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LICHENS

ERGOSTEROL PEROXIDE FROM *PELTIGERA APHTHOSA* AND *P. DOLICHORRHIZA*

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Plant. Peltigera aphthosa (L.) Willd. and *Peltigera dolichorrhiza* (Nyl.) Nyl., both collected on Mount Fuji. *Previous work.* Unknown compound X_3, m.p. 183–184°, from the above lichens.[1]

Thallus. Extracted hexane, chromatographed. Ergosterol peroxide, $C_{28}H_{44}O_3$, m.p 183–184°, $[\alpha]_D$ −23·9°. Ergosterol peroxide acetate,[2] m.p. 198–201° (m.m.p., TLC and IR).

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[1] R. TAKAHASHI, O. TANAKA and S. SHIBATA, *Phytochem.* **9**, 2037 (1970).
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Key Word Index—Peltigera aphthosa; *Peltigera dolichorrhiza*; Lichens; ergosterol.

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FILICINAE

ASPIDIACEAE

A NEW ACYLPHLOROGLUCINOL FROM *DRYOPTERIS DICKINSII*

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Recently, Penttilä and Sundman[1] reported the isolation and synthesis of filixic acids BBB, PBB and PBP from *Dryopteris filix-mas*, while the presence of filixic acids ABB, ABP and ABA was only presumed. In this communication we report the isolation, characterization and synthesis of filixic acid ABA.

RESULTS

Dried rhizomes of *Dryopteris dickinsii* were percolated with Et_2O and the Et_2O extract was treated with MgO. The raw filicin obtained by Aebi's method[2] was chromatographed on silica and eluted with cyclohexane-$CHCl_3$ (1:1).

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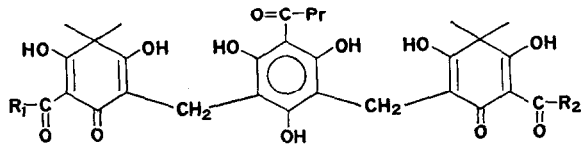

Pr = $CH_2CH_2CH_3$

Filixic acid BBB (I) $R_1 = R_2 = Pr$
ABB (II) $R_1 = CH_3$, $R_2 = Pr$
ABA (III) $R_1 = R_2 = CH_3$

Filixic acid BBB (I). $C_{36}H_{44}O_{12}$, m.p. 168–170° (from acetone), IR, UV, NMR, TLC and m.m.p. with authentic sample. *Filixic acid* ABB (II). $C_{34}H_{40}O_{12}$, m.p., IR, UV and NMR, not identified with certainty. *Filixic acid* ABA (III). $C_{32}H_{36}O_{12}$, m.p. 163–166° (yellow needles from acetone), IR ν_{max}^{KBr} cm^{-1}, 3140 (—OH), 2960, 1640–1610 (enolic 1,3-diketo system or 2-hydroxyaryl ketone), 1260, 1198, UV λ_{max}^{EtOH} nm (log ϵ), 228 (4·56), 292 (4·41), 343 (4·12), UV $\lambda_{max}^{EtOH+NaOH}$ nm (log ϵ), 241 (4·62), 319 (4·47), R_f 0·58 on TLC in $CHCl_3$–MeOH–H_2O (7:3:1, lower), spot gave yellow orange with diazotized benzidine and dark brown with $FeCl_3$. The NMR spectrum (NMR analysis in $CDCl_3$ showed ppm) of (III) shows signal attributable to: 1·02 (3H, t —$COCH_2CH_2C\underline{H}_3$), about 1·77 (2H, m —$COCH_2C\underline{H}_2CH_3$), 3·18 (2H, t —$COC\underline{H}_2CH_2CH_3$), all due to butyryl group. 1·45, 1·55 (12H, each s two gem dimethyl groups), 2·71 (6H, s two acetyl groups), 3·55 (4H, s methylene bridge between two acylphloroglucinol structure groups). 9·91 (2H, s), 11·33 (1H, s), 12·58 (1H, s), 15·34 (1H, s) and 17·22 (2H, s), all due to hydrogen bonded hydroxy groups.

After alkaline cleavage of III, phloroglucinol, methylphloroglucinol, phlorobutyrophenone, methylphlorobutyrophenone and acetylfilicinic acid were identified by TLC comparisons with authentic samples. The structure of (III) was confirmed by synthesis. Acetylfilicinic acid, phlorobutyrophenone and formalin were reacted together in dilute alkaline solution and the required compound, (III) separated. Natural filixic acid ABA was completely identical with synthetic material by IR, UV, NMR, TLC, m.p. and m.m.p.

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Key Word Index—Dryopteris dickinsii; Aspidiaceae; filixic acids ABA, ABB and BBB.