

FILICINAE

ASPIDIACEAE

PHLOROGLUCINOL DERIVATIVES OF *DRYOPTERIS DICKINSII*
AND SOME RELATED FERNS

S. HISADA, K. SHIRAISHI and I. INAGAKI

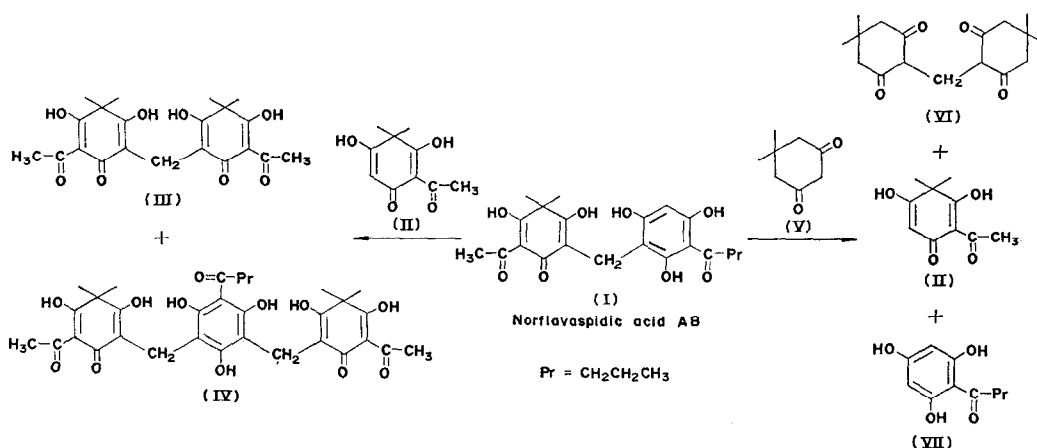
Faculty of Pharmaceutical Sciences, Nagoya City University, Mizuho-ku, Nagoya, Japan

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Key Word Index—*Dryopteris dickinsii*; Aspidiaceae; ferns; acylphloroglucinols; norflavaspidic acid AB.

In the previous paper¹ we reported that three filixic acids *BBB*, *ABB* and *ABA* were isolated from *Dryopteris dickinsii* (Fr. et Sav.) C. Chr. Here, we report the isolation of a new constituent, norflavaspidic acid *AB* (I) from the rhizomes of this fern. The raw filicin obtained by MgO method was chromatographed on silica and eluted with cyclohexane—CHCl₃ (1:1)¹ then with CHCl₃ alone. CHCl₃ elution afforded I, C₂₁H₂₄O₈, m.p. 105–107°, *m/e* 404 (M⁺), significant peaks at *m/e* 208, 196, 165, 153. IR ν_{\max}^{KBr} cm⁻¹; 3200 (OH), 2900, 1640 (conjugated C=O), 1605 (conjugated C=C), 1233, 1193, 1147. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ); 226.5 (4.34), 292.5 (4.31), 341 (4.07), UV $\lambda_{\max}^{\text{EtOH}+\text{NaOH}}$ nm (log ϵ); 242.5 (4.41), 321 (4.37). The NMR spectrum (NMR analysis in CDCl₃ + D₂O using TMS as internal reference showed ppm) of I shows signal attributable to: 1.01 (3H, t—COCH₂—CH₂CH₃), about 1.72 (2H, m—COCH₂CH₂CH₃), 3.16 (2H, t—COCH₂CH₂CH₃) all due to butyryl group. 1.45 (weak), 1.53 (6H, each s gem-dimethyl), 2.77 (3H, s—COCH₃), 3.62 (2H, s methylene bridge between acetylfilicinic acid and phlorobutyrophenone), 6.03 (1H, s free H of aromatic ring).

After alkaline cleavage of I, phloroglucinol, methylphloroglucinol, phlorobutyrophenone, methylphlorobutyrophenone, filicinic acid, and acetylfilicinic acid were identified by TLC comparisons with authentic samples. The structure of I was further confirmed by the following two chemical reactions.



SCHEME 1. REACTIONS OF NORFLAVASPIDIC ACID AB.

I and acetylfilicinic acid (II) in the presence of 3.7% formalin were reacted together in dilute alkaline solution to obtain albaspidin AA (III), $C_{21}H_{24}O_8$, m.p. 170–173° and filixic acid ABA (IV), $C_{32}H_{36}O_{12}$, m.p. 164–167°. In the next, I and excess dimedone (V) were reacted together in dilute alkaline solution to yield II, $C_{10}H_{14}O_4$, m.p. 170–173°, methylene-bis-dimedone (VI), $C_{17}H_{24}O_4$, m.p. 189° and phlorobutyrophenone (VII), $C_{10}H_{12}O_4$, m.p. 184–187°. All reaction products (II, III, IV, VI and VII) were identical with authentic samples.

TABLE 1. CONSTITUENTS OF SOME *Dryopteris* SPECIES

<i>Dryopteris</i> spp.	Locality	Filixic acid			Norflavaspidic acid AB
		BBB	ABB	ABA	
<i>D. dickinsii</i>	Toyama	+	+	+	+
	Kumamoto	(+)	(+)	(+)	(+)
	Mie	+	+	+	+
	Shiga	(+)	(+)	+	+
	Kumamoto	(+)	(+)	+	+
<i>D. tasiroi</i>	Kumamoto	(+)	+	+	+
	Kumamoto	(+)	+	+	+
<i>D. commixta</i>	Kumamoto	(+)	(+)	(+)	+

+, Isolated; (+), TLC spot; TLC-Plate, Kieselgel H; Solvent system, $CHCl_3$ -MeOH- H_2O = 7:3:1 (lower); Colour reag., Diazotized benidine.

We have also investigated the occurrence of phloroglucinol derivatives in the several sources of *D. dickinsii*, and *D. tasiroi* Tagawa and *D. commixta* Tagawa. The results were showed in Table 1.

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¹ S. HISADA, K. SHIRAIISHI and I. INAGAKI, *Phytochem.* **11**, 1850 (1972).

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DENNSTAEDTIACEAE

STEROLS AND TRITERPENES OF *OLEANDRA PISTILLARIS**

A. S. C. WAN

School of Pharmacy, University of Singapore, Singapore

and

R. T. AEXEL and H. J. NICHOLAS

Institute of Medical Education and Research and Department of Biochemistry, St. Louis University School of Medicine, St. Louis, MO 63104, U.S.A.

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Plant. *Oleandra pistillaris*, Dennstaedtiaceae (Oleanroideae). *Source.* Cameron Highlands (Malaysia). *Previous work.* None.

Present work. Ground plant material (whole plant; 660 g) extracted with hot EtOH

* Part III in a series "Malaysian Plants". For part II see *Phytochem.* **11**, 456 (1972).