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CHEMISTRY OF THE PODOCARPACEAE—I

CONSTITUENTS OF THE HEARTWOOD OF *PODOCARPUS SPICATUS*

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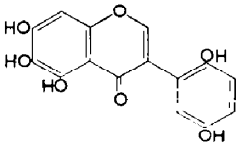
Abstract—Quercetin and a new *iso*flavone, podospicatin, have been isolated from *Podocarpus spicatus*. Podospicatin trimethyl ether has been shown to be 5:6:7:2′:5′-pentamethoxy*iso*flavone.

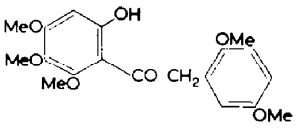
THE heartwood of *Podocarpus spicatus* (Maori name—"Matai") has already been shown to contain the lignans, matairesinol,[1,2] conidendrin[3] and a third constituent, m.p. 212°.[1,3,4] While working on the mother liquors for a further supply of the third component, quercetin has been isolated in small yield.

The third compound has now been shown to be a new *iso*flavone, podospicatin, $C_{17}H_{14}O_7$. Podospicatin contains two methoxyl groups while complete methylation affords podospicatin trimethyl ether indicating the partial structure, $C_{15}H_5O_2(OCH_3)_5$, for the trimethyl ether. Spectral properties of podospicatin (λ_{max} 262, 302 mμ)[5] indicate an *iso*flavone structure which has been confirmed by degradation.

Mild alkaline hydrolysis of the trimethyl ether with ethanolic potassium hydroxide gave a phenol, $C_{14}H_7O_2(OCH_3)_5$, in high yield, the loss of one carbon atom being accounted for by the isolation of formic acid. More vigorous alkaline treatment afforded two fragments, an acid, identified as the dimethyl ether of homogentisic acid by comparison with a synthetic sample, and a phenol, agreeing in properties with those of antiarol (3:4:5-trimethoxyphenol). Podospicatin can thus be formulated as a dimethyl ether of 2′:5:5′:6:7-pentahydroxy*iso*flavone (I) and the product from mild alkaline treatment of the trimethylether as the benzyl ketone (II).



I



II

In only four cases has the 2′:5′-hydroxylation pattern been noted in naturally occurring flavones and this is the first record in an *iso*flavone.

EXPERIMENTAL

Microanalyses were carried out by Dr. A. R. Campbell, University of Otago. Ultra-violet spectra were measured in ethanol.

Isolation of podospicatin. The mother liquors from the crystallization of matairesinol[1] were

[1] L. H. Briggs, D. A. Peak and J. L. D. Woolloxall, *J. Proc. Roy. Soc. N.S.W.* **69**, 61 (1935).
[2] R. D. Haworth and T. Richardson, *J. Chem. Soc.* 633 (1935).
[3] R. D. Haworth, T. Richardson and G. Sheldrick, *J. Chem. Soc.* 1576 (1935); L. H. Briggs and D. A. Peak, *J. Chem. Soc.* 724 (1936).
[4] H. V. Brewerton, *New Zealand J. Sci.* **1**, 220 (1958).
[5] W. K. Warburton, *Quart. Rev.* **8**, 67 (1954).

evaporated, the residue finely ground and suspended in dilute sodium carbonate solution. Acidification of the filtered solution gave a black viscous product which was dissolved in hot alcohol (charcoal). After some weeks the deposited crystalline material was filtered, washed with alcohol and repeatedly crystallized from acetic acid to give podospicatin, pale yellow needles, m.p. 214–216°.

(Found: C, 61·9; H, 4·3; OMe, 18·8; Calc. for $C_{17}H_{14}O_7$: C, 61·8; H, 4·2; 2 OMe, 18·8%.)

Ultra-violet spectrum: λ_{max} 262 mμ (log ε 4·37), 302 mμ (log ε 4·11).

Isolation of quercetin. The alcoholic mother liquors from which podospicatin had been obtained were allowed to dry spontaneously. The residue was alternately crystallized from acetic acid (60%) and aqueous ethanol (50%) to give quercetin, m.p. and mixed m.p. 314–314·5°. The acetate[6] had m.p. 190–191°.

Bromopodospicatin. A solution of bromine (188 mg) in ethylene dibromide (11 ml) was added to a solution of podospicatin (200 mg) in the same solvent (49 ml). Extraction with sodium hydrogen carbonate solution (4 × 25 ml), followed by acidification, afforded material (200 mg) crystallizing from acetic acid (60%) in yellow needles, m.p. 202°.

(Found: C, 49·4; H, 3·4; Br, 19·2; Calc. for $C_{17}H_{13}O_7Br$: C, 49·9; H, 3·2; Br, 19·6%.)

Podospicatin trimethyl ether. Podospicatin was methylated with dimethyl sulphate in acetone solution in the presence of anhydrous potassium carbonate. The trimethyl ether, after repeated crystallization from absolute ethanol, formed prisms, m.p. 160–162°.

(Found: C, 64·5; H, 5·4; OMe, 41·6; Calc. for $C_{20}H_{20}O_7$: C, 64·5; H, 5·4; 5 OMe, 41·7%.)

Ultra-violet spectrum: λ_{max} 253 mμ (log ε 3·33), 299 mμ (log ε 3·11).

Alkaline degradations of podospicatin trimethyl ether. A solution of the trimethyl ether (279 mg) in ethanolic potassium hydroxide (20%; 5 ml) was refluxed for 5 hr. After dilution with water (15 ml) and removal of ethanol *in vacuo*, saturation with carbon dioxide precipitated a gum which was removed with ether. Repeated crystallization of this material from aqueous ethanol gave colourless needles of the benzyl ketone (II), m.p. 102–104° (248 mg).

(Found: C, 63·3; H, 6·5; OMe, 40·5; Calc. for $C_{19}H_{22}O_7$: C, 63·0; H, 6·1; 5 OMe, 42·8%).

Ultra-violet spectrum: λ_{max} 281 mμ (log ε 3·31), 3·22 mμ (log ε 3·07).

Steam distillation of the acidified aqueous mother liquors gave an acid distillate which readily reduced Tollens' reagent. After neutralization with sodium hydroxide (0·79 equivalent) an aqueous solution of S-benzylthiourea hydrochloride (150 mg), was added and the solution allowed to evaporate at room temp. The product, after crystallization from aqueous ethanol, had m.p. and mixed m.p. 146° with S-benzyl thiourea formate.

The benzyl ketone (II; 160 mg) was dissolved in water (0·25 ml) containing sodium hydroxide (1·5 g) and the solution heated to 220° for 45 min. The products of the fusion were divided into acid and phenolic fractions in the usual manner. The major acid component crystallized from water in rods, m.p. 120–121° (24 mg). (Found: C, 61·4; H, 6·0; $C_{10}H_{12}O_4$ requires: C, 61·2; H, 6·2%.) The melting point was not depressed by homogentisic acid dimethyl ether (m.p. 120–121°) prepared by ozonolysis of 2:5-dimethoxyallylbenzene.[7]

The major phenolic product from the alkaline fusion crystallized from benzene in plates, m.p. 148–149° (33 mg). (Found: C, 58·9; H, 6·6; OMe, 48·6; $C_9H_{12}O_4$ requires: C, 58·7; H, 6·6; 3 OMe, 50·5%.) Chapman, Perkin and Robinson[8] record m.p. 147° for antiarol (3:4:5-trimethoxyphenol).

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