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FLAVONE GLUCURONIDES OF THE NEW ZEALAND LIVERWORT *MARCHANTIA MACROPORA*

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Key Word Index—*Marchantia macropora*; liverworts; apigenin 7-*O*-glucuronide; chrysoeriol 7-*O*-glucuronide; luteolin 7-*O*-glucuronide; luteolin 3′-*O*-glucuronide; luteolin 7,3′-di-*O*-glucuronide.

Plant. Marchantia macropora Mitt. (Marchantiaceae) is a thallose liverwort found only in New Zealand [1].

Source. Supplied by Miss Ella O. Campbell, Massey University, Palmerston North (Voucher specimen No. MPN 17004).

Present work. Fresh gametophyte tissue was extracted with acetone–water as described previously [2]. The flavonoids were separated by successive 1-D PC in TBA and 15% HOAc. The PC homogeneous flavonoids were identified from their UV spectra, hydrolyses and identification of the constituent aglycone and sugar, and co-chromatography with the relevant flavone glucuronide previously isolated from other *Marchantia* species [2,3].

The major flavonoids of *Marchantia macropora* are luteolin, luteolin 3′-*O*-glucuronide and luteolin 7,3′-di-*O*-glucuronide. These are accompanied by lesser amounts of the 7-*O*-glucuronides of apigenin, chrysoeriol and luteolin.

The present work completes our survey of *Marchantia* species native to New Zealand. *M. macropora* displays features in its flavonoid chemistry common to *M. polymorpha* [1], *M. foliacea* [3] and *M. berteroana* [4].

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TRITERPENES FROM RHIZOMES OF *POLYPODIUM LEUCOTOMOS*

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Key Word Index—*Polypodium leucotomos*; Polypodiaceae; fern; triterpenes; fernene; dryocrassol; neriifoliol.

Plant. Polypodium leucotomos (syn. *P. decumanum, Phlebodium decumanum* [1], "Calaguala"). *Source.* Wild specimens growing on *Palma africana* trees along the northern seashore of Honduras. *Uses.* Folk medicines. *Previous work.* Infusions of rhizomes are active against malignant tumours and leukaemias [2]. *Plant part examined.* Rhizomes.

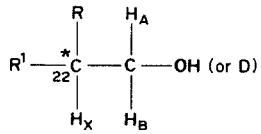
Present work. Fern-9(11)-ene and dryocrassol were isolated and characterized. Spectroscopic evidence is presented and discussed which fully supports the conclusion from chemical reactivity [3,4] that dryocrassol is the C-22 epimer of neriifoliol [5].

Dryocrassol and neriifoliol [5] give virtually

identical MS and therefore possess identical atomic skeletons. Their IR spectra are similarly interpreted and only differ significantly between 950 and 1100 cm^{-1} which is the region of C–O stretching. This suggests that $-CH_2OH$ group has a slightly different environment in the two compounds.

The PMR spectrum of dryocrassol indicates 7 Me-groups. The signals of 6 of these are almost identical with those of neriifoliol and, since these are singlets, they must be attached to quaternary C-atoms. (A *gem*-dimethyl is indicated by the IR peaks at 1389, 1374, 1210 and 1182 cm^{-1}. 4 of the 6 Me-groups are therefore angular). The remaining Me-group gives a doublet at $\tau = 8{\cdot}92$ and 8·96 ppm and is therefore attached to a CH group; this must be in $-CH(Me)CH_2OH$. With neriifoliol this doublet is found at $\tau = 9{\cdot}04$ and 9·105 ppm. In addition, the signals around $\tau = 6{\cdot}5$ ppm due to the CH_2 protons of $-CH_2OH$ are arranged slightly differently for dryocrassol and neriifoliol. These facts suggest that the two compounds are epimers which differ in the configuration of the asymmetric centre at C-22.

Addition of D_2O causes negligible change in the PMR spectrum of both dryocrassol and neriifoliol, which indicates that the exchangeable –OH proton does not couple significantly with the other protons. Analysis of the signals around $\tau = 6{\cdot}5$ ppm for both compounds shows they arise from H_A and H_B of the ABX system



whose chemical shifts (Hz) from TMS at 100 MHz and whose coupling constants (Hz) are as follows: for dryocrassol; $\nu_A = 361{\cdot}5$, $\nu_B = 337{\cdot}4$, $J_{AX} = 2{\cdot}6$, $J_{BX} = 6{\cdot}1$, $J_{AB} = 10{\cdot}6$; for neriifoliol; $\nu_A = 373{\cdot}2$, $\nu_B = 334{\cdot}3$, $J_{AX} = 2{\cdot}7$, $J_{BX} = 6{\cdot}3$, $J_{AB} = 10{\cdot}25$. Agreement between the position and intensities of the observed signals and those of a computer simulated PMR spectrum calculated from the above figures is good for each compound.

EXPERIMENTAL

Extraction and fractionation. Powdered rhizomes were extracted with Et_2O or CH_2Cl_2. The evaporated extract (3·0–3·5% of the original weight) was dissolved in *n*-hexane and chromatographed on a column (25 × 2·5 cm) of neutral Al_2O_3 (Merck, activity I). The column was eluted consecutively with 1·5 l. of *n*-hexane, C_6H_6, $CHCl_3$ and EtOAc. 200 g of the extract was dissolved in 1 l. of purified castor oil and subjected to molecular distillation at 10^{-5} mmHg at 160–200°. The distillate was taken up in *n*-hexane and rechromatographed as described.

The *n*-hexane fractions afforded hexagonal crystals whose yield was augmented by saponification of the evaporated mother liquors with KOH in EtOH. Recrystallization of the solid from hot EtOH afforded plates whose properties (mp, mmp, I_2 value, $[\alpha]_D^{25}$, ORD, MS, PMR, UV, IR) were identical with those of fern-9(11)-ene [7–9] (Found: C, 87·98; H, 12·22. Calc. for $C_{30}H_{50}$: C, 87·73; H, 12·27%. ORD in *n*-hexane under N_2: negative Cotton effect at 207 nm).

Dryocrassol. The EtOAc eluate was evaporated to dryness and extracted with *n*-hexane. The filtered extract was evaporated and after recrystallization twice from hot C_6H_6 afforded needles, mp 247–249°, $[\alpha]_D^{28} + 52°$ (*c*, 0·24 in $CHCl_3$), $[\alpha]_D^{22{\cdot}5} + 58{\cdot}1°$ (*c*, 1·38 in $CHCl_3$), $[\alpha]_{546\,nm}^{25} + 58{\cdot}1$ (*c*, 0·5 in $CHCl_3$) (Found: C, 84·0; H, 12·5. $C_{30}H_{52}O$ requires: C, 84·0; H, 12·2%); UV spectrum in EtOH transparent down to 200 nm; *m/e* (*I*% in parenthesis) 428·4024 (6·3) (M^+ corresponding to $C_{30}H_{52}O = 428{\cdot}4018$), 413 (48), 369·3534 (7·4) ($C_{27}H_{45} = 369{\cdot}3521$), 207·1751 (100) ($C_{14}H_{23}O$) = 207·1749), 191 (60), 177 (6·3), 163 (11), 149·1327 (27) ($C_{11}H_{17} = 149{\cdot}1330$), 137 (15), 123 (17), 109 (18), 95 (35), 81 (24·5), 69 (22), 55 (16), 41 (9·8); τ (ppm in $CDCl_3$) 8·92 (1·5H), 8·98 (1·5H), 9·04 (6H), 9·145 (3H), 9·175 (3H), 9·20 (3H), 9·27 (3H) (all Me), 6·5 region (2H, >CH–CH_2–O(H), two AB-quartets, 369·5, 366·5, 358·5, 356, 344·5, 338·5, 344, 328, Hz from TMS at 100 MHz). Identity of IR spectra and mmp (247–249°) proves that the compound is dryocrassol.

Neriifoliol [5]. The following additional measurements were made. τ (ppm in $CDCl_3$) 9·04 (7·5H), 9·105 (1·5H), 9·15 (3H), 9·18 (3H), 9·205 (3H), 9·28 (3H) (all Me), 6·5 region (2H, >CH–CH_2–O(H), two AB-quartets, 380·5, 377·5, 370, 367·5, 342, 335·5, 331·5, 325·5 Hz from TMS at 100 MHz).

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