# Chemical and Chemotaxonomical Studies of Ferns. LXXX.[1] Proanthocyanidins of *Arachniodes sporadosora* NAKAIKE and *A. exilis* CHING

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**Three new trimeric proanthocyanidins were isolated in lactone form (1L, 2L and 3L) and acid form (1A, 2A and 3A) from the fronds of both *Arachniodes sporadosora* NAKAIKE and *A. exilis* CHING. Their structures were determined by spectroscopic methods and thiolytic degradation.**

**Keywords** *Arachniodes sporadosora*; *Arachniodes exilis*; Aspidiaceae; fern; proanthocyanidin; sweet substance; $^{13}$C-NMR

There has been considerable progress in the chemistry of proanthocyanidins in the last two decades. Recently, Nishioka and his co-workers, who have made an important contribution in this field, reported the presence of many proanthocyanidins in several ferns.[2] Hori *et al.* have also isolated new proanthocyanidins from a Pteridaceous fern, *Dennstaedtia distenta*.[3] In a continuation of our chemical studies of ferns, three more new proanthocyanidins were isolated not only as their lactone forms, **1L**, **2L** and **3L**, but also as acid forms, **1A**, **2A** and **3A**, from *Arachniodes sporadosora* (KUNZ.) NAKAIKE and *A. exilis* CHING. In this paper, we describe the structure determination of these compounds.

*A. sporadosora* and *A. exilis* are Aspidiaceous ferns found in the region from south of the Kanto district, Japan, to Taiwan, China. They frequently grow in the same area, and hybridize readily with each other. Their methanol extracts showed similar chromatographic patterns on silica gel, suggesting a closs relationship between them. From the methanol extract of the air-dried fronds of either *A. sporadosora* or *A. exilis*, the above-mentioned six compounds were isolated by repeated chromatography on Sephadex LH-20.

Compound **1L**, a pale brown amorphous solid, $[\alpha]_D^{20}$ +65° ($c$=1.0, MeOH), was positive to the ferric chloride reagent and gave a red color with HCl in EtOH, suggesting it to be a proanthocyanidin. In the secondary ion mass spectrum (SI-MS), **1L** gave the $[M+H]^+$ ion peak at $m/z$ 905. In the carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectrum, **1L** showed thirty-six signals assignable to the A- and B-ring carbons of three epicatechin-type units, indicating that **1L** is a trimeric proanthocyanidin (Table I). The remaining eleven signals included a ketal carbon signal at $\delta$ 104.9, suggesting that **1L** possesses a proanthocyanidin A-type unit (**8**) in the molecule.[4] A typical trimer **9** containing a proanthocyanidin A-type unit has been isolated from the root bark of *Cinnamomum zeylanicum*.[5] The $^{13}$C-NMR spectral data of **9** (in Chart 2) were in good agreement with those of **1L** except that the C-2 and C-3 signals of the bottom unit of **1L** showed an upfield shift (−4.3 ppm) and a downfield shift (+3.6 ppm), respectively, and the signal of C-4 of the bottom unit of **9** ($\delta$ 29.2) was replaced by three signals at $\delta$ 36.1 (CH), 39.9 ($CH_2$) and 176.3 (COO). These spectral data indicated that the bottom unit of **1L** possesses a carboxymethylene unit at C-4. Considering its molecular weight and the fact that **1L** gave a tridecaacetate [field desorption mass spectrum (FD-MS) $m/z$: 1450 ($M^+$)] with acetic anhydride in pyridine, this carboxymethylene unit was expected to form a lactone ring with the hydroxyl group at C-5.[6] A compound similar to this putative bottom unit has been isolated from an Aspidiaceous fern, *Dryopteris filix-mas*, and named dryopterin (**6**).[7] The $^{13}$C-NMR data of the C-ring of **6** are in good agreement with those of the bottom unit of **1L**.

On degradation with acid in the presence of benzylmercaptan, **1L** gave a dimeric proanthocyanidin thioether **4** and the bottom unit **6**. Their properties and spectral data were the same as those of proanthocyanidin A-2 4′-benzylthio-

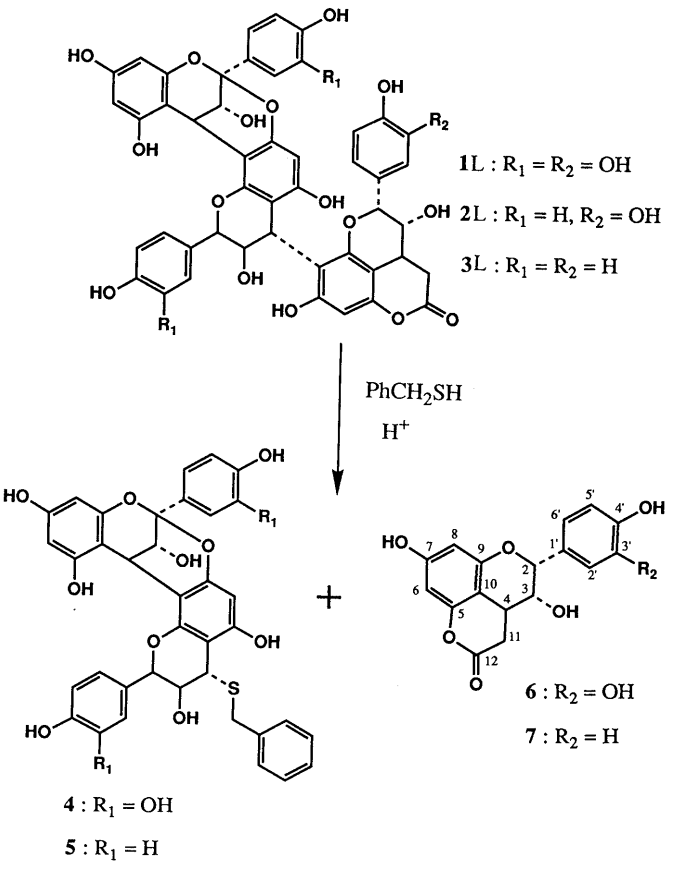
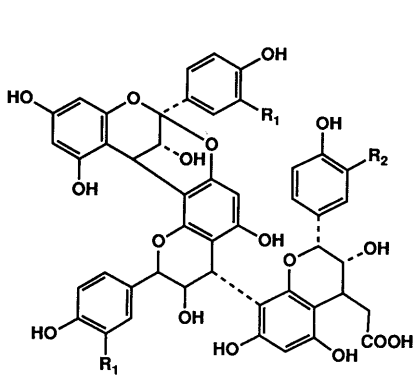
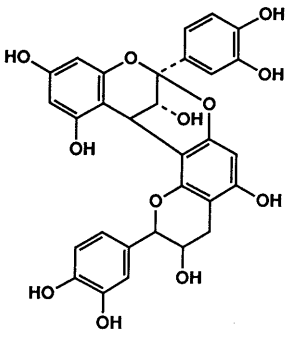



Chart 1



1A : $R_1 = R_2 = OH$
2A : $R_1 = H$, $R_2 = OH$
3A : $R_1 = R_2 = H$



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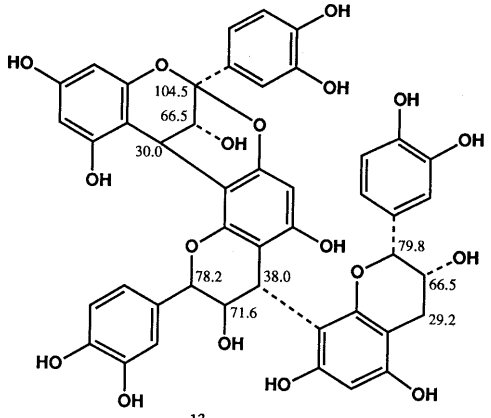


9 ($^{13}$C-NMR data in $D_2O$ - acetone-$d_6$)

Chart 2

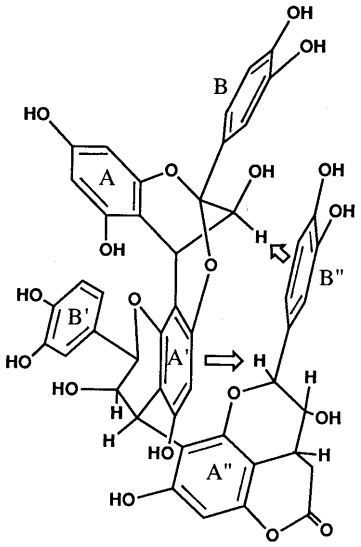


Fig. 1

ether (**4**)[5] and dryopterin (**6**).[8] Therefore, **1L** was determined to be a coupling product of proanthocyanidin A-2 (**8**) and dryopterin (**6**) with the position of the interflavonoid linkage remaining to be confirmed as either (4$\beta$-6) or (4$\beta$-8).[9] In the proton nuclear magnetic resonance ($^1$H-NMR) spectrum of **1L**, the signals corresponding to those of C-3-H ($\delta$ 4.06) of **4** and C-2-H ($\delta$ 4.80) of **6** appeared at $\delta$ 3.28 and 4.38, respectively. These remarkable upfield shifts are attributable to the magnetic anisotropic effects of the B″-ring and the A′-ring which can be located just in front of the protons only when **1L** possesses a (4′$\beta$-8) linkage (see Fig. 1). Therefore, the structure of **1L** was determined as epicatechin-(4$\beta$→8,2$\beta$→O→7)-epicatechin-(4$\beta$→8)-dryopterin.[10]

Compound **2L**, a pale brown amorphous solid, $[\alpha]_D^{20}$ + 62° ($c$=1.2, MeOH), showed the $[M+H]^+$ ion peak at $m/z$ 873 in the SI-MS, indicating that **2L** possesses a molecular formula smaller than that of **1L** by two oxygen atoms. The $^1$H- and $^{13}$C-NMR data of **2L** were almost the same as those of **1L** except that the signals corresponding to two of the three catechol-type B-rings of **1L** were replaced by those of two *p*-hydroxyphenyl groups (Tables I and II).

On thiolytic degradation, **2L** gave a dimeric proanthocyanidin thioether **5**, a pale brown amorphous solid, $[\alpha]_D^{20}$ + 64° ($c$=0.7, acetone), and dryopterin (**6**). The structure of **5** was confirmed as epiafzelechin-(4$\beta$→8,2$\beta$→O→7)-epiafzelechin 4′-benzylthioether by comparison of its $^1$H- and $^{13}$C-NMR data with those of **4** (Table II). Therefore, the structure of **2L** was determined as epiafzelechin-(4$\beta$→8, 2$\beta$→O→7)-epiafzelechin-(4$\beta$→8)-dryopterin.

Compound **3L**, a pale brown amorphous solid, $[\alpha]_D^{20}$ + 71° ($c$=1.5, MeOH), was found to have a molecular formula with one less oxygen atom than **2L** basing on the $[M+H]^+$ ion peak at $m/z$ 857 in the SI-MS. The $^1$H- and $^{13}$C-NMR data were almost the same as those of **2L** except that the catechol-type B-ring of the bottom unit of **2L** was displaced by a *p*-hydroxyphenyl group. On thiolytic degradation, **3L** gave the dimeric proanthocyanidin thioether **5** and a bottom unit **7**, a colorless amorphous powder, $[\alpha]_D^{20}$ − 30° ($c$=0.2, MeOH). The structure of **7** was confirmed as 3′-deoxydryopterin by comparison of its $^1$H- and $^{13}$C-NMR data with those of dryopterin **6** (Table II). Therefore, the structure of **3L** was determined as epiafzelechin-(4$\beta$→8,2$\beta$→O→7)-epiafzelechin-(4$\beta$→8)-3′-deoxydryopterin.

Compounds **1A**, **2A** and **3A** gave $[M+H]^+$ ion peaks at $m/z$ 923, 891 and 875 in the SI-MS, indicating that they have larger molecular weights by 18 mass units than **1L**, **2L** and **3L**, respectively. Compound **1A** showed almost the same $^1$H- and $^{13}$C-NMR spectra as those of **1L** except for the signals due to H-11$\alpha$, C-11 and C-12 (Tables I and II). The differences in the chemical shifts suggested that the lactone group of **1L** had been hydrolyzed in the case of **1A**. This suggestion was supported by the fact that **1A** gave an undecamethylate with methyl iodide and $K_2CO_3$ in acetone, FD-MS $m/z$: 1090 [$M^+$]. On thiolytic degradation, **1A** gave the same products, **4** and **6**, as those of **1L**, forming the lactone ring under these reaction conditions. Thus, the structure of **1A** was assigned as the free acid form of **1L**.[12] Similarly, the structures of **2A** and **3A** were assigned as the free acid forms of **2L** and **3L**, respectively.

Compounds **1L**, **2L** and **3L** (alternatively, **1A**, **2A** and **3A**) are examples of a new type of proanthocyanidin which possesses a terminal two-carbon unit, probably originating from malonyl coenzyme A. Compounds **1L** and **1A** have a sweet taste, similarly to compound **9**.[13] However,

TABLE I. $^{13}$C-NMR Data in $D_2O$–Acetone-$d_6$ (1 : 1)

| C | 1L | 1A | 2L | 2A | 3L | 3A |
|---|---|---|---|---|---|---|
| 2 | 104.9 | 104.8 | 105.0 | 105.0 | 104.9 | 104.6 |
| | 78.0 | 77.9 | 78.1 | 78.2 | 78.3 | 77.9 |
| | 75.5 | 75.4 | 75.7 | 75.7 | 75.7 | 75.4 |
| 3 | 71.4 | 71.3 | 71.5 | 71.6 | 71.8 | 71.5 |
| | 70.1 | 70.2 | 70.2 | 70.7 | 70.5 | 70.6 |
| | 66.5 | 66.4 | 66.6 | 66.6 | 66.6 | 66.3 |
| 4 | 38.2 | 38.1 | 38.3 | 38.4 | 38.4 | 38.1 |
| | 36.1 | 36.2 | 36.2 | 36.6 | 36.5 | 36.5 |
| | 28.2 | 28.1 | 28.4 | 28.4 | 28.4 | 28.1 |
| 5,7,9 | 156.9 | 156.8 | 157.0 | 157.0 | 156.8 | 156.4 |
| | 155.9 | 155.8 | 156.1 | 156.1 | 156.1 | 155.8 |
| | 155.5 | 155.4 | 155.6 | 155.7 | 155.7 | 155.4 |
| | 155.1 | 155.0 | 155.2 | 155.3 | 155.3 | 155.0 |
| | 155.1 | 155.0 | 155.2 | 155.1 | 155.2 | 154.7 |
| | 155.0 | 154.8 | 155.1 | 154.9 | 155.0 | 154.5 |
| | 153.7 | 153.6 | 153.8 | 153.8 | 153.8 | 153.5 |
| | 151.4 | 151.2 | 151.5 | 151.4 | 151.2 | 151.1 |
| | 150.5 | 150.4 | 150.6 | 150.6 | 150.4 | 150.3 |
| 6,8,10 | 108.2 | 108.1 | 108.3 | 108.3 | 108.3 | 108.0 |
| | 106.4 | 106.3 | 106.5 | 106.6 | 106.5 | 106.3 |
| | 105.9 | 105.8 | 106.0 | 106.0 | 105.8 | 105.6 |
| | 102.8 | 103.2 | 102.9 | 104.1 | 103.7 | 104.3 |
| | 99.5 | 99.4 | 99.8 | 99.8 | 99.8 | 99.5 |
| | 98.2 | 98.1 | 98.3 | 98.3 | 98.4 | 98.1 |
| | 96.8 | 96.9 | 96.9 | 97.2 | 97.2 | 96.9 |
| | 96.7 | 96.6 | 96.8 | 96.8 | 96.8 | 96.5 |
| | 95.8 | 95.8 | 95.9 | 96.1 | 96.0 | 95.7 |
| 11 | 39.9 | 41.3[a] | 40.1 | 43.4[a] | 39.8 | 44.6[a] |
| 12 | 176.3 | 177.4[a] | 176.3 | 179.1[a] | 176.2 | 180.2[a] |
| 3,4-Dihydroxyphenyl | | | | | | |
| 1′ | 132.3 | 132.3 | 132.5 | 132.7 | | |
| | 131.9 | 131.8 | | | | |
| | 131.3 | 131.2 | | | | |
| 2′ | 116.8 | 116.6 | 115.3 | 115.3 | | |
| | 115.6 | 115.5 | | | | |
| | 115.3 | 115.2 | | | | |
| 3′,4′ | 145.9 | 145.8 | 145.3 | 145.2 | | |
| | 145.6 | 145.4 | 144.8 | 144.7 | | |
| | 145.3 | 145.1 | | | | |
| | 145.0 | 144.9 | | | | |
| | 144.8 | 144.7 | | | | |
| | 144.7 | 144.5 | | | | |
| 5′ | 116.6 | 116.4 | 115.9 | 116.0 | | |
| | 116.2 | 116.1 | | | | |
| | 116.1 | 116.0 | | | | |
| 6′ | 121.3 | 121.2 | 119.4 | 119.5 | | |
| | 119.8 | 119.8 | | | | |
| | 119.5 | 119.4 | | | | |
| *p*-Hydroxyphenyl | | | | | | |
| 1′ | | | 131.4 | 131.4 | 131.7 | 131.8 |
| | | | 130.8 | 130.8 | 131.1 | 131.4 |
| | | | | | 130.6 | 130.8 |
| 2′,6′ | | | 130.7 | 130.7 | 130.4 | 130.7 |
| | | | 129.2 | 129.2 | 128.9 | 129.2 |
| | | | | | 128.8 | 129.1 |
| 3′,5′ | | | 116.6 | 116.2 | 116.0 | 116.6 |
| | | | 115.9 | 115.9 | 115.5 | 115.8 |
| | | | | | 115.3 | 115.6 |
| 4′ | | | 157.8 | 157.8 | 157.5 | 157.9 |
| | | | 157.4 | 157.4 | 157.1 | 157.5 |
| | | | | | 156.7 | 157.1 |

The numbering system for the flavane skeleton is adopted. The numbers 11 and 12 represent an additional carboxymethylene unit. *a*) The chemical shifts changed with concentration.[11]

compounds **2L**, **2A**, **3L** and **3A** have an astringent taste.

## Experimental

Melting points were determined with a Yanagimoto micromelting 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. Circular dichroism (CD) spectra were recorded on a JASCO J-600 spectrometer. Mass spectra (MS) were measured with Hitachi M-80A and JEOL SX-102 spectrometers.

**Isolation Procedure** The air-dried fronds (800 g) of *Arachniodes sporadosora* NAKAIKE, collected in October at Uchiurayama, Chiba Prefecture, 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 about 500 ml under reduced pressure and 1 l of acetone was added. The gummy precipitates were removed and the remaining solution was evaporated. The residue (11 g) was repeatedly chromatographed on Sephadex LH-20 using acetone–water, EtOH and EtOH–water as eluents to yield compounds **1L** (1.1 g), **1A** (0.2 g), **2L** (0.5 g), **2A** (0.5 g), **3L** (0.3 g) and **3A** (0.2 g).

The air-dried fronds (650 g) of *A. exilis* CHING, collected in October at Uchiurayama, Chiba Prefecture, were extracted and separated in a similar manner as above to yield compounds **1L** (0.9 g), **1A** (0.3 g), **2L** (0.4 g), **2A** (0.1 g), **3L** (0.2 g) and **3A** (0.1 g).

**Compound 1L** A pale brown amorphous powder, $[\alpha]_D^{20}$ +65° ($c$=1.0, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 284 (4.10). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3370, 1700, 1605, 1520, 1210, 1110, 1060, 1005, 820, 780. SI-MS $m/z$: 905 $[M+H]^+$.

**Compound 1A** A pale brown amorphous powder, $[\alpha]_D^{20}$ +79° ($c$=1.0, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 284 (4.04). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3370, 1700, 1610, 1510, 1210, 1110, 1060, 1005, 820, 780. SI-MS $m/z$: 923 $[M+H]^+$.

**Compound 2L** A pale brown amorphous powder, $[\alpha]_D^{20}$ +62° ($c$=1.2, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 224 (4.86), 279 (3.72). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3380, 1700, 1610, 1515, 1210, 1140, 1115, 1090, 1065, 1005, 830. SI-MS $m/z$: 873 $[M+H]^+$.

**Compound 2A** A pale brown amorphous powder, $[\alpha]_D^{20}$ +78° ($c$=1.0, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 225 (4.91), 280 (3.90). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3400, 1695, 1605, 1505, 1210, 1140, 1115, 1090, 1065, 1005, 830. SI-MS $m/z$: 891 $[M+H]^+$.

**Compound 3L** A pale brown amorphous powder, $[\alpha]_D^{20}$ +71° ($c$=1.5, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 225 (4.92), 277 (3.78). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3380, 1700, 1610, 1510, 1210, 1115, 1090, 1065, 1005, 830. SI-MS $m/z$: 857 $[M+H]^+$.

**Compound 3A** A pale brown amorphous powder, $[\alpha]_D^{20}$ +84° ($c$=1.1, MeOH), UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 224 (4.97), 277 (3.94). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3400, 1700, 1610, 1510, 1210, 1115, 1090, 1060, 1000, 835. SI-MS $m/z$: 875 $[M+H]^+$.

**The Tridecaacetate of 1L** A mixture of **1L** (50 mg), pyridine (2 ml) and acetic anhydride (2 ml) was allowed to stand for 19 h at room temperature, then poured into ice-water. The products were extracted with EtOAc. The extract was washed with 10% $Na_2CO_3$ solution, 10% HCl solution and water, then dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was chromatographed on Sephadex LH-20 using 10% MeOH in benzene as an eluent to yield the tridecaacetate (38 mg). A colorless amorphous powder, $[\alpha]_D^{20}$ +37° ($c$=0.3, $CHCl_3$). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 278 (3.90). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 2940, 1770, 1615, 1600, 1500, 1440, 1370, 1210, 1110, 1060, 1015, 900, 840. FD-MS $m/z$: 1450 $[M^+]$.

**The Undecamethylate of 1A** Compound **1A** (40 mg) was dissolved in dry acetone (20 ml) and then methyl iodide (8 ml) and anhydrous $K_2CO_3$ (6 g) were added. The mixture was stirred under reflux for 8 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 20% acetone in $CHCl_3$ as an eluent to yield 38 mg of the undecamethylate of **1A**. A colorless amorphous powder, $[\alpha]_D^{20}$ +25° ($c$=1.6, $CHCl_3$). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 281 (4.32). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3450, 3000, 2950, 2850, 1720, 1600, 1505, 1450, 1260, 1120, 1020, 810, 760. FD-MS $m/z$: 1090 $[M^+]$.

**Degradation of 1L** Compound **1L** (520 mg) was dissolved in EtOH (17 ml) containing benzylmercaptan (7 ml) and glacial acetic acid (5 ml), and the solution was refluxed under argon for 20 h. After removal of the volatile solvent, the residual oil was chromatographed on Sephadex LH-20 using EtOH as an eluent to yield **4** (27 mg) and **6** (8 mg).

**4**: A pale brown amorphous powder, $[\alpha]_D^{20}$ +87° ($c$=1.3, acetone). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 282 (4.17). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3350, 1610, 1510, 1435, 1280, 1140, 1060. SI-MS $m/z$: 699 $[M+H]^+$.

**6**: A colorless amorphous powder, $[\alpha]_D^{20}$ −59° ($c$=0.6, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 282 (3.88). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3370, 1700, 1600, 1510, 1455, 1270, 1140, 1100, 1020, 820. CD : $[\theta]_{282}$ −1270° ($c$=0.01, MeOH).

TABLE II. $^1$H-NMR Data in $D_2O$–Acetone-$d_6$ (1 : 1)

| | 1L | 1A | 4 | 6 | | 2L | 2A | | 3L | 3A | 5 | 7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Top unit | | | | | | | | | | | | |
| H-3 | 3.28 d (3) | 3.26 d (3) | 4.06 d (3) | | H-3 | 3.30 d (4) | 3.29 d (4) | H-3 | 3.19 d (4) | 3.18 d (3) | 4.05 d (3) | |
| H-4 | 4.12 d (3) | 4.10 d (3) | 4.36 d (3) | | H-4 | 4.12 d (4) | 4.10 d (4) | H-4 | 4.00 d (4) | 3.99 d (3) | 4.35 d (3) | |
| H-6 | 5.92 d (2) | 5.91 d (2) | 5.98 d (2) | | H-6 | 5.91 d (2) | 5.91 d (2) | H-6 | 5.91 d (2) | 5.90 d (2) | 5.97 d (2) | |
| H-8 | 6.03 d (2) | 6.02 d (2) | 6.07 d (2) | | H-8 | 6.02 d (2) | 6.02 d (2) | H-8 | 6.01 d (2) | 6.00 d (2) | 6.05 d (2) | |
| H-2′ | 7.01 d (2) | 7.00 d (2) | 7.12 d (2) | | H-2′6′ | 7.30 d (9) | 7.30 d (9) | H-2′6′ | 7.28 d (9) | 7.27 d (9) | 7.42 d (9) | |
| H-5′ | 6.87 d (8) | 6.86 d (9) | 6.84 d (8) | | H-3′5′ | 6.86 d (9) | 6.86 d (9) | H-3′5′ | 6.85 d (9) | 6.85 d (9) | 6.84 d (9) | |
| H-6′ | 6.80 dd (8, 2) | 6.80 dd (9, 2) | 6.89 dd (8, 2) | | | | | | | | | |
| Middle unit | | | | | | | | | | | | |
| H-2 | 5.59 br s | 5.56 br s | 5.23 br s | | H-2 | 5.63 br s | 5.61 br s | H-2 | 5.62 br s | 5.59 br s | 5.28 br s | |
| H-3 | 4.14 br s | 4.14 br s | 3.95 d (2) | | H-3 | 4.15 br s | 4.16 br s | H-3 | 4.12 br s | 4.12 br s | 3.94 d (3) | |
| H-4 | 4.42 br s | 4.39 br s | 4.04 d (2) | | H-4 | 4.42 br s | 4.39 br s | H-4 | 4.41 br s | 4.38 br s | 4.06 d (3) | |
| H-6 | 6.14 s | 6.11 s | 6.11 s | | H-6 | 6.13 s | 6.10 s | H-6 | 6.11 s | 6.07 s | 6.11 s | |
| H-2′ | 7.34 d (2) | 7.31 d (2) | 7.19 d (2) | | H-2′6′ | 7.65 d (9) | 7.64 d (9) | H-2′6′ | 7.61 d (9) | 7.60 d (9) | 7.45 d (9) | |
| H-5′ | 6.88 d (9) | 6.86 d (9) | 6.84 d (8) | | H-3′5′ | 6.88 d (9) | 6.87 d (9) | H-3′5′ | 6.87 d (9) | 6.86 d (9) | 6.84 d (9) | |
| H-6′ | 7.15 dd (9, 2) | 7.14 dd (9, 2) | 6.98 dd (8, 2) | | | | | | | | | |
| Bottom unit | | | | | | | | | | | | |
| H-2 | 4.38 br s | 4.37 br s | Benzyl $CH_2$ | 4.80 br s | H-2 | 4.37 br s | 4.38 br s | H-2 | 4.45 br s | 4.87 br s | Benzyl $CH_2$ | 4.87 br s |
| H-3 | 3.59 br s | 3.58 br s | 3.93 s | 3.86 br s | H-3 | 3.58 br s | 3.59 br s | H-3 | 3.58 br s | 3.58 br s | 3.94 s | 3.86 br s |
| H-4 | 3.29 m | 3.26 m | H-4 7.16 br t (8) | 3.30 ddd (10, 4, 2) | H-4 | 3.30 m | 3.26 m | H-4 | 3.27 m | 3.23 m | H-4 7.18 br t (7) | 3.31 ddd (11, 4, 2) |
| H-6 | 5.79 s | 5.78 s | H-3,5 7.24 br t (8) | 5.90 d (2) | H-6 | 5.73 s | 5.79 s | H-6 | 5.79 s | 5.79 s | H-3,5 (2) | 5.89 d (2) |
| H-8 | | | | 5.98 d (2) | | | | H-8 | | | 7.25 br t (7) | 5.98 d (2) |
| H-11α | 2.92 dd (17, 3) | 2.80 dd (16, 4) | H-2,6 7.32 d | 2.89 dd (16, 4) | H-11α | 2.89 dd (16, 4) | 2.71 dd (16, 4) | H-11α | 2.75 dd (16, 4) | 2.57 dd (11, 4) | H-2,6 7.33 d | 2.90 dd (16, 4) |
| H-11β | 2.22 dd (17, 12) | 2.20 dd (16, 10) | (7) | 2.38 dd (16, 10) | H-11β | 2.21 dd (16, 12) | 2.19 dd (16, 9) | H-11β | 2.22 dd (16, 9) | 2.18 dd (11, 8) | (7) | 2.39 dd (16, 11) |
| H-2′ | 6.80 d (2) | 6.79 d (2) | | 6.79 br s | H-2′ | 6.79 d (2) | 6.81 d (2) | H-2′6′ | 7.19 d (9) | 7.20 d (8) | | 7.29 d (8) |
| H-5′ | 6.84 d (8) | 6.86 d (9) | | 6.79 br s | H-5′ | 6.80 d (8) | 6.80 d (9) | H-3′5′ | 6.77 d (9) | 6.76 d (8) | | 6.80 d (8) |
| H-6′ | 6.74 dd (8, 2) | 6.74 dd (9, 2) | | 6.96 br s | H-6′ | 6.73 dd (8, 2) | 6.75 dd (9, 2) | | | | | |

Chemical shifts: ppm. Multiplicity: s, singlet; d, doublet; br s, broad singlet; br t, broad triplet; m, multiplet. Coupling constants (in parentheses): Hz.

MS *m/z*: 330 [$M^+$].

**Degradation of 2L** Compound **2L** (150 mg) was degraded in the same way as compound **1L** to yield **5** (11 mg) and **6** (3 mg).

**5**: A pale brown amorphous powder, $[\alpha]_D^{20}$ +64° (*c*=0.7, acetone). UV $\lambda_{max}^{MeOH}$ nm (log ε): 225 (4.84), 278 (4.00). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3350, 1610, 1505, 1440, 1220, 1140, 1110, 1060, 830. SI-MS *m/z*: 667 [M+H]$^+$.

**Degradation of 3L** Compound **3L** (150 mg) was degraded in the same way as compound **1L** to yield **5** (8 mg) and **7** (3 mg).

**7**: A colorless amorphous powder, $[\alpha]_D^{20}$ −30° (*c*=0.2, MeOH). UV $\lambda_{max}^{MeOH}$ nm (log ε): 278 (3.67). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3400, 1700, 1610, 1505, 1460, 1250, 1145, 1095. CD: $[\theta]_{282}$ −1900° (*c*=0.01, MeOH). MS *m/z*: 314 [$M^+$].

**Degradation of 1A** Compound **1A** (150 mg) was degraded in the same way as compound **1L** to yield **4** (17 mg) and **6** (3 mg).

## References and Notes


1) Part LXXIX: K. Hori, T. Satake, Y. Saiki and T. Murakami, *Yakugaku Zasshi*, **110**, 315 (1990).
2) T.-H. Hwang, Y. Kashiwada, G. Nonaka and I. Nishioka, *Phytochemistry*, **29**, 279 (1990); Y. Kashiwada, M. Morita, G. Nonaka and I. Nishioka, *Chem. Pharm. Bull.*, **38**, 856 (1990).
3) K. Hori, T. Satake, Y. Saiki, T. Murakami and C.-M. Chen, *Chem. Pharm. Bull.*, **36**, 4301 (1988).
4) D. Jacques, E. Haslam, G. R. Bedford and D. Greatbanks, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 2263.
5) G. Nonaka, S. Morimoto and I. Nishioka, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 2139.
6) As the H-3 signal of the bottom unit appears at δ 3.59 in the $^1$H-NMR spectrum of **1L**, C-3-OH is not considered to form the lactone ring.
7) C. Karl, P. Alsted and G. Muller, *Z. Naturforsch.*, **36C**, 607 (1981).
8) The absolute configuration of dryopterin (**6**) had not been determined.[7] We determined it as (2*R*), (3*R*) and (4*S*) by comparing the circular dichroism (CD) spectrum of **6**, $[\theta]_{282}$ −1280° (MeOH), with that of (−)-epicatechin, $[\theta]_{282}$ −2320° (MeOH).
9) Usual epicatechin-type proanthocyanidins possess 4β-configuration, avoiding steric interaction between the oxygen substituents at C-3 and C-5 and those in the *ortho*-positions on the A-ring of the linked

unit. The possibility of 4α-configuration is ruled out by the evidence described below and also the nuclear Overhauser effect (NOE) correlation two-dimensional NMR spectrum (NOESY) of **1**L where NOE between C-2-H of the middle unit and C-2-H of the bottom unit was observed.

10) Nomenclature of proanthocyanidins: R. W. Hemingway, L. Y. Foo and L. J. Porter, *J. Chem. Soc., Perkin Trans. 1,* **1982**, 1209.

11) The chemical shifts of C-11 and C-12 changed with concentration in this solvent system in the range of several ppm. This phenomenon is considered to be related to the equilibrium between the dimeric form of carboxylic acid and the hydrogen-bonded comlex of carboxylic acid with solvent. See: G. E. Maciel and D. D. Traficante, *J. Am. Chem. Soc.*, **88**, 220 (1966).

12) Recently, I. Nishioka and his co-workers isolated compound **1**A from an Aspidiaceous fern, *Polysticum polyblepharum*; M. Morita, Y. Kashiwada, G. Nonaka and I. Nishioka, Abstracts of Papeprs, The 36th Annual Meeting of the Japanese Society of Pharmacognosy, Kumamoto. Oct. 1989, p. 170. We also isolated **1**A from *P. tsus-simense* and a Polypodiaceous fern, *Loxogramma saziran.*

13) I. Nishioka, *Kagaku To Seibutsu*, **24**, 428 (1986).