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Chemical and Chemotaxonomical Studies of Ferns. LXXXI.[1] Characteristic Lignans of Blechnaceous Ferns

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Four lignans, blechnic acid (1), 7-epiblechnic acid (3), 8-epiblechnic acid (6) and brainic acid (2), were isolated from six Blechnaceous ferns, *Blechnum orientale, Struthiopteris amabilis, S. niponica, Woodwardia orientalis, W. prolifera* and *Brainea insignis*. Their structures were determined by spectroscopic methods and chemical conversion.

Keywords Blechnaceae; *Blechnum orientale*; *Struthiopteris amabilis*; *Struthiopteris niponica*; *Woodwardia orientalis*; *Woodwardia prolifera*; *Brainea insignis*; lignan; fern; chemotaxonomy

During the course of our studies on fern constituents, six Blechnaceous ferns were investigated and four characteristic compounds of this family, named blechnic acid (**1**), 7-epiblechnic acid (**3**), 8-epiblechnic acid (**6**) and brainic acid (**2**), were isolated.

Both 7-epiblechnic acid (**3**), a colorless crystalline powder, mp 231.5—232.5 °C, $[\alpha]_D^{23}$ $-145°$ ($c=1.0$, MeOH), and 8-epiblechnic acid (**6**), a colorless crystalline powder, mp 231—232 °C, $[\alpha]_D^{23}$ $+142°$ ($c=1.1$, MeOH), showed the same physical properties and spectral data except for the sign of optical rotation, indicating they are antipodal to each other. They are formulated as $C_{18}H_{14}O_8$ from high resolution mass spectra (HR-MS). Their proton nuclear magnetic resonance (^1H-NMR) spectra (in CD_3OD) showed the presence of a 1,3,4-trisubstituted benzene ring [6.78 (1H, d, $J=1.8$ Hz), 6.75 (1H, d, $J=7.9$ Hz), 6.71 (1H, dd, $J=7.9$, 1.8 Hz)], a 1,2,3,4-tetrasubstituted benzene ring [7.18 (1H, d, $J=8.5$ Hz), 6.81 (1H, d, $J=8.5$ Hz)], a *trans*-disubstituted double bond [7.76 (1H, d, $J=15.9$ Hz), 6.27 (1H, d, $J=15.9$ Hz)] and vicinally arranged two methines [5.88 (1H, d, $J=4.9$ Hz), 4.32 (1H, d, $J=4.9$ Hz)] in the molecule. Further, their carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra suggested the presence of two carboxyl groups in the molecule (Table I), and also suggested that both benzene rings are substituted by two oxygen functions in the same manner as catechol.[2] As one of the methines was considered to bear an oxygen function (δ 88.4 in the ^{13}C-NMR spectra), one catechol type oxygen was expected to be linked with this methine. Based on these data and the fact that they gave pentamethylates with methyl iodide and K_2CO_3 in acetone, structures as **3** and **6** in Chart 1 were deduced for them. Such a lignan-type compound as **6** has been reported as the hydrolysis product of lithospermic acid B (**7**).[3] The properties, including the sign of optical rotation and spectral data of the pentamethylate (**8**) of **6** were superimposable on those reported for its pentamethylate. Thus, the structures of **3** and **6** were determined as shown in Chart 1.

Blechnic acid (**1**), colorless needles, mp 198.0—198.5 °C, $[\alpha]_D^{23}$ $-28°$ ($c=1.0$, MeOH), were also formulated as $C_{18}H_{14}O_8$ from HR-MS. The ^1H-NMR spectrum (in CD_3OD) closely resembled those of **3** and **6**, showing the presence of a 1,3,4-trisubstituted benzene ring [6.96 (1H, d, $J=1.8$ Hz), 6.84 (1H, dd, $J=7.9$, 1.8 Hz), 6.75 (1H, d, $J=7.9$ Hz)], a 1,2,3,4-tetrasubstituted benzene ring [7.13 (1H, d, $J=8.5$ Hz), 6.80 (1H, d, $J=8.5$ Hz)], a *trans*-disubstituted double bond [7.56 (1H, d, $J=15.9$ Hz), 6.26 (1H, d, $J=15.9$ Hz)] and vicinally arranged two methines [5.93 (1H, d, $J=9.2$ Hz), 4.59 (1H, d, $J=9.2$ Hz)]. The significant difference between the spectrum of **1** and those of **3** and **6** is the coupling constants of the methine signals, 9.2 Hz for **1** and 4.9 Hz for **3** and **6**. This indicated that **1** is an epimer at one of these methines.

In such an alkaline condition as Na_2CO_3 in MeOH, **1** epimerizes to **3** easily. To determine the epimerizing position, the reaction was carried out in a CD_3OD solution containing 0.5% CD_3ONa at room temperature, monitoring the reaction with ^1H-NMR. After 20 h, almost all the starting material (**1**) was epimerized to **3** without any exchange of protons at C-7 and C-8 to deuteriums. This means the epimerization occurs at C-7 through a mechanism

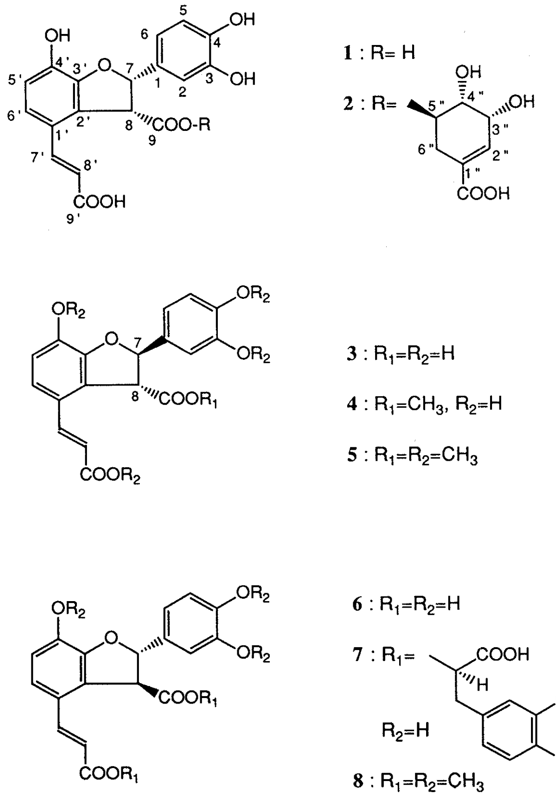

Chart 1

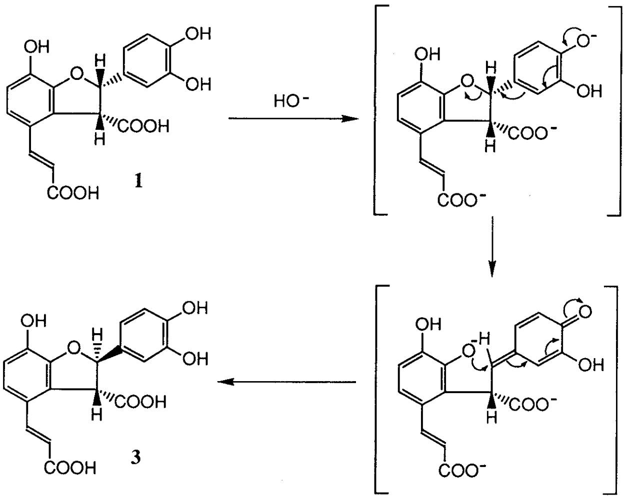

Chart 2

Table I. ^{13}C-NMR Data in Acetone-d_6

C	1	2	3(6)
1	129.5	129.3	133.8
2	115.2	115.1	113.8
3	145.8	146.0	146.4
4	146.3	146.5	146.6
5	116.0	116.4	116.6
6	119.9	119.6	118.6
7	88.0	87.6	88.4
8	54.8	55.0	57.1
9	171.7	169.9	173.5
1′	124.5	124.4	125.0
2′	129.4	128.7	127.5
3′	149.4	149.5	148.8
4′	145.0	145.1	144.7
5′	118.4	118.5	118.6
6′	122.7	123.2	121.7
7′	143.1	143.1	143.2
8′	117.8	118.1	117.8
9′	169.2	169.3	169.0
Shikimic acid			
1″		128.7 (129.3)	
2″		140.2 (138.9)	
3″		66.8 (66.8)	
4″		67.8 (68.8)	
5″		71.7 (71.2)	
6″		27.1 (28.1)	
-COOH		169.0 (168.9)	

The values in parentheses are the reported chemical shifts of 5-*O*-galloyl shikimic acid.4)

shown in Chart 2, but not at C-8 through enolization. Thus, the structure of **1** was determined as the C-7 epimer of **3**.

Table II. Lignan Contents (%) in the Dried Fronds of Blechnaceous Ferns

Fern	Lignan 1	2	3	6
Blechnum orientale	0.009	0.019	N.D.	0.021
Struthiopteris amabilis	0.034	0.029	0.12	N.D.
Struthiopteris niponica	0.024	N.D.	N.D.	N.D.
Woodwardia orientalis	0.063	0.025	0.029	N.D.
Woodwardia prolifera	0.071	0.029	0.036	N.D.
Brainea insignis	N.D.	0.017	N.D.	N.D.

N.D.: not detected.

Brainic acid (**2**), a colorless amorphous powder, $[\alpha]_D^{24}$ $-42°$ ($c=1.0$, MeOH), was formulated as $C_{25}H_{22}O_{12}$ from secondary ion mass spectrum (SI-MS) data, *m*/*z* 515 $(M+H)^+$, and elemental analysis. The ^{1}H-NMR spectrum of **2** was composed of the signals superimposable on those of **1** and additional signals at δ 6.63 (1H, ddd, $J=4.3$, 2.1, 1.2 Hz), 4.83 (1H, dt, $J=3.4$, 4.6 Hz), 3.78 (1H, tdd, $J=4.3$, 2.1, 1.2 Hz), 3.28 (1H, dd, $J=4.6$, 4.3 Hz), 2.47 (1H, ddt, $J=18.9$, 4.6, 2.1 Hz) and 2.08 (1H, ddt, $J=18.9$, 3.4, 1.2 Hz). These additional signals were suggestive of those of shikimic acid, of which the hydroxyl group at C-5 was considered to be acylated because of the down-field shift of the corresponding signal (δ 4.83). The ^{13}C-NMR data of **2** were also superimposable on those of **1** and shikimic acid moiety of 5-*O*-galloyl shikimic acid (Table I).4)

On alkaline methanolysis, **2** gave shikimic acid and monomethyl ester **4**. As the coupling constant of the methine protons at C-7 and C-8 of **4** was 4.9 Hz, the epimerization at C-7 was considered to have occurred in the reaction condition. On methylation with methyl iodide and K_2CO_3 in acetone, **4** was converted into pentamethylate **5**.

Based on these evidences, the structure of **2** was limited to 5-*O*-blechnoyl shikimic acid. The carboxyl group which forms the ester linkage was determined as C-9 from the long-range ^{1}H–^{13}C shift-correlated spectrum of **2**, where the proton signals at C-8 and C-5″ (shikimic acid) are correlated to the carbon signal of C-9. Thus, the structure of **2** was determined as shown in Chart 1.

Blechnic acid (**1**), 7-epiblechnic acid (**3**), 8-epiblechnic acid (**6**) and brainic acid (**2**) are the rare examples of lignan-type compounds isolated from ferns.5) The Blechnaceous ferns investigated and the contents of these compounds are listed in Table II. It is unusual that such a pair of antipodes as **3** and **6** is present in the same family, but, the fact was confirmed by the repeated examination. The fact indicates that **3** and **6** are not artifacts derived by epimerization.

As the constituents of these ferns, a flavonoid6) in *B. insignis*, a triterpene7) and phytoecdysones8) in *W. orientalis* and phytoecdysones8) in *S. amabilis* and *S. niponica* have been reported sporadically. It is noteworthy that these lignans are distributed in all the species investigated and have not been isolated from any other family so far. They must be useful chemical markers to classify Blechnaceous ferns or to elucidate the relationships of Blechnaceae with other families.

Experimental

Melting points were determined with a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were taken with a JASCO DIP-360 automatic polarimeter. The ^{1}H-NMR and ^{13}C-NMR spectra were measured with a JEOL GSX-500 spectrometer. Ultraviolet (UV) spectra were recorded on a Hitachi 323 spectrometer and infrared (IR) spectra on a Shimadzu IR-460 spectrometer. Mass spectra (MS) were measured with a Hitachi M-80A spectrometer.

Fern Materials The ferns investigated were collected at the following places. *Blechnum orientale* L.; Amami-Ohshima Island, Kagoshima Prefecture, in December. *Struthiopteris amabilis* (Makino) Ching; Shingu, Wakayama Prefecture, in August. *Struthiopteris niponica* (Kunze) Nakai; Kiso, Nagano Prefecture, in August. *Woodwardia orientalis* Sw.; Shimoda, Shizuoka Prefecture, in September. *Woodwardia prolifera* Hook. *et* Arn.; Amami-Ohshima Island, Kagoshima Prefecture, in November. *Brainea* *insignis* (Hook.) J. Sm.; Kuantaochi, Nantou Prefecture, Taiwan, in December.

General Isolation Procedure The air-dried fronds (1 kg) were extracted twice with 3 l of MeOH under reflux for 6 h. The combined extracts (6 l) and then 10 l of MeOH were passed over activated charcoal (100 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. The fractions containing the lignans were collected and repeatedly chromatographed on Sephadex LH-20 using 70% MeOH to isolate the lignans.

Blechnic Acid (1) Colorless needles, mp 198.0—198.5 °C (from H_2O), $[\alpha]_D^{23}$ $-28°$ ($c=1.0$, MeOH). UV (MeOH) λ_{max} nm (log ε): 253 (4.13), 292 (4.11), 305 (4.10), 327 (4.02). IR (KBr) ν_{max} cm^{-1}: 3300, 2600, 1720, 1690, 1610, 1500. ^{1}H-NMR (in CD_3OD) δ: 7.56 (1H, d, $J=15.9$ Hz, H-7′), 7.13 (1H, d, $J=8.5$ Hz, H-6′), 6.96 (1H, d, $J=1.8$ Hz, H-2), 6.84 (1H, dd, $J=7.9$, 1.8 Hz, H-6), 6.80 (1H, d, $J=8.5$ Hz, H-5′), 6.75 (1H, d, $J=7.9$ Hz, H-5), 6.26 (1H, d, $J=15.9$ Hz, H-8′), 5.93 (1H, d, $J=9.2$ Hz, H-7), 4.59 (1H, d, $J=9.2$ Hz, H-8). ^{1}H-NMR (in acetone-d_6) δ: 7.66 (1H, d, $J=16.2$ Hz, H-7′), 7.27 (1H, d, $J=8.5$ Hz, H-6′), 7.08 (1H, d, $J=1.8$ Hz, H-2), 6.94 (1H, d, $J=8.5$ Hz, H-5′), 6.93 (1H, dd, $J=7.9$, 1.8 Hz, H-6), 6.86 (1H, d, $J=7.9$ Hz, H-5), 6.40 (1H, d, $J=16.2$ Hz, H-8′), 6.04 (1H, d, $J=9.2$ Hz, H-7), 4.75 (1H, d, $J=9.2$ Hz, H-8). EI-MS *m/z*: 358, 314, 270, 255, 160, 123. HR-MS Calcd for $C_{18}H_{14}O_8$: 358.069. Found: 358.068.

7-Epiblechnic Acid (3) A colorless crystalline powder, mp 231.5—232.5 °C, $[\alpha]_D^{23}$ $-145°$ ($c=1.0$, MeOH). UV (MeOH) λ_{max} nm (log ε): 254 (4.15), 295 (4.09), 307 (4.10), 327 (4.03). IR (KBr) ν_{max} cm^{-1}: 3300, 2600, 1720, 1690, 1610, 1500. ^{1}H-NMR (in CD_3OD) δ: 7.76 (1H, d, $J=15.9$ Hz, H-7′), 7.18 (1H, d, $J=8.5$ Hz, H-6′), 6.81 (1H, d, $J=8.5$ Hz, H-5′), 6.78 (1H, d, $J=1.8$ Hz, H-2), 6.75 (1H, d, $J=7.9$ Hz, H-5), 6.71 (1H, dd, $J=7.9$, 1.8 Hz, H-6), 6.27 (1H, d, $J=15.9$ Hz, H-8′), 5.88 (1H, d, $J=4.9$ Hz, H-7), 4.32 (1H, d, $J=4.9$ Hz, H-8). EI-MS *m/z*: 358, 314, 270, 255, 191, 147, 136, 123. HR-MS Calcd for $C_{18}H_{14}O_8$: 358.069. Found: 358.067.

8-Epibechnic Acid (6) A colorless crystalline powder, mp 231—232 °C, $[\alpha]_D^{23}$ $+142°$ ($c=1.1$, MeOH). Spectral data are the same as those of **3**.

Brainic Acid (2) A colorless amorphous powder, $[\alpha]_D^{24}$ $-42°$ ($c=1.0$, MeOH). UV (MeOH) λ_{max} nm (log ε): 250 (4.12), 292 (4.15), 327 (4.02). IR (KBr) ν_{max} cm^{-1}: 3300, 1720, 1700, 1620, 1520. ^{1}H-NMR (in CD_3OD) δ: 7.51 (1H, d, $J=15.9$ Hz, H-7′), 7.12 (1H, d, $J=8.5$ Hz, H-6′), 6.90 (1H, d, $J=1.8$ Hz, H-2), 6.82 (1H, d, $J=8.5$ Hz, H-5′), 6.81 (1H, dd, $J=8.2$, 1.8 Hz, H-6), 6.78 (1H, d, $J=8.2$ Hz, H-5), 6.63 (1H, ddd, $J=4.3$, 2.1, 1.2 Hz, H-2″), 6.22 (1H, d, $J=15.9$ Hz, H-8′), 5.93 (1H, d, $J=9.2$ Hz, H-7), 4.83 (1H, dt, $J=3.4$, 4.6 Hz, H-5″), 4.70 (1H, d, $J=9.2$ Hz, H-8), 3.78 (1H, tdd, $J=4.3$, 2.1, 1.2 Hz, H-3″), 3.28 (1H, dd, $J=4.6$, 4.3 Hz, H-4″), 2.47 (1H, ddt, $J=18.9$, 4.6, 2.1 Hz, H-6″-a), 2.08 (1H, ddt, $J=18.9$, 3.4, 1.2 Hz, H-6″-b). ^{1}H-NMR (in acetone-d_6) δ: 7.52 (1H, d, $J=15.9$ Hz, H-7′), 7.20 (1H, d, $J=8.2$ Hz, H-6′), 6.97 (1H, d, $J=1.8$ Hz, H-2), 6.89 (1H, d, $J=8.2$ Hz, H-5′), 6.85 (1H, d, $J=8.1$ Hz, H-5), 6.83 (1H, dd, $J=8.1$, 1.8 Hz, H-6), 6.66 (1H, ddd, $J=4.3$, 2.1, 1.2 Hz, H-2″), 6.27 (1H, d, $J=15.9$ Hz, H-8′), 6.00 (1H, d, $J=9.2$ Hz, H-7), 4.89 (1H, dt, $J=3.4$, 4.6 Hz, H-5″), 4.78 (1H, d, $J=9.2$ Hz, H-8), 3.81 (1H, tdd, $J=4.3$, 2.1, 1.2 Hz, H-3″), 3.33 (1H, dd, $J=4.6$, 4.3 Hz, H-4″), 2.50 (1H, ddt, $J=18.9$, 4.6, 2.1 Hz, H-6″-a), 2.16 (1H, ddt, $J=18.9$, 3.4, 1.2 Hz, H-6″-b). SI-MS *m/z*: 515 $(M+H)^+$. *Anal.* Calcd for $C_{25}H_{22}O_{12}$: C, 58.37; H, 4.31. Found: C, 58.10; H, 4.59.

Methylation of 7-Epiblechnic Acid (3) 7-Epiblechnic acid (150 mg) was dissolved in dry acetone (30 ml) and then methyl iodide (10 ml) and anhydrous K_2CO_3 (1.5 g) were added. The mixture was stirred under reflux for 18 h and poured into ice-water. The products were extracted with EtOAc. The extract was washed with water, dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel using *n*-hexane and EtOAc as eluents to yield pentamethylate (**5**, 110 mg). A colorless syrup, $[\alpha]_D^{22}$ $-147°$ ($c=2.0$, $CHCl_3$). UV (MeOH) λ_{max} nm (log ε): 245 (4.11), 289 (4.03), 301 (4.05), 328 (3.93). IR ($CHCl_3$) ν_{max} cm^{-1}: 3000, 2900, 1740, 1710, 1610, 1510. ^{1}H-NMR (in $CDCl_3$) δ: 7.71 (1H, d, $J=15.9$ Hz, H-7′), 7.21 (1H, d, $J=9.3$ Hz, H-6′), 6.91 (1H, dd, $J=8.9$, 1.8 Hz, H-6), 6.89 (1H, d, $J=9.3$ Hz, H-5′), 6.88 (1H, d, $J=1.8$ Hz, H-2), 6.83 (1H, d, $J=8.9$ Hz, H-5), 6.28 (1H, d, $J=15.9$ Hz, H-8′), 6.03 (1H, d, $J=15.9$ Hz, H-8′), 6.03 (1H, d, $J=5.6$ Hz, H-7), 4.48 (1H, d, $J=5.6$ Hz, H-8), 3.94, 3.87, 3.86, 3.80, 3.78 (each 3H, s, $-OC\underline{H}_3$). EI-MS *m/z*: 428, 396, 368, 337, 309, 181, 151, 138. HR-MS Calcd for $C_{23}H_{24}O_8$: 428.147. Found: 428.144.

Methylation of 8-Epiblechnic Acid (6) 8-Epiblechnic acid (**6**, 80 mg) was methylated in the same way as **3** to yield pentamethylate **8** (55 mg). A colorless syrup, $[\alpha]_D^{24}$ $+145°$ ($c=1.0$, $CHCl_3$). The spectral data are the same as those of **5**.

Epimerization of Blechnic Acid (1) Blechnic acid (**1**, 50 mg) was dissolved in MeOH (15 ml) and Na_2CO_3 (100 mg) was added. The mixture was refluxed for 4 h and filtered. The filtrate was weakly acidified with dil. HCl and concentrated. The residue was chromatographed on Sephadex LH-20 using MeOH as an eluent to yield 7-epiblechnic acid (**3**, 32 mg).

Alkaline Methanolysis of Brainic Acid (2) Brainic acid (**2**, 200 mg) was dissolved in MeOH (20 ml) and Na_2CO_3 (200 mg) was added. The mixture was refluxed for 5 h and filtered. The filtrate was weakly acidified with dil. HCl and concentrated. The residue was chromatographed on Sephadex LH-20 using MeOH as an eluent to yield compound **4** (70 mg) and shikimic acid (22 mg).

Compound 4 A colorless amorphous powder, $[\alpha]_D^{22}$ $-20°$ ($c=1.0$, MeOH). UV (MeOH) λ_{max} nm (log ε): 245 (4.19), 292 (4.12), 325 (4.02). IR (KBr) ν_{max} cm^{-1}: 3300, 1720, 1700, 1620, 1520. ^{1}H-NMR (in CD_3OD) δ: 7.54 (1H, d, $J=15.9$ Hz, H-7′), 7.13 (1H, d, $J=8.2$ Hz, H-6′), 6.78 (1H, d, $J=8.2$ Hz, H-5′), 6.77 (1H, d, $J=1.8$ Hz, H-2), 6.74 (1H, d, $J=8.2$ Hz, H-5), 6.69 (1H, dd, $J=8.2$, 1.8 Hz, H-6), 6.28 (1H, d, $J=15.9$ Hz, H-8′), 5.83 (1H, d, $J=4.9$ Hz, H-7), 4.41 (1H, d, $J=4.9$ Hz, H-8), 3.76 (3H, s, $C\underline{H}_3-O-$). *Anal.* Calcd for $C_{19}H_{16}O_8$: C, 61.29; H, 4.33. Found: C, 61.01; H, 4.59.

Shikimic Acid Colorless needles, mp 188—190 °C, $[\alpha]_D^{21}$ $-159°$ ($c=0.7$, MeOH). IR (KBr) ν_{max} cm^{-1}: 3500, 3400, 1680, 1650, 1455, 1300, 1280, 1100, 1070, 940. ^{1}H-NMR (in CD_3OD) δ: 6.74 (1H, dt, $J=4$, 2 Hz, H-2), 4.35 (1H, tt, $J=4$, 2 Hz, H-3), 3.97 (1H, dt, $J=8$, 6 Hz, H-5), 3.65 (1H, dd, $J=8$, 4 Hz, H-4), 2.71 (1H, ddt, $J=18.5$, 6, 2 Hz, H-6-a), 2.16 (1H, ddt, $J=18.5$, 6, 2 Hz, H-6-b). The properties and spectral data were identical with those of an authentic sample.

Methylation of 4 Compound **4** (50 mg) was dissolved in dry acetone (10 ml) and then methyl iodide (15 ml) and anhydrous K_2CO_3 (1.0 g) were added. The mixture was stirred under reflux for 3 h and filtered. The filtrate was concentrated and chromatographed on Sephadex LH-20 using MeOH as an eluent to yield pentamethylate of 7-epiblechnic acid (**5**, 30 mg).

References and Notes

1) Part LXXX: N. Tanaka, R. Orii, K. Ogasa, H. Wada, T. Murakami, Y. Saiki and C.-M. Chen, *Chem. Pharm. Bull.*, **39**, 55 (1991).
2) J. B. Harborne and T. J. Mabry, "The Flavonoids: Advances in Research," Chapman and Hall, New York, 1982, p. 21.
3) T. Tanaka, S. Morimoto, G. Nonaka, I. Nishioka, T. Yokozawa, H. Y. Chung and H. Oura, *Chem. Pharm. Bull.*, **37**, 340 (1989).
4) G. Nonaka, M. Ageta and I. Nishioka, *Chem. Pharm. Bull.*, **33**, 96 (1985).
5) Another example, lericiresinol 9-*O*-*β*-D-glucoside and its related lignan, has been isolated from a Pteridaceous fern, *Pteris vittata*: T. Satake, T. Murakami, Y. Saiki and C.-M. Chen, *Chem. Pharm. Bull.*, **26**, 1619 (1978).
6) T. Murakami, H. Wada, N. Tanaka, T. Kido, H. Iida, Y. Saiki and C.-M. Chen, *Yakugaku Zasshi*, **106**, 982 (1986).
7) T. Murakami and C.-M. Chen, *Chem. Pharm. Bull.*, **19**, 25 (1971).
8) H. Hikino, T. Okuyama, H. Jin and T. Takemoto, *Chem. Pharm. Bull.*, **21**, 2292 (1973).