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Diarylheptanoids from *Myrica gale* var. *tomentosa* and Revised Structure of Porson

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From the stems of *Myrica gale* var. *tomentosa* (Myricaceae), two new diarylheptanoids (3 and 4) were isolated together with myricanone, porson, gallic acid and myricetin 3-*O*-(6″-galloyl)-β-D-galactopyranoside. On the basis of spectroscopic and chemical evidence, the structures of 3 and 4 have been determined as 12-dehydroporson and 12-hydroxymyricanone, respectively. The structure of porson was reinvestigated, and a revised structure, 12-hydroxy-5-*O*-methylmyricanone, was proposed.

Key words *Myrica gale* var. *tomentosa*; diarylheptanoid; porson; 12-dehydroporson; 12-hydroxymyricanone; Myricaceae

The family Myricaceae consists of about 50 species of trees and shrubs growing mainly in subtropical to mild-temperate regions of the world. *Myrica gale* with its variety *tomentosa* is a deciduous shrub distributed in the subarctic zone. One of the characteristic features of most members of the Myricaceae is the presence of aromatic foliage, and the leaves and branches of *M. gale* (bog myrtle) have been used as an insect repellent and a flavoring agent in alcoholic beverages in Europe.[1] Mono- and sesquiterpenoids in the essential oil of *M. gale* have been investigated.[2] Non-volatile ingredients of the plant are also known; triterpenoids,[3] flavonoids,[4] unusual chalcone derivatives[5] and four diarylheptanoids (myricanone,[1] porson,[6] galeon and hydroxygaleon[7]).

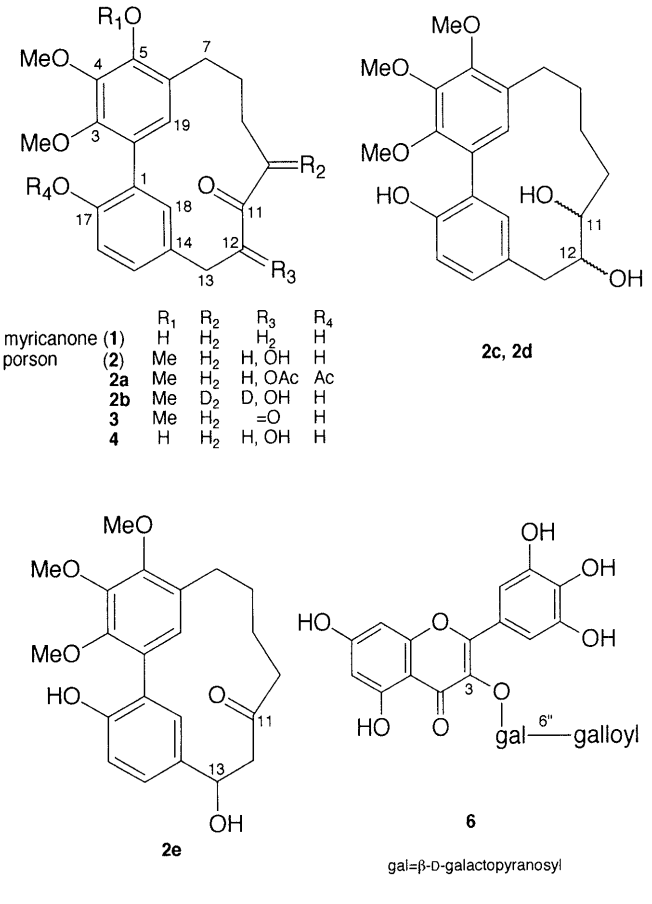
This paper deals with phenolic constituents, especially diarylheptanoids, in the branches of *M. gale* L. var. *tomentosa* C. DC. (yachi-yanagi in Japanese) distributed on marshlands in Northern Japan, Sakhalin and Eastern Siberia, and is, as far as we know, the first report on chemical constituents of this plant.

The methanolic extract from the branches was extracted successively with benzene, ethyl acetate and water. The benzene solution was washed with saturated $NaHCO_3$, and then extracted with 2N NaOH to give a phenolic fraction. Repeated chromatographic separation of the phenolic fraction on silica gel afforded diarylheptanoids **1**, **2**, **3** and **4**. On the other hand, the water-soluble fraction of the methanol extract afforded two phenolic compounds **5** and **6**. Compound **1** was directly identified by comparison with an authentic sample of myricanone isolated from the bark of *M. rubra*.[8]

Compound **2** was obtained as colorless needles, mp 186—187 °C, $C_{22}H_{26}O_6$ with negligible optical rotation. Its IR spectrum exhibited hydroxyl absorptions (3550, 3350 cm^{-1}) and a carbonyl absorption (1701 cm^{-1}). Its UV spectrum showed absorption maxima at 213 (log ε 4.59), 248 (4.09) and 294 (3.78) nm. The ^{13}C-NMR spectrum of **2** indicated the presence of a carbonyl, five methylenes, three methoxyls and a secondary alcoholic methine together with twelve aromatic carbons. These spectral properties led us to presume that **2** is a biphenyl-type diarylheptanoid with an alcoholic hydroxy group and a ketonic carbonyl on the heptane chain. The ^1H- and ^{13}C-NMR chemical shifts of **2** were assigned with the aid of ^1H–^1H correlation spectroscopy (COSY) and ^1H–^{13}C COSY spectra (Table 1). On acetylation, **2** afforded a diacetate **2a**, colorless needles, mp 168—169 °C.

Based on the comparison of the physical and spectroscopic data (MS, IR, ^1H- and ^{13}C-NMR spectra) of **2** and **2a** with those of porson and its acetate, **2** is identical with porson, which has been isolated from *M. gale* by Anthonsen *et al.*[6] and also from the gall of *M. rubra* by Takeda *et al.*[9] The chemical structure **2e** (Chart 1) was proposed for porson (**2**) by Anthonsen *et al.*

Compound **3**, pale yellow needles, mp 191—192 °C has the molecular formula $C_{22}H_{24}O_6$ from the high-resolution MS (HR-MS), *i.e.*, two protons less than porson (**2**). The



	R_1	R_2	R_3	R_4
myricanone (**1**)	H	H_2	H_2	H
porson (**2**)	Me	H_2	H, OH	H
2a	Me	H_2	H, OAc	Ac
2b	Me	D_2	D, OH	H
3	Me	H_2	=O	H
4	H	H_2	H, OH	H

2c, 2d

2e

6

gal=β-D-galactopyranosyl

Chart 1

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Table 1. ^{13}C-NMR Chemical Shifts of Compounds **2**, **3** and **4** in $CDCl_3$

	2	3	4
1	126.6	126.1	123.5
2	126.5	124.8	122.5
3	147.4	147.3	148.0
4	145.7	145.7	138.8
5	152.5	152.5	146.1
6	130.3	130.1	126.7
7	28.2	27.3	27.8
8	24.7	25.4	24.5
9	20.7	21.5	20.6
10	43.0	41.9	43.1
11	217.9	204.5	218.1
12	77.1	198.5	77.2
13	40.0	39.0	40.0
14	126.8	126.5	126.9
15	131.5	129.5	131.4
16	117.4	118.3	117.2
17	153.2	152.9	152.9
18	133.2	132.7	133.1
19	128.8	128.5	129.1
OCH_3	60.5	60.5	61.4
OCH_3	61.2	61.2	61.6
OCH_3	61.9	62.0	

^{13}C-NMR spectrum of **3** was similar to that of **2**, except for the signals due to two carbonyl groups at δ_C 198.5 and 204.5. The ^{1}H–^{1}H COSY spectrum of **3** disclosed that the five methylenes consisted of a chain of four methylenes and an isolated methylene, and that 7-H_2 and 19-H had a long-range coupling with each other. Thus, **3** was presumed to be a ketonic derivative of porson (**2**). In fact, oxidation of **2** with MnO_2 in chloroform yielded a diketone, mp 190—191 °C, with which **3** was identical.

Compound **4**, a white amorphous powder, has the molecular formula $C_{21}H_{24}O_6$. In the UV spectrum of **4**, the absorption maxima at 213 ($\log\varepsilon$ 4.55), 257 (4.01) and 294 (3.84) nm resemble those of porson (**2**). The ^{13}C-NMR spectrum of **4** showed two methoxy groups, which seemed to be of an *ortho*-disubstituted anisole type on the basis of their chemical shifts (δ_C 61.4 and 61.6).

Begley *et al.*[10] and we also[8] have reported that the IR spectrum of myricanone (**1**) in a diluted solution (CCl_4) shows two hydroxyl bands at 3530 and 3350 cm^{-1}; the former absorption is assigned to 5-OH hydrogen-bonded with 4-OMe, and the latter, to 17-OH hydrogen-bonded with 3-OMe. The IR spectrum of **4** in CCl_4 showed two absorptions at 3530 and 3375 cm^{-1} in addition to an alcoholic hydroxyl absorption at 3550 cm^{-1}. The IR spectrum of porson (**2**) lacked the absorption band at 3530 cm^{-1}. This finding indicated that one of the hydroxy groups in **4** must be located at C-5, as in myricanone (**1**): the structure of **4** was determined to be the 5-demethyl derivative of porson (**2**). Selective methylation at the 5-hydroxy group of **4** with diazomethane gave a methyl ether, mp 185—186 °C,[10] which was identifical with **2** on the basis of TLC and mixed melting point determination.

During the above investigation, doubt arose about the structure **2e** (13-OH structure) proposed for porson (**2**). Firstly, the UV spectra of **2** and **3** are not significantly different. It has been reported that the UV spectrum of *p*-hydroxyacetophenone[11] has a strong absorption maximum ($\log\varepsilon$ 4.13) at 276 nm, and that in alkaline solution, the maximum shifts to 320 nm. The UV spectra of **3** did not show such an absorption at about 270 nm, and addition of alkali, did not cause a striking change. Secondly, on comparison of the ^{13}C-NMR spectrum of **2** with that of myricanone, hydroxylation at the benzylic position C-13 of myricanone (**1**) is expected to cause some downfield shift of the β-carbon C-14 signal of **1**,[12] if porson (**2**) had the structure **2e** (13-OH structure). In fact, the chemical shift of C-14 was observed at δ_C 126.8 in **2** and at δ_C 132.3 in **1**.[8] Namely, the C-14 signal of **2** appears at higher field by 5.5 ppm than that of 1, contrary to expectation.

In conclusion, we propose a revision of the structure **2e** (β-ketol) for porson to the 12-OH structure **2** (α-ketol) (Chart 1). The following experiments were conducted in order to confirm this.

Deuteriation of porson (**2**) with NaOMe in CD_3OD afforded deuteriated-**2** (**2b**), colorless needles, mp 186—187 °C, $C_{22}H_{23}D_3O_6$. In the ^{1}H-NMR spectrum of **2b**, three signals assignable to methine (12-H) and a methylene (10-H_2) adjacent to the carbonyl group at C-11 disappeared. Namely, three deuterium atoms (10, 10, 12-D_3) (*m/z* 389) were introduced into **2**, and at the same time the benzyl methylene signals due to 13-H_2 at δ_H 2.85 (m) and 3.55 (br d, J=13 Hz) in **2** changed into a typical AB pattern (J=13 Hz) in **2b**. This finding supports the new structure **2** proposed for porson.

Reduction of **2** with $NaBH_4$ yielded two diastereomeric dihydro derivatives, **2c**, colorless needles, mp 217—218 °C, $C_{22}H_{28}O_6$ and **2d**, an amorphous powder, $C_{22}H_{28}O_6$. In the ^{1}H–^{1}H COSY spectrum of **2d**, a cross peak was observed between two carbinol methine protons: one multiplet at δ_H 4.05 (12-H) and another multiplet at δ_H 3.81 (11-H). In the ^{1}H-NMR spectrum of **2d**, irradiation at δ_H 4.05 (12-H) collapsed two double doublets due to 13-H_2 at δ_H 2.98 (J=8, 15 Hz) and δ_H 3.11 (J=4, 15 Hz) into a pair of signals in an AB coupling system (J=15 Hz). Consequently, the alcoholic hydroxyl of **2** must be adjacent to the carbonyl, namely at C-12, not at C-13.

The similarity of the UV spectrum of porson (**2**) to that of compound **3**, described previously, can reasonably be explained on the basis of the new structure proposed for **2**. Compound **3** seems to exist as the α-diketo form, not as its tautomeric form (α-hydroxy enone), since **3** showed two signals assignable to carbonyl in the ^{13}C-NMR spectrum. Furthermore, the upfield shift of the C-14 signal of porson (**2**) in comparison with that of myricanone (**1**), described previously, can be accounted for by the γ-gauche effect of the hydroxyl introduced at C-12 on the C-14 chemical shift of **1**.[13]

On the basis of the revised structure **2** of porson, compounds **3** and **4** were determined as 12-dehydroporson and 12-hydroxymyricanone (Chart 1), respectively.

Compound **5** was identified as gallic acid by direct comparison with an authentic sample. Compound **6**, pale yellow prisms, mp 229—230 °C, has the molecular formula $C_{28}H_{24}O_{17}$. It was identified as myricetin 3-*O*-(6″-galloyl)-β-D-galactopyranoside[14] by the comparison of the ^{1}H- and ^{13}C-NMR spectra with those of an authentic sample.

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Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-181 automatic polarimeter at 20 °C. Mass spectra were recorded with a JEOL JMS D-300 spectrometer, and with a JEOL JMS SX-102 spectrometer. UV spectra were recorded with a Shimadzu UV-250 spectrometer. IR spectra were recorded with a Hitachi IR 260-10 spectrometer. NMR spectra were recorded with JEOL JMN GX-270 and JEOL JMN GX-400 spectrometers. Tetramethylsilane was used as the internal standard. Chemical shifts are given on the δ scale (ppm). The following abbriviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (J values) are given in hertz (Hz). Column chromatography was performed on Kieselgel 60 (Merck, 70—230 mesh). TLC was performed on precoated Kieselgel 60 F_{254} plates (Merck) and detection was carried out by UV irradiation and by spraying 10% H_2SO_4 followed by heating.

Extraction and Isolation The powdered, dried stems (1.7 kg) of *Myrica gale* var. *tomentosa*, which were collected at Hokkaido, in August 1990, were refluxed with MeOH (3 l × 4, each 3 h) to give a MeOH extract (170 g). The extract was refluxed with benzene (200 ml × 3, each 2 h). After washed with saturated $NaHCO_3$, the combined benzene solution was extracted with 2 N NaOH (600 ml × 3). The aqueous layers were acidified with 2 N HCl, and extracted with Et_2O to give a phenolic fraction (11 g), which was chromatographed repeatedly, eluting with hexane–EtOAc (3 : 2) or benzene–EtOAc (7 : 3) to affords compounds **1** (4 mg), **2** (77 mg), **3** (4.8 mg) and **4** (6.1 mg). The benzene-insoluble portion was refluxed with EtOAc. The EtOAc-insoluble portion (100 g) was refluxed with H_2O. The H_2O extract (0.8 l) was chromatographed on Polyamide C-200 with H_2O, H_2O–MeOH (1 : 1) and MeOH. The MeOH eluate was concentrated, and the residue was chromatographed on Sephadex LH-20 with MeOH–H_2O (4 : 1) to give **5** (10 mg) and **6** (80 mg).

Myricanone (1) Colorless prisms (from EtOH), mp 192—193 °C (lit. mp 190—192 °C). MS m/z: 356 (M^+, 100). UV λ_{max}^{EtOH} nm (log ε): 212 (4.52), 260 (4.05), 297 (3.86). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3530, 3375 (OH), 1710 (C=O). Compound **1** was identified as myricanone by the comparison of TLC behavior and IR and ^{1}H-NMR spectra with those of an authentic sample and by mixed melting point determination.

Porson (2) Colorless needles (from MeOH), mp 186—187 °C (lit. mp 186—187 °C). $[\alpha]_D$ −1.8° (c=2.31, $CHCl_3$–MeOH (1 : 1)). MS m/z: 386 (M^+, 100), 315 ($M^+ - C_4H_7O$, 18), 287 ($M^+ - C_5H_7O_2$, 22). HR-MS m/z: Calcd for $C_{22}H_{26}O_6$; 386.1727. Found 386.1721. UV λ_{max}^{EtOH} nm (log ε): 213 (4.59), 248 (4.09), 294 (3.78). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550, 3350 (OH), 1701 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.55 (1H, m, H-8), 1.70 (1H, m, H-9), 2.00 (1H, m, H-9), 2.10 (1H, m, H-8), 2.15 (1H, d, J=6 Hz, OH), 2.68 (1H, m, H-7), 2.85 (3H, m, H-7, 10, 13), 3.15 (1H, ddd, J=11, 6, 2 Hz, H-10), 3.55 (1H, br d, J=13 Hz, H-13), 3.83, 3.90, 3.96 (each 3H, s, 3 × OMe), 4.38 (1H, ddd, J=7, 6, 2 Hz, H-12), 6.46 (1H, s, H-19), 6.66 (1H, d, J=2 Hz, H-18), 6.90 (1H, d, J=8 Hz, H-16), 7.07 (1H, dd, J=2, 8 Hz, H-15), 7.73 (1H, s, phenol-OH). ^{13}C-NMR: Table 1. Compound **2** was identified as porson by comparison of the MS, ^{1}H- and ^{13}C-NMR spectra with those of an authentic sample.

Diacetate (2a) of 2 A solution of **2** (1 mg) in Ac_2O (0.5 ml) and pyridine (0.5 ml) was acetylated at room temperature overnight. After usual work-up, the diacetate (**2a**) was obtained as colorless needles (from MeOH), mp 168—169 °C (lit. mp 168—169 °C). MS m/z: 470 (M^+, 100), 428 ($M^+ - CH_3CO$, 50). HR-MS m/z: Calcd for $C_{26}H_{30}O_8$; 470.1939. Found 470.1936. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 1710. ^{1}H-NMR ($CDCl_3$) δ: 2.09, 2.23 (each 3H, s, 2 × OAc), 3.62, 3.89, 3.93 (each 3H, s, 3 × OMe), 5.30 (1H, m, H-12), 6.31 (1H, s, H-19), 6.73 (1H, d, J=2 Hz, H-18), 7.04 (1H, d, J=8 Hz, H-16), 7.15 (1H, dd, J=2, 8 Hz, H-15).

Deuteriation of 2 A 0.1% NaOMe solution in CD_3OD (0.2 ml) was added to a solution of **2** (2 mg) in CD_3OD (0.1 ml), and reaction mixture was kept at room temperature overnight. After removal of the CD_3OD under an air stream, the residue was acidified with 2.5% HCl, and extracted with ether. The ether extract was washed with H_2O, dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography with benzene–EtOAc (2 : 1) to give **2b** (1 mg). **2b**: colorless needles, mp 186—187 °C (from MeOH). MS m/z: 389 (M^+, 100), 316 ($M^+ - C_4H_5D_2O$, 18), 287 ($M^+ - C_5H_4D_3O_2$, 22). HR-MS m/z: Calcd for $C_{22}H_{23}D_3O_6$; 389.1918. Found 389.1918. ^{1}H-NMR ($CDCl_3$) δ: 1.55 (1H, m, H-8), 1.70 (1H, m, H-9), 2.06 (2H, m, H-9, H-8), 2.02 (1H, s, OH), 2.70 (1H, m, H-7), 2.80 (1H, m, H-7), 2.91 (1H, d, J=14 Hz, H-13), 3.54 (1H, d, J=14 Hz, H-13), 3.83, 3.90, 3.95 (each 3H, s, 3 × OMe), 6.47 (1H, s, H-19), 6.67 (1H, d, J=2 Hz, H-18), 6.93 (1H, d, J=8 Hz, H-16), 7.09 (1H, dd, J=8, 2 Hz, H-15), 7.72 (1H, s, OH).

Reduction of 2 A solution of **2** (14 mg) in MeOH (5 ml) was treated with $NaBH_4$ (40 mg), and the mixture was stirred at room temperature under a N_2 atmosphere for 2 h, then concentrated to dryness. Boric acid was removed by co-distillation with MeOH. The residue, was taken up in H_2O and extracted with EtOAc. The EtOAc extract was washed with H_2O, and then dried over Na_2SO_4. Removal of the solvent under reduced pressure gave two products, which were purified by repeated column chromatography ($CHCl_3$–MeOH (9 : 1), benzene–EtOAc (7 : 3)), to afford **2c** (3 mg) and **2d** (4 mg). **2c**: colorless needles, mp 217—218 °C (from MeOH). MS m/z: 388 (M^+, 100), 287 (32). HR-MS m/z: Calcd for $C_{22}H_{28}O_6$; 388.1884. Found 388.1884. ^{1}H-NMR ($CDCl_3$) δ: 1.40 (1H, dd, J=11, 14 Hz, H-10), 1.55 (1H, m, H-9), 1.67 (1H, m, H-9), 1.93 (2H, m, H_2-8), 1.96 (1H, m, 11-OH, disappeared with D_2O), 2.33 (2H, m, H-10, 12-OH, changed with D_2O to 1H, m), 2.55 (1H, m, H-7), 2.83 (1H, m, H-7), 2.91 (1H, dd, J=11, 16 Hz, H-13), 3.11 (1H, dd, J=4, 16 Hz, H-13), 3.91, 3.92, 3.97 (each 3H, s, 3 × OMe), 4.16 (1H, m, H-11, changed with D_2O to d, J=11 Hz), 4.33 (1H, m, H-12, changed with D_2O to dd, J=4, 11 Hz), 6.82 (1H, s, H-19), 6.90 (1H, d, J=8 Hz, H-16), 7.00 (1H, d, J=2 Hz, H-18), 7.07 (1H, dd, J=2, 8 Hz, H-15), 7.80 (1H, s, OH, disappeared with D_2O). **2d**: white powder. MS m/z: 388 (M^+, 100), 287 (34). HR-MS m/z: Calcd for $C_{22}H_{28}O_6$; 388.1884. Found 388.1881. ^{1}H-NMR ($CDCl_3$) δ: 1.46 (1H, m, H-9), 1.57 (1H, m, H-8), 1.68 (1H, br s, 11-OH, disappeared with D_2O), 1.79 (1H, m, H-10), 1.95 (1H, br s, 12-OH, disappeared with D_2O), 2.08 (2H, m, H-9, H-10), 2.15 (1H, m, H-8), 2.62 (1H, m, H-7), 2.82 (1H, m, H-7), 2.98 (1H, dd, J=8, 15 Hz, H-13), 3.11 (1H, dd, J=4, 15 Hz, H-13), 3.81 (1H, m, H-11), 3.90, 3.91, 3.97 (each 3H, s, 3 × OMe), 4.05 (1H, m, H-12, changed with D_2O to dd, J=4, 8 Hz), 6.89 (1H, d, J=8 Hz, H-16), 6.92 (1H, s, H-19), 7.09 (1H, dd, J=2, 8 Hz, H-15), 7.35 (1H, d, J=2 Hz, H-18), 7.89 (1H, s, OH, disappeared with D_2O). Irradiation of the multiplet at 4.05 changed two double doublets at 2.98 and 3.11 into AB type signals, J=15 Hz). Irradiation of the multiplet at 3.81 collapsed the multiplet ($W_{1/2}$=16 Hz) at 4.05 into a multiplet ($W_{1/2}$=14 Hz).

Oxidation of 2 A solution of **2** (19.3 mg) in $CHCl_3$ (3 ml) was treated with activated MnO_2 (22 mg) and the whole mixture was stirred at room temperature overnight. The precipitates were removed by filtration. The filtrate was evaporated under reduced pressure. The residue was purified by column chromatography with benzene–EtOAc (20 : 1) to give **3** (8 mg) as pale yellow needles (CH_2Cl_2–MeOH (1 : 10)), mp 190—191 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.90 (4H, m, H_2-8, H_2-9), 2.73 (2H, m, H_2-7), 3.03 (2H, t, J=7 Hz, H_2-10), 3.85, 3.90, 3.95 (each 3H, s, 3 × OMe), 3.98 (2H, s, H_2-13), 6.40 (1H, s, H-19), 6.77 (1H, d, J=2 Hz, H-18), 6.95 (1H, d, J=8 Hz, H-16), 7.09 (1H, dd, J=2, 8 Hz, H-15).

12-Dehydroporson (3) Pale yellow needles (from CH_2Cl_2–MeOH (1 : 10)), mp 191—192 °C. MS m/z: 384 (M^+, 100), 296 (80), 265 (85). HR-MS m/z: Calcd for $C_{22}H_{24}O_6$; 384.1573. Found 384.1573. UV λ_{max}^{MeOH} nm (log ε): 213 (4.36), 249 (3.83), 294 (3.52), (MeOH + 1 N NaOH): unchanged, (MeOH + 1 N HCl): unchanged, (MeOH + NaOAc): unchanged. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3375 (OH), 1700 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.90 (4H, m, H_2-8, H_2-9), 2.74 (2H, m, H_2-7), 3.03 (2H, t, J=7 Hz, H_2-10), 3.86, 3.90, 3.96 (each 3H, s, 3 × OMe), 3.98 (2H, s, H_2-13), 6.40 (1H, s, H-19), 6.77 (1H, d, J=2 Hz, H-18), 6.96 (1H, d, J=8 Hz, H-16), 7.10 (1H, dd, J=2, 8 Hz, H-15). ^{13}C-NMR: Table 1. Compound **3** was confirmed to be identical with **3** obtained from **2** on the basis of mixed melting point dertermination, co-chromatography on TLC and ^{1}H-NMR spectral comparison.

12-Hydroxymyricanone (4) White powder, $[\alpha]_D$ −6.1° (c=0.49, $CHCl_3$). MS m/z: 372 (M^+, 100), 301 (20), 273 (25). HR-MS m/z: Calcd for $C_{21}H_{24}O_6$; 372.1573. Found 372.1581. UV λ_{max}^{MeOH} nm (log ε): 213 (4.55), 257 (4.01), 294 (3.84). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550, 3530, 3375, 1708 (C=O). ^{1}H-NMR (C_5D_5N) δ: 1.60 (1H, m, H-8), 2.10 (3H, m, H-8, H_2-9), 3.05 (3H, m, H_2-7, H-10), 3.10 (1H, m, H-13), 3.65 (1H, m, H-10), 3.77 (3H, s, OMe), 3.80 (1H, m, H-13), 3.91 (3H, s, OMe), 4.82 (1H, dd, J=5, 2 Hz, H-12), 6.82 (1H, s, H-19), 7.20 (1H, d, J=6 Hz, H-16), 7.21 (1H, d, J=1 Hz, H-18), 7.23 (1H, dd, J=1, 6 Hz, H-15). ^{13}C-NMR: Table 1.

Methylation of 4 A solution of **4** (2 mg) in MeOH (0.5 ml) was methylated with an excess of CH_2N_2–Et_2O at room temperature for 2 h. The solvent was removed with an air stream, and the residue was recrystallized from MeOH to give colorless needles (**2**), mp 185—186 °C. This product was identified with porson (**2**) on the basis of mixed melting point determination and co-TLC.

Gallic Acid (5) Slightly-yellow needles (from MeOH), mp 233—

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235 °C (lit. mp 235—240 °C). Compound **5** was identified as gallic acid by TLC comparison and mixed melting point determination with an authentic sample.

Myricetin 3-*O*-(6″-Galloyl)-β-D-galactopyranoside (6) Pale yellow prisms (from MeOH–H_2O), mp 229—230 °C, $[\alpha]_D$ +31.3° (c=1.1, MeOH). Positive FABMS m/z: 633 $[M+H]^+$. Negative FABMS m/z: 631 $[M-H]^-$. Positive HR-FABMS m/z: Calcd for $C_{28}H_{25}O_{17}$; 633.1092 $[M+H]^+$. Found 633.1093. EIMS m/z: 318 (100), 170 (20), 153 (70). UV λ_{max}^{MeOH} nm (log ε): 370 (4.33), 268 (4.41), 211 (4.76). IR ν_{max}^{KBr} cm^{-1}: 3500—3100 (OH), 1670, 1650 (C=O). ^{1}H-NMR (CD_3OD) δ: 7.40 (2H, s, H-2′, H-6′), 6.93 (2H, s, H-2‴, H-6‴), 6.38, 6.21 (each 1H, d, J=2 Hz, H-6, H-8), 5.09 (1H, d, J=8 Hz, H-1′). ^{13}C-NMR (CD_3OD) δ: 180.0 (C-4), 168.6 (C-7‴), 166.6 (C-7), 163.4 (C-5), 159.3 (C-2), 158.9 (C-9), 146.9 (C-3′, 5′, 3‴, 5‴), 140.5 (C-4‴), 138.8 (C-4′), 136.5 (C-3), 122.3 (C-1′), 121.7 (C-1‴), 110.8 (C-2′, C-6′), 110.7 (C-2‴, C-6‴), 106.2 (C-10, C-1″), 100.6 (C-6), 95.4 (C-8), 75.6 (C-3″), 75.1 (C-5″), 73.8 (C-2″), 70.7 (C-4″), 64.3 (C-6″).

Acid Hydrolysis of Compound 6 A solution of **6** (10 mg) in 50% MeOH containing 10% H_2SO_4 (10 ml) was refluxed for 2 h. Usual work-up gave myricetin, gallic acid and galactose. TLC: $CHCl_3$–MeOH–AcOMe–H_2O (5:3:6:1); *Rf* 0.60 (myricetin), *Rf* 0.42 (gallic acid). Propanol–$CHCl_3$–H_2O (6:2:1); *Rf* 0.27 (galactose). Compound **6** was identified as myricetin 3-*O*-(6″-galloyl)-β-D-galactopyranoside by comparison of the ^{1}H- and ^{13}C-NMR spectra with those of an authentic sample.

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