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TRITERPENOIDS FROM *PORIA CARBONICA*

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Key Word Index—*Poria carbonica*; Polyporaceae; triterpenoids; eburicoic acid; dehydroeburicoic acid.

Plant. Poria carbonica. Source. Isolated from Douglas-fir utility poles in Oregon, U.S.A.[1] *Previous work.* Isolation and characterization of eburicoic acid and dehydroeburicoic acid from several species of *Fomes*,[2] *Polyporus*[2] and *Lenzites*,[3] and from *Poria cocus*.[4]

Present work. Light petrol. extraction of *Poria carbonica* grown on malt extract agar yielded, on concentration, a mixture of eburicoic acid and dehydroeburicoic acid, $C_{31}H_{50}O_3$ and $C_{31}H_{48}O_3$ respectively, m.p. 281-3°, $[\alpha]_D^{25}$ +39·5° ($CHCl_3$). UV, 235, 243, 252 nm (EtOH). Methyl esters (m.p., UV, IR, NMR and MS).

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DRYOCRASSIN: A NEW ACYLPHLOROGLUCINOL FROM *DRYOPTERIS CRASSIRHIZOMA*

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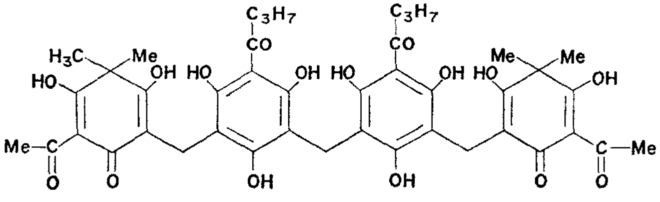
Key Word Index—*Dryopteris crassirhizoma*; Aspidiaceae; fern; acylphloroglucinols; dryocrassin.

Plant. Dryopteris crassirhizoma Nakai. *Uses.* Oreoresin of the dried rhizome and frond bases was used as a taenifuge in Japan.[1] *Previous work.* Filixic acid-like substance.[2] *Present*

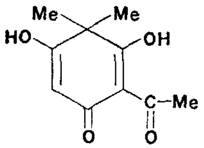
[1] *Japanese Pharmacopoeia* 6th edn (1951).
[2] HISADA, S. and NORO, Y. (1961) *Yakugaku Zasshi* **81**, 1270.

work. The filixic acid-like substance proved to be a new four ring phloroglucinol derivative, and its structure was established as I and named dryocrassin.

Dried material was percolated with Et_2O, and extract was evapolated. The raw filicin obtained by MgO method was dissolved in Et_2O. When the Et_2O solution was allowed to stand, a crystalline precipitate was obtained. By recyrstallization from acetone, the precipitate gave I, $C_{43}H_{48}O_{16}$, yellow crystals, m.p. 209–214°, IR ν_{max}^{KBr} cm^{-1}; 3100, 2700, 1625, 1610, 1480, 1200, 1160, 1030, UV λ_{max}^{EtOH} nm (ϵ); 222 (42 000), 306 (27 000), 351 (26 000), NMR (in pyridine-d_5, i. s. tetramethylsilane, showed ppm); 0·88 (6H, *t* 2× $-COCH_2CH_2C\underline{H}_3$, *J* 7 Hz), 1·72 (4H, *m* 2× $-COCH_2C\underline{H}_2Me$, *J* 7 Hz), 3·25 (4H, *t* 2 × $-COC\underline{H}_2CH_2Me$, *J* 7 Hz), 1·51 (12H, *s* two gem-dimethyl), 2·66 (6H, *s* 2× -COMe), 3·92 (4H, *s* two methylene bridges between acetylfilicinic acid and phlorobutyrophenone rings), 4·31 (2H, *s* methylene bridge between two phlorobutyrophenone rings).

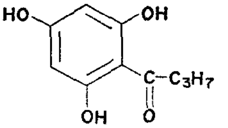


Dryocrassin (I)



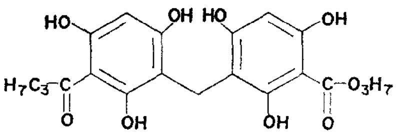
(II)

+



(III)

II +



(IV)

Alkaline creavage of I was carried out on the two different conditions, and both decomposition products were examined. (a) The NaOH solution of I was heated with Zn dust at 100° for 5 min. Acetylfilicinic acid (II), $C_{10}H_{12}O_4$, m.p. 166–167° and phlorobutyrophenone (III), $C_{10}H_{12}O_4$, m.p. 184–185° were isolated from the reaction mixture. (b) The Na_2CO_3 solution of I was heated with $Na_2S_2O_4$ at 100° for 5 min, and II and methylene-bis-phlorobutyrophenone (IV), $C_{21}H_{24}O_8$ m.p. 214–216° were obtained. Those decomposition products were identified with authentic samples by TLC, IR, MS and NMR.

The structure of I was further confirmed by its synthesis. II, IV and formalin were reacted together in dilute alkaline solution and the required compound (I) was separated. Natural dryocrassin was completely identical with synthetic substance by TLC, UV and IR.

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

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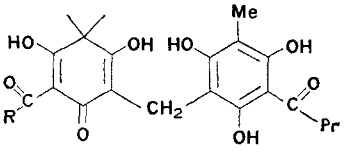
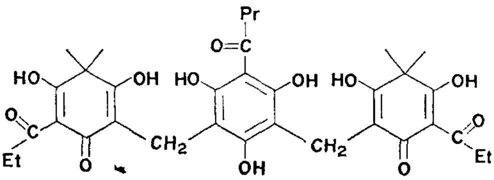
Key Word Index—*Dryopteris sieboldii*; Aspidiaceae; ferns; acylphloroglucinols; flavaspidic acid-*AB* and -*PB*; filixic acid -*PBP*.

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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