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PODOCARPACEAE

SOME CONSTITUENTS OF *PODOCARPUS SALIGNA**

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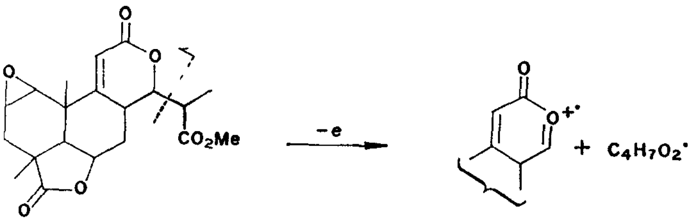
BECAUSE of the current interest in *Podocarpus* species[1–4] and our project dealing with Chilean flora,[5] a preliminary examination of *Podocarpus saligna* D. Don, a plant indigenous to Chile, has been made The leaves were collected August 1968, 15 km north of Concepcion. After cold extraction with ethanol, the soluble material was re-extracted in turn with benzene, ethyl acetate, and *n*-butanol From the benzene extract was isolated the saturated hydrocarbon fraction, the major component being nonacosane, and also β-sitosterol, identified by conversion into its acetate Fern-9(11)-ene was isolated from the ethyl acetate fraction together with some of its isomer, probably isofernene. A lactone, $\nu_{\max}^{\text{Nujol}}$ 1770, 1735 and 1710 cm^{-1} was also isolated from this fraction. Its mass spectrum showed a molecular weight of 376, corresponding to $C_{20}H_{24}O_7$, and it showed a base peak at *m*/*e* 289, due to loss of 87 mass units and analysed as loss of $C_4H_7O_2$ Its NMR spectrum was reminiscent of those from the highly oxygenated norditerpenes such as the nagilactones,[6] podolactones,[7] and inumakilactones,[8] isolated from similar species. On the basis of extensive proton decoupling experiments[9] the lactone has been assigned structure (I) Mass spectral fragmentation occurs preferentially to form the ion *a*.



(I)

m/*e* 289
a

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[1] K NAKANISHI, M KOREEDA, S SASAHI, M L CHANG and H Y HSU, *Chem Commun* 915 (1966).

[2] S IMAI, S FUJIOKA, E MURATA, Y SASKAWA and K NAKANISHI, *Tetrahedron Letters* 3887 (1968)

[3] M N GALBRAITH and D H S HORN, *Chem Commun* 905 (1966)

[4] J JIZBA, V HEROUT and F SORM, *Tetrahedron Letters* 1689 (1967)

[5] M SILVA, G POBLETE and P G SAMMES, *Phytochem* In press

[6] I HAYASHI, S TAKAHASHI, H ONA and T SAKAN, *Tetrahedron Letters* 2071 (1963)

[7] M N GALBRAITH, D H S HORN, J M SASSE and D ADAMSON, *Chem Commun* 170 (1970).

[8] S ITO, M KODAMA, M SUNAGAWA and T TAKAHASHI, *5th Int Symp Chemistry of Natural Products*, London (1968), S ITO, M KODAMA, M SUNAGAWA, T TAKAHASHI, H IMAMURA and O HONDA, *Tetrahedron Letters* 2065 (1968)

[9] Carried out at Imperial College We thank Mr P N Jenkins for his help with these experiments, the full details of which will be published elsewhere

A further lactone of related, but as yet undefined constitution has also been isolated in small amounts from this extract Cyanidin and delphinidin were isolated from the leaves after extraction and which are therefore present originally as leucoanthocyanidins The leaves did not show any insect moulting hormone activity [10]

EXPERIMENTAL

Instruments used were as described previously [11] Material for chromatography was supplied by Merck

The dried, ground leaves (10 8 kg) were extracted to exhaustion with EtOH at room temp After removal of solvent *in vacuo* the residue (2 9 kg) was treated with H_2O and the precipitate (880 g) discarded The solution was extracted with benzene, EtOAc and *n*-BuOH The solvents were removed *in vacuo* at $<45°$ to yield the fraction from benzene (16 7 g), EtOAc (160 g) and *n*-BuOH (820 g)

The benzene fraction (16 g) was chromatographed through alumina (grade III, 200 g) to yield the following compounds

Hydrocarbon fraction 25 mg eluted with light petroleum After recrystallizations from MeOH had m p 57–60° Mass spectral analysis showed the principal component to be nonacosane This fraction was not further investigated

β-Sitosterol 40 mg eluted with benzene–light petroleum, m p (EtOH) 132–135°, un-depressed by mixed m p with authentic material Acetylation with Ac_2O in pyridine at room temp afforded the *acetate*, m p and mixed m p 120–122°

A portion (48 g) of the EtOAc fraction was chromatographed through silica gel (loading ratio 1 200) to give the following compounds

Hydrocarbon fraction 3 4 g eluted with benzene, m p 50–70° TLC on silica gel G—10% $AgNO_3$, using cyclohexane as solvent, indicated two major components The first was identical to authentic fern-9(11)-ene (R_f 0 61) and the second component of the same R_f as isofernene (R_f 0 65) Direct spectral comparison (IR) of the former with an authentic sample confirmed the assignment [12]

Lactone A 370 mg eluted with 1 1 EtOAc–benzene, m p (EtOAc) 259–260°, $[\alpha]_D^{20}$ +40 3° (c 0 77) pyridine), ν_{max}^{KBr} 2900, 2866, 1770, 1735 and 1710 cm^{-1}, λ_{max}^{EtOH} 218 nm (ϵ 9750), NMR bands ($CDCl_3$ + 1 drop D_5-pyridine) τ 8 76 (3Hs, Me_{20}), 8 75 (3Hd, J 7 Hz, Me_{16}), 8 60 (3Hs, Me_{18}), 8 39 (1Hd, J 5 3 Hz, 5-H) 8 1–8 5 (2Hm, 7α-H, 7β-H), 7 48–7 85 (2Hm, 8-H), 6 92 (1Hd, J 1 9 Hz, 1-H), 6 70 (1Hm, 2-H), 6 40 (3Hs, MeO), 5 77 (1Hdd, J 2 4, 11 5 Hz, 14-H), 5 14 (1Hm, 6-H), 4 32 (1Hd, J 2 5 Hz, 11-H) Mass spectral bands at *m/e* 376(M^+, 0 8%, corresponding to $C_{20}H_{24}O_7$), 358 (0 1), 361 (0 1), 346 (1 2), 332 (1 0), 317 (0 2), 289 (100), 274 (2 0), 260 (7), 245 (10), 105 (10), 91 (10) (Found C, 61 53, H, 6 05 $C_{20}H_{24}O_7$ H_2O requires C, 60 90, H, 6 65%) After attempted acetylation (Ac_2O/pyridine) starting material was recovered $NaBH_4$ reduction in EtOH at room temp gave a complex mixture The material was stable to brief treatment with dil HCl but reacted after a prolonged period

Lactone B 35 mg eluted by EtOAc, m p 280–300°, contaminated by traces of lactone A The structure of this lactone is under investigation TLC investigation of the *n*-BuOH extract showed no further major components

Detection of leucoanthocyanidins The powdered, dried leaves (200 g) were refluxed in 2 N HCl for 40 min [13] The acid was extracted with amyl alcohol and chromatographed on Whatman paper No 3 using both the Forestal and BAW solvent systems [14] The R_f values for the two compounds detected corresponded to cyanidin and delphinidin

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[10] We thank Dr D H S Horn for carrying out the tests for insect moulting hormone activity

[11] M SILVA, M A CRUZ and P. G SAMMES, *Phytochem* **10**, 3255 (1971)

[12] Carried out at Imperial College with samples provided by Dr G Mellows

[13] E C BATE-SMITH and N H LERNER, *Biochem J* **58**, 126 (1953)

[14] J B HARBORNE, *Comparative Biochemistry of the Flavonoids*, p 7, Academic Press, London (1967)

Key Word Index—Podocarpus saligna, Podocarpaceae, terpenes, fern-9(11)-ene, norditerpene, leucoanthocyanidins