A Novel Flavonoid Glycoside from Drymaria diandra

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Abstract: A novel flavonoid glycoside, drymariatin A, was isolated from the whole plants of Drymaria diandra (Caryophyllaceae). By spectroscopic analysis, its structure was elucidated as 6-trans-[2'-O-(α-rhamnopyranosyl)]-ethenyl-5,7,4-trihydroxyflavone.

Previous chemical studies of the genus Drymaria have not been very extensive. An alkaloid, nortriterpenes and their glycosides, triterpenoids and mixtures of long chain fatty acids were isolated from this genus (1–4). Drymaria diandra Bl. (Caryophyllaceae) is used as a folk drug for treatment of acute hepatitis in China (5). In a search for its biologically active compounds, a chemical study on this plant was carried out and a novel flavonoid glycoside, named drymariatin A (1), was obtained from the n-butanol fraction of its ethanol extract by column chromatography.

Drymariatin A was obtained as a yellow powder. Its negative FAB-MS exhibited the molecular ion peak at m/z 457 ([M – 1]⁻, base peak) and one fragment peak at m/z 311 ([M – 146]⁻). The molecular formula was established by HR-FABMS as C₂₅H₂₂O₁₀. The IR spectrum had adsorptions at 3400 and 1627 cm⁻¹ corresponding to the hydroxy and hydrogen bonded unsaturated carbonyl groups. The UV spectrum showed bands at 270.5, 309.0 and 338.0 nm. This information along with the analysis of its ¹H- and ¹³C-NMR signals indicated that 1 was a flavone glycoside.

The ¹H-NMR spectrum of this compound revealed a high field methyl doublet at δ 1.61 (J = 6.0 Hz), two olefinic doublets at δ 8.48 and 7.20, two aromatic singlets at δ 8.68 and 6.89, an AX pair of aromatic doublets at δ 7.84 (2H, J = 8.8 Hz) and 7.16 (2H, J = 8.8 Hz) characteristic of a para-disubstituted aromatic ring, and the signals of the sugar portion in the low-field aliphatic region. The DEPT spectrum showed one carbonyl, eight quaternary carbon, eleven methine carbon and one methyl signals. The NMR data and HMBC, HMBC spectra indicated that the sugar was rhamnose, and its anomeric proton and carbon were at δ 5.84 (s) and 102.2, respectively, suggesting the presence of a α-O-glycosidic bond.

Compared with ¹³C-NMR signals of 5,7,4-trihydroxyflavone (6), it had two additional olefinic carbons. The HMBC spectrum showed correlations between one olefinic proton (H-2') and C-6, H-2' and C₆H₄O, and correlations between another olefinic proton (H-1') and C-5, H-1' and C-2', H-6 and C-2' were also observed. This indicated that the olefinic carbon C-1' was linked to C-6, and the olefinic carbon C-2'

References

was the binding site for the sugar unit. The value of the coupling constants for two olefinic protons (J = 12.4 Hz) indicated that the two olefinic protons were in a trans-position (7). Therefore the structure of drymariatin A was determined as 6-trans-[2'-O-(α-rhamnopyranosyl)ethenyl]-5,7,4-trihydroxyflavone (Fig. 1). It is a novel flavonoid derivative, and its 1H- and 13C-NMR data are summarized in Table 1.

![Structure of drymariatin A (1).](image)

**Table 1** 1H- and 13C-NMR data of drymariatin A (1) (500 MHz for 1H-NMR, 125 MHz for 13C-NMR, in pyridine-d6).

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<td>162.6</td>
<td>1'</td>
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<tr>
<td>3</td>
<td>103.8</td>
<td>2'</td>
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<td>10</td>
<td>122.4</td>
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<td>2', 6'</td>
<td>3'</td>
<td>128.9</td>
<td>7.84 (d, 8.8)</td>
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<td>3'5'</td>
<td>116.9</td>
<td>7.16 (d, 8.8)</td>
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<td>4'</td>
<td>159.9</td>
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30:70) column chromatography and gave drymariatin A (6 mg).

**Drymariatin A (1):** C21H22O10, yellow powder, IR (KBr): \( \lambda_{\text{max}} = 3400, 1627 \text{ cm}^{-1} \); HRFAB-MS: m/z requires: 457.1135, found 457.1048 [M – H]⁺, 311 [M – Rha – H]⁺; UV (MeOH): \( \lambda_{\text{max}} = 270, 309, 338 \text{ nm} \); 1H-NMR and 13C-NMR data are listed in Table 1.

**Acknowledgements**

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**References**


**Materials and Methods**

Spectra were recorded with the following instruments. IR: Bio-Rad FTS-135 spectrometer; NMR: Bruker DRX-500 MHz; MS: VG Auto Spec-3000; UV: Shimadzu UV 2104; 200–300 mesh and 300–400 mesh silica gel, RP-18, Sephadex HL-20 and resin D-101 were used for column chromatography.

The whole plants of *Drymba diandra* (Caryophyllaceae) were collected in Xishuangbanna, Yunnan, China, in July 1997. A voucher specimen (No. 11397) of the plant is deposited at the herbarium of Kunming Institute of Botany, Academia Sinica. The botanical identification was made by Mr. Hong Wang, Xishuangbanna Tropical Botanical Garden, Academia Sinica.

The whole plants of *D. diandra* BL. (18.6 kg) were extracted with hot ethanol four times to afford a ETOH extract that was suspended in water, extracted with ethyl acetate and n-butanol, respectively. The BuOH residue was chromatographed on resin D-101 using H2O-MeOH (from 90:10 to 10:90) gradient system. The fraction eluted with 70% MeOH was further subjected to silica gel (CHCl3-MeOH, 85:15), Sephadex HL-20 (H2O-MeOH, 20:80) and RP-18 (H2O-MeOH, 30:70) column chromatography and gave drymariatin A (6 mg).