each, 3H, s), 0.95 (9H, s), 0.97 (3H, s), 3.18 (1H, m, H-3), 5.41 (1H, dd, *J*=6.8, 4.7 Hz, H-15), 9.10 (1H, s, CHO). ^{13}C-NMR (C_5D_5N): 79.0 (C-3), 114.3 (C-15), 163.2 (C-14), 204.7 (C-28). MS *m/z*: 440 (M^+), 203, 189 (100). Reduction of **8** with $NaBH_4$ gave compound **15**, mp 271—272 °C, which was identical with an authentic sample of myricadiol (TLC, mixed melting point and IR spectrum).

Vanillic Acid (9)——An off-white powder. UV λ_{max}^{EtOH} nm (log ε): 205 (4.5), 255 (4.2), 290 (3.9). High *m/z*: 168.0392 (M^+) (Calcd for $C_8H_8O_4$, 168.0422). ^{1}H-NMR (C_5D_5N): 3.78 (3H, s, OCH_3), 7.24 (1H, d, *J*=8.1 Hz, H-5), 8.0, 8.00 (1H, d, *J*=2.0 Hz, H-2), 8.09 (1H, dd, *J*=8.1, 2.0 Hz, H-6), 10.4 (1H, br s, COOH). ^{13}C-NMR (C_5D_5N): 55.6 (OCH_3), 113.7 (C-2), 115.9 (C-5), 123.4 (C-1), 124.7 (C-6), 148.0 (C-3), 152.4 (C-4), 169.0 (COOH).[13] Methylation of **9** with diazomethane gave a methyl ester (**9a**), mp 61—62 °C. Compounds **9** and **9a** were identical with the respective authentic samples (TLC, mixed melting point, and ^{1}H-NMR spectra).

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