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FILICINAE

POLYPODIACEAE

PHYTOECDYSONES FROM *PHYMATODES NOVAE-ZELANDIAE*

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The fern *Phymatodes novae-zelandiae* which is endemic to New Zealand has been shown to give extracts with pronounced insect moulting hormone activity in the house-fly ligature bioassay.[1] The activity of this plant is due to the presence of crustecdysone, polypodine B and α-ecdysone, which have now been isolated from frond tissue.

The alcoholic concentrate of dried, milled fronds (1 kg) was partitioned between light petroleum and 80% MeOH, water and the concentrated methanolic layer re-partitioned between $CHCl_3$–MeOH–H_2O (1:1:1). The $CHCl_3$ fraction was eluted through a column of alumina (10% H_2O) with EtOAc–EtOH (1:1) to give an ecdysone rich fraction. Further chromatography on silica gel with $CHCl_3$–EtOH (19:1) gave a series of fractions from which α-ecdysone (m.p. 237–239°, 100 mg), polypodine B (m.p. 253–255°, 180 mg) and crustecdysone (m.p. 239–241°, 70 mg) were crystallized. The identities of these compounds were established by a direct comparison with authentic samples (m.m.p., TLC, IR, UV, NMR and MS).

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[1] G. B. RUSSELL and P. FENEMORE, *N.Z. Jl. Sci.* **14**, 31 (1971).

Key Word Index—Phymatodes novae-zelandiae; Polypodiaceae; crustecdysone; polypodine B; α-ecdysone.

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ANGIOSPERMAE
DICOTYLEDONAE

ARALIACEAE

CONSTITUENTS OF THREE-LEAVED *ACANTHOPANAX*

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Plant. Acanthopanax trifoliatus (Linn.) Merr. *Occurrence.* Taipei, Taiwan (Formosa). *Uses.* Folk medicinal, anti-paralysis. *Previous work.* On sister species: *Acanthopanax innovans*[1] and *A. sciadophylloides.*[2]

[1] M. YASUE *et al.*, *Yakugaku Zasshi* **87**, 247, 732 (1967); **88**, 390 (1968); **90**, 1113, 1172 (1970); *Chem. Pharm. Bull. Tokyo* **18**, 856 (1970).

[2] M. YASUE, Y. KATO, Y. M. LIN and J. SAKAKIBARA, *Yakugaku Zasshi* **88**, 738 (1968); **89**, 872 (1969); **90**, 341 (1970).

Present work. From the aqueous soluble fraction of the methanol-extracts of the leaves, KCl, scyllitol, and myoinositol were isolated. From the benzene soluble fraction taraxeryl acetate, taraxerol, β-sitosterol with an unidentified steroid, a mixture of all *n*-alkanes between C_{29} and C_{33} containing hentriacontane as the major components, and a mixture of two primary alcohols, triacontanol and dotriacontanol, were obtained.

EXPERIMENTAL

The air dried and powdered leaves (820 g) was completely exhausted with hot MeOH (34 l.). The extract was concentrated to 800 ml, diluted with H_2O (800 ml) and extracted with benzene.

Water soluble components. Subsequent treatment with 90% MeOH yielded three crystalline compounds I, II, and III. *Compound* I. Colourless prisms, m.p. >500°; IR was shown to be KCl confirmed by IR, hexyl calcium, $NaClO_4$, $Na_3Co(No_2)_6$, picric acid, and $AgNO_3$ tests. *Compound* II. Colourless prisms, m.p. 344–346° (50% MeOH); $C_6H_{12}O_6$; ν_{max}(KBr) 3485, 3300 (OH) cm^{-1}; acetylation (pyridine–Ac_2O) gave an *hexaacetate*: m.p. 292–293°, ν_{max}(KBr) 1740, 1230 (CH_3CO O) cm^{-1}; NMR (in DMSO-d_6): δ 5·45(6H, s, =CHOCOCH₃), 1·93 (18H, s, 6 × CH_3CO·O). These data suggested that the compound was scyllitol which was confirmed by comparison with an authentic sample (paper chromatography, IR and m.m.p.). *Compound III.* Colourless Crystal, m.p. 230° (50% MeOH), $C_6H_{12}O_6$, ν_{max}(KBr) 3370, 3200 (OH) cm^{-1}; *hexaacetate*: m.p. 216°. These data suggested that compound III was *myo*inositol which was further confirmed by comparison with an authentic sample (paper chromatography, IR and m.m.p.). *Benzene soluble compounds.* The *n*-hexane soluble fraction was chromatographed on SiO_2 gave compounds IV, V, VI. Chromatography of the *n*-hexane insoluble fraction afforded compounds VII and VIII. *Compound* IV. Colourless prisms, m.p. 293–295°, ν_{max}(KBr) 1731, 1247 (CH_3CO·O), 3030, 1638, 810 =C=CH— cm^{-1}; NMR: δ5·57 (1H, dd, J = 4 Hz, 7 Hz) indicated an olefinic proton in =C=CHCH₂, 4·50 (1H, t, J = δ Hz, =CH·OCOCH₃), 2·03 (3H, s, CH_3CO), 1·10 (3H, s), 0·96 (6H, s), 0·93 (6H, s) 0·88 (6H, s), 0·83 (3H, s), indicated eight Me groups. From the above data the compound IV appeared to be taraxeryl acetate which was further confirmed by comparison with an authentic sample (TLC, IR, and m.m.p.). *Compound* V. Colourless crystals, m.p. 275–276° (benzene); ν_{max}(KBr) 3495 (OH), 3040, 1640, 812 (=C=CH—) cm^{-1}; *Acetate*: colourless prisms, m.p. 293–295°, the IR spectra and TLC were identical with that of compound IV, taraxeryl acetate. So compound V must be taraxerol which was confirmed by comparison with an authentic sample (TLC, IR, and m.m.p.). *Compound* VI. Colourless crystals, m.p. 155–156°, IR spectra almost identical with that of β-sitosterol. Analysed by GLC indicated contamination by an unidentified sterol probably campesterol. *Compound* VII. Colourless plates, m.p. 62–63°, ν_{max}(KBr), 2925, 2860 (C–H), 1478, 1468 (CH_2 and CH_3), 730, 720($(CH_2)_n$), indicating the presence of *n*-alkanes with a long chain, which was analysed by GLC: five peaks were identified as C_{29-33} *n*-alkanes by comparison with authentic specimens. The percentages in the mixture were: *n*-$C_{29}H_{60}$ 8·8; *n*-$C_{30}H_{62}$ 3·0; *n*-$C_{31}H_{64}$ 63·2; *n*-$C_{32}H_{66}$ 5·9; *n*-$C_{33}H_{68}$ 19·1%. *Compound* VIII. Colourless crystals, m.p. 84–85°, ν_{max}(KBr) 3500, 1050 (RCH_2OH), 1470, 730, 720 ($(CH_2)_n$)); the *acetate*, colourless crystals, m.p. 62°, was analysed by GLC shown two peaks which were identified to triacontanyl and dotriacontanyl acetates respectively by comparison with authentic specimens. The percentage in the mixture were triacontanyl acetate 30·2 and dotriacontanyl acetate 69·8%. So the compound VIII was a mixture of $C_{30}H_{61}OH$ and $C_{32}H_{65}OH$.

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Key Word Index—Acanthopanax trifoliatus; Araliaceae; sterols; alkanes; fatty alcohols; taraxerol.