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ANTIFUNGAL AND OTHER COMPOUNDS ISOLATED FROM THE ROOTS OF NEW ZEALAND FLAX PLANTS (THE GENUS *PHORMIUM*)

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New Zealand flax, the genus *Phormium* (Agavaceae), occurs widely throughout the country and has been used by the Maori for curing various ills, but no compounds of antifungal value have so far been isolated in reported investigations of the seeds and rhizomes. The roots have not previously been investigated. Cucurbitacins, antibacterial (1) and anticancer (2), were isolated from the leaves.

EXPERIMENTAL

Phormium tenax J.R. & G. Forst. was collected from damp pasture near DSIR and *Phormium cookianum* Le Jolis from the grounds of DSIR, both in early December (summer). Herbarium samples were deposited with Botany Division, DSIR, Christchurch, New Zealand, and authenticated by Dr. E. Edgar.

Hexane extracts of the air-dried, powdered roots of the two species were investigated by column chromatography on Si gel. Elution with hexane-Et_2O (90:10) yielded three main fractions which were each rechromatographed. From the first fraction a yellow solid, chrysophanol, musizin (0.05%), and stypandrone were obtained successively. These were purified by repeated crystallization and characterized by comparison (tlc, uv, and mmp) with authentic samples. From the second fraction, in *P. tenax* only, hexacosanol was isolated, recrystallized, and characterized by comparison (tlc, ir, and mmp) with an authentic sample. β-Sitosterol was isolated from the third fraction.

Experimental details, including a full assignment of the ^{1}H-nmr spectrum of musizin (provided by Dr. H. Wong, Chemistry Division, DSIR, Petone, New Zealand) in DMSO-d_6, are available on request to the senior author.

Musizin, which has useful antifungal activity (3), has not previously been reported in species of the Agavaceae family. It is easily recognizable on tlc by its green coloration in iodine vapor. Stypandrone has been isolated from plants containing musizin and shown to be an in vivo oxidation product of musizin (4).

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TRITERPENOIDS AND OTHER COMPONENTS OF *POA HUECU*

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In continuation of our work on *Poa huecu* Par. (Gramineae) (1,2), a perennial Argentinian plant toxic to livestock, we report here the identification of the components of both the petroleum ether and methanolic extracts. Antimicrobial tests showed that the cinnamic acid derivatives were responsible for the activity against *Mycobacterium phlei*. The occurrence of triterpenic ketones seems to be a chemotaxonomical feature of *P. huecu*. This species also shows to be deficient in alkaloids. Gramine, although widespread in Gramineae (3), was not here detected.

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EXPERIMENTAL

PLANT MATERIAL.—Whole plants of *P. huecu* were collected in Estancia Llamuco, Neuquén, Argentina, by INTA (Argentina). Voucher specimens were deposited in the Herbarium of Instituto de Botánica Darwinion (Buenos Aires, Argentina) under the Nr. SI 14036.

EXTRACTION, ISOLATION AND IDENTIFICATION OF THE COMPOUNDS.—Dried, ground, whole plants were extracted as previously reported (2). The petroleum ether extract (1.9% rel. to dry plant) yielded the triterpenic ketones identified as germanicone, lupenone, cyclolaudenone, hopenone; the triterpenic alcohol lupeol; lineal alcohols ($C_{24}H_{50}O$ to $C_{34}H_{70}O$; the main component was *n*-hexacosanol: $C_{26}H_{54}O$); *iso*-alcohols of 24, 26, 28, 30, and 34 carbons; the steroidal ketones: campesterone and sitosterone; the cinnamic acid derivatives: sinapic, *p*-coumaric, caffeic, and ferulic acids. The latter was the main component. Gallic and cinnamic acids were not present.

The methanolic extract (6.8% rel. to dry plant) was worked up as previously reported (2). It was percolated on polyamide with $CHCl_3$, H_2O, and, finally, MeOH. The chloroformic percolate yielded sitosterol 3-*O*-β-D-glucopyranoside, campesterol 3-*O*-D-glucopyranoside, and cholesterol 3-*O*-D-glucopyranoside. The aqueous percolate through Sephadex LH-20 gave mainly the free sugars identified as glucose, galactose, mannose, arabinose, and rhamnose; and the quarternary ammonium compounds choline and acetylcholine. Amino acids were also detected.

ANTIMICROBIAL ASSAYS.—The petroleum ether extract as well as chloroformic, methanolic, and aqueous percolates were tested against gram positive and gram negative bacteria and the acid fast, *Mycobacterium phlei* (ATCC 11, 758). Dilution and inoculation of media were carried out as previously reported (4). Growth inhibition of *M. phlei* was observed with the petroleum ether extract (MIC 500 μg/ml), MeOH percolate (MIC 1,000 μg/ml), $CHCl_3$ percolate (2,000 μg/ml), and aqueous percolate (MIC 250 μg/ml). The petroleum ether extract also produced inhibition of *Micrococcus luteus* (Collection of Cátedra de Microbiología, FCEN, UBA) (MIC 1,000 μg/ml). No growth inhibition of the other tested microorganisms was observed (MIC>4,000 μg/ml). Each fraction of column chromatography of the petroleum ether extract was assayed against *M. phlei*. Only the fraction that contained the cinnamic acid derivatives caused growth inhibition of *M. phlei*.

Full details on the isolation and identification of the compounds are available on request to the senior author.

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