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ISOLATION OF FLAVASPIDIC ACID-*PB* FROM *DRYOPTERIS SIEBOLDII*

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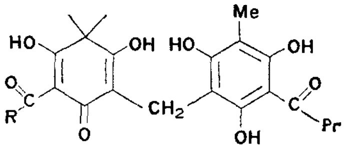
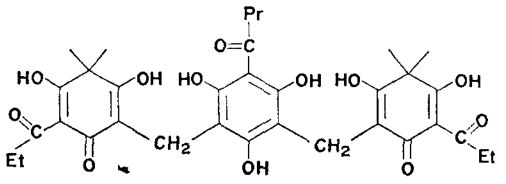
Key Word Index—*Dryopteris sieboldii*; Aspidiaceae; ferns; acylphloroglucinols; flavaspidic acid-*AB* and -*PB*; filixic acid -*PBP*.

Plant. Dryopteris sieboldii (van Houtte) O. Ktze. *Source.* Kagoshima Prefecture, Japan. *Previous work.* The presence of flavaspidic acid and filixic acid was detected by paper electrophoresis,[1] and the existence of flavaspidic acid-*PB* was only reported in *D. filix-mas* by PPC.[2]

Present work. Dried rhizomes of *D. sieboldii* were percolated with Et_2O and crude filicin was obtained by MgO method.[3] The Et_2O solution of crude filicin gave flavaspidic acid-*AB* (I). Mother liquor after removal of I was chromatographed on silica and eluted with cyclohexane–$CHCl_3$ (1 : 1). The elution afforded filixic acid-*PBP* (II) and then flavaspidic acid-*PB* (III).



Flavaspidic acid-*AB* (I) R = Me
Flavaspidic acid-*PB* (III) R = Et



Filixic acid -*PBP* (II)

Flavaspidic acid-*AB* (I). $C_{22}H_{26}O_8$, m.p. 205–7° (from C_6H_6) IR, UV, NMR and m.m.p. with authentic sample. Filixic acid-*PBP* (II). $C_{30}H_{40}O_{12}$, m.p. 192–194° (light yellow needles from acetone). IR ν_{max}^{KBr} cm^{-1} 3140 (OH), 2940 (methylene), 1640–1610 (enolic 1,3-diketo system or 2-hydroxyarylketone), 1192. UV λ_{max}^{EtOH} nm (log ϵ) 225 (4·42), 297 (4·24), 345 (4·12). UV $\lambda_{max}^{EtOH+NaOH}$ nm (log ϵ) 242 (4·37), 315 (4·26). R_f 0·75 on TLC in $CHCl_3$–MeOH–H_2O (7:3:1, lower) spot color gave orange yellow with diazotized benzidine and dark brown with $FeCl_3$. The NMR spectrum (NMR analysis in $CDCl_3$ using TMS as internal reference showed ppm) shows signal attributable to: 0·96 (3H, *t* $-COCH_2CH_2C\underline{H}_3$), 1·12 (6H, *t* $-COCH_2C\underline{H}_3$), 1·40, 1·46 (12H, each *s gem*-dimethyl), about 1·76 (2H, *m* $-COCH_2C\underline{H}_2CH_3$), 3·15 (6H, *t* $-COC\underline{H}_2CH_2CH_3$, $-COC\underline{H}_2CH_3$), 3·52 (4H, *s* two methylene bridges), 9·97 (2H, *s*), 11·39 (1H, *s*), 12·62 (1H, *s*), 15·57 (1H, *s*), 17·78 (2H, *s*), all due to hydrogen bonded hydroxy groups and quenched by addition of D_2O. The MS, 640 (M^+), significant peaks at *m/e* 418, 222, 210, 193, 181, 165, 153.

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Flavaspidic acid-*PB* (III). $C_{23}H_{28}O_8$, m.p. 154–6° (yellow powder from *n*-hexane). IR ν_{max}^{KBr} cm^{-1} 3520, 3230 (OH), 2960 (methylene), 1640–1610 (enolic 1,3-diketo system or 2-hydroxyarylketone), 1195, 1153. UV λ_{max}^{EtOH} nm (log ϵ) 223 (4·94), 299 (4·79), 349 (4·93). UV $\lambda_{max}^{EtOH+NaOH}$ nm (log ϵ) 239 (4·79), 317 (5·00). R_f 0·14 on TLC in $CHCl_3$–MeOH–H_2O (7:3:1, lower) spot color gave orange-red with diazotized benzidine and dark brown with $FeCl_3$. The NMR spectrum (NMR analysis in pyridine-d_5 using TMS as internal reference showed ppm) shows signal attributable to: 0·90 (3H, *t* $-COCH_2CH_2C\underline{H}_3$), 1·25 (3H, *t* $-COCH_2C\underline{H}_3$), 1·56 (6H, *s* *gem*-dimethyl), about 1·85 (2H, *m* $-COCH_2C\underline{H}_2Me$), 2·38 (3H, *s* aromatic $C\underline{H}_3$), 3·26 (4H, *m* $-COC\underline{H}_2CH_2CH_3$, $-COC\underline{H}_2CH_3$), 3·99 (2H, *s* methylene bridge between propionylfilicinic acid and methylphlorobutyrophenone), 9·33 (5H, *br* OH) quenched by addition of D_2O. The MS, *m/e* 432 (M^+), significant peaks at *m/e* 222, 210, 193, 167.

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BIFLAVONES IN THE LEAVES OF TWO *JUNIPERUS* PLANTS

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Key Word Index—*Juniperus horizontalis*; *Juniperus recurva*; Cupressaceae: biflavones; sciadopitysin; 7,7″-di-*O*-methylcupressuflavone

A number of *Juniperus* plants has already been examined[1–3] for biflavones. We now report the isolation of sciadopitysin[4] (I, 7,4′,4‴-tri-*O*-methylamentoflavone) from *Juniperus horizontalis* Moench[5] and 7,7″-di-*O*-methylcupressuflavone[6,7] (II) from *J. recurva* Buch.-Ham.[5] Some other biflavones including cupressuflavone and its monomethyl ether are detected in the leaf extracts of the two plants by TLC examinations. This constitutes the

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[5] Place of collection and identification: Lyod Botanical Garden, Darjeeling, India.

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