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CHEMISTRY OF THE PODOCARPACEAE—III*

A NEW LIGNAN, SECO-ISOLARICIRESINOL AND FURTHER CONSTITUENTS OF THE HEARTWOOD OF *PODOCARPUS SPICATUS*

L. H. BRIGGS, R. C. CAMBIE and J. L. HOARE
Department of Chemistry, University of Auckland, New Zealand

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Abstract—A new lignan for which the name seco-isolariciresinol is proposed, has been isolated from the heartwood of *Podocarpus spicatus*. The structure has been shown to be 2:3-bis(4′-hydroxy-3′-methoxybenzyl)-butan-1:4-diol (II, R = H), and confirmed by an absolute synthesis from (−)-matairesinol (I, R = H). A further examination of the extractives of the heartwood has resulted in the isolation of the minor constituents, (−)-taxifolin, (+)-aromadendrin, kaempferol and sequoyitol, in addition to the previously reported compounds, matairesinol, α-conidendrin, quercetin, genistein and podospicatin.

PREVIOUS investigations of the constituents of *Podocarpus spicatus* have shown the presence, in the heartwood or heartshakes, of the lignans, matairesinol,[1–4] and conidendrin.[5,6] A third constituent, podospicatin, m.p. 212°,[2,5,7] has recently been shown to be 2′:5:7-trihydroxy-5′:6-dimethoxyisoflavone.[4,8] The isolation of quercetin[8] from the heartshakes and genistein[4] from the heartwood has also been reported.

In the present communication, a complete re-examination of the heartwood constituents is reported. In order to facilitate the isolation of minor constituents the concentrate from a methanolic extract was intimately mixed with Celite and successively re-extracted with solvents of increasing polarity. The concentrate from each extract, where possible, was fractionally crystallized and non-crystalline residues fractionated with aqueous alkalies of increasing basicity. Liberal use was made of paper chromatographic techniques to monitor each purification step and for initial indentification of the constituents. The scheme of extraction and the products isolated from each extract shown in Table 1.

By these means the following previously reported compounds were isolated and identified by comparison with authentic samples: matairesinol (2·26% yield), α-conidendrin (0·005% yield), quercetin (0·83% yield), genistein (0·05% yield) and podospicatin (0·13% yield). In addition the following compounds not previously detected in *Podocarpus spicatus* were isolated: (+)-taxifolin (0·002% yield), (+)-aromadendrin (0·001% yield), kaempferol (0·002% yield), sequoyitol (0·009% yield) and a new lignan (0·012% yield).

* Part II: L. H. Briggs and T. P. Cebalo, *Tetrahedron* **6**, 145 (1959).

[1] T. H. Easterfield and J. Bee, *J. Chem. Soc.* **97**, 1028 (1920).
[2] L. H. Briggs, D. A. Peak and J. L. D. Woolloxall, *J. Proc. Roy. Soc. N.S.W.* **69**, 61 (1935)
[3] R. D. Haworth and T. Richardson, *J. Chem. Soc.* 633 (1935).
[4] L. H. Briggs and T. P. Cebalo, *Tetrahedron* **6**, 145 (1959).
[5] R. D. Haworth, T. Richardson and G. Sheldrick, *J. Chem. Soc.* 1576 (1935).
[6] L. H. Briggs and D. A. Peak, *J. Chem. Soc.* 724 (1936)
[7] H. V. Brewerton, *New Zealand J. Sci.* **1**, 220 (1958).
[8] L. H. Briggs and B. F. Cain, *Tetrahedron* **6**, 143 (1959).

TABLE 1. *Podocarpus spicatus* HEARTWOOD EXTRACTIVES

HEARTWOOD

Extracted with methanol

Extract on Celite

Light petroleum extract	Benzene extract	Ether extract	Chloroform extract	Ethyl acetate extract	Butan-1-ol extract
(i) *crystallization* podospicatin (ii) *chromatography* matairesinol	(i) *crystallization* matairesinol podospicatin (ii) Na_2CO_3 *solubles* podospicatin (iii) 4% NaOH *solubles* matairesinol	(i) *crystallization* matairesinol podospicatin genistein quercetin (ii) $NaHCO_3$ *solubles* (+)-taxifolin (+)-aroma-dendrin (iii) Na_2CO_3 *solubles* podospicatin genistein quercetin kaempferol (iv) 0·2% NaOH *solubles* matairesinol seco-isolari-ciresinol (v) 4% NaOH *solubles* matairesinol	(i) *crystallization* matairesinol (ii) Na_2CO_3 *solubles* seco-isolari-ciresinol podospicatin genistein quercetin kaempferol (iii) 0·2% NaOH *solubles* seco-isolari-ciresinol (iv) 4% NaOH *solubles* matairesinol α-conidendrin	(ii) Na_2CO_3 *solubles* quercetin kaempferol (ii) 4% NaOH *solubles* matairesinol	(i) *water solubles* sequoyitol

The new lignan, isolated from the ether and chloroform extracts, is a laevorotatory crystalline solid, m.p. 112·5–113·5°, which gives a positive ferric chloride reaction. The compound has the formula, $C_{20}H_{26}O_6$, and a Zeisel determination shows the presence of two methoxyl groups. The infra-red spectrum shows hydroxyl stretching at 3448 cm^{-1}, phenolic deformation in the regions 1200 cm^{-1} and 1410–1310 cm^{-1} and a band compatible with primary hydroxyl deformation at 1050 cm^{-1}.[9]

Difficulty was experienced in crystallizing acyl derivatives of the lignan. The presence of four hydroxyl groupings was demonstrated, however, by the formation of a tetra-acetate and a tetra-benzoate. The acetate was obtained only as a glass on acetylation in pyridine solution or with fused sodium acetate while the benzoate was obtained as a microcrystalline mono-hydrate by purification from aqueous methanol. Both derivatives showed no hydroxyl absorption in the infra-red.

Two of the hydroxyl groups present in the lignan were shown to be phenolic by the formation of a di-O-methyl ether, $C_{22}H_{30}O_6$, by methylation in aqueous alkali. This derivative had a constant melting point 59–60° when initially crystallized from aqueous methanol but crystallization from chloroform–light petroleum raised the melting point to 120–123°. Prolonged methylation with dimethyl sulphate and potassium carbonate in boiling acetone gave a further di-O-methyl ether, m.p. 120·5–121°, depressed on admixture with the former derivative and which showed major differences in the infra-red spectrum. The formula of the latter derivative, $C_{22}H_{28}O_5$, and the absence of hydroxyl absorption in the infra-red spectrum suggested that it was derived

[9] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (2nd Ed.) p. 95. Methuen, London (1958).

from the former by the loss of the elements of water. That this was so was subsequently shown by dehydration of the former derivative, $C_{22}H_{30}O_6$, to the latter compound with potassium hydrogen sulphate.

Comparison of the ultra-violet spectrum with those of the lignans, matairesinol, α-conidendrin and isolariciresinol (Fig. 1), indicated a close relationship with this

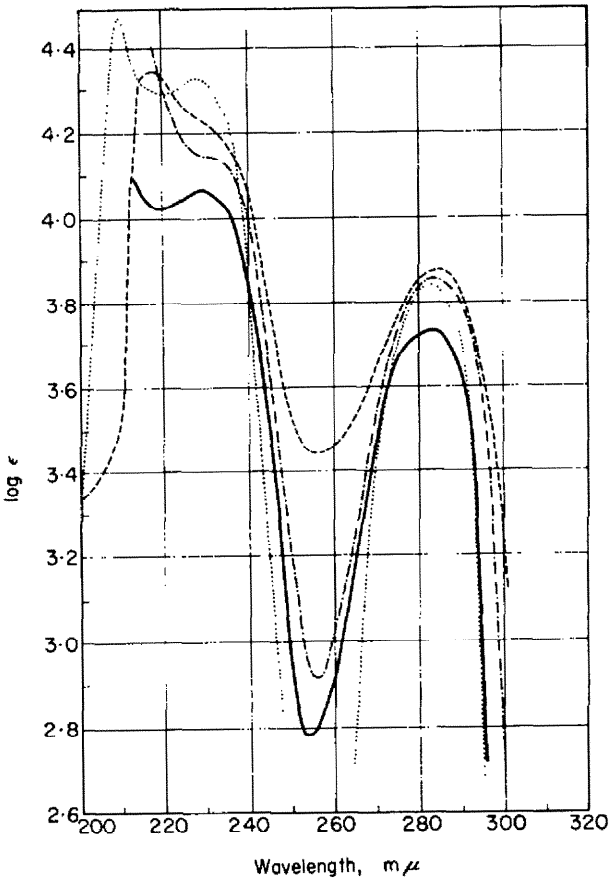
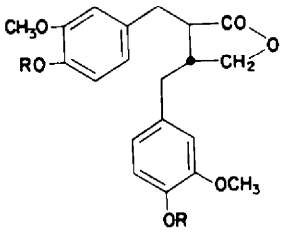


FIG. 1. Ultra-violet spectra of seco-isolariciresinol (II: R = H) ....., matairesinol (I: R = H) ———, isolariciresinol – – – – –, and conidendrin (VIII) –·–·–·–

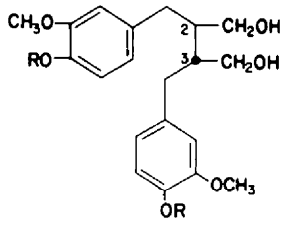
class of compound. Since all the oxygen functions are accounted for by two methoxyl and four hydroxyl groups, the formula, $C_{20}H_{26}O_6$, is only compatible with a lignan possessing a fully saturated aliphatic portion, with two aliphatic hydroxyl groups capable of dehydration. On the assumption that the substitution pattern in the aromatic nuclei is of the common 3-methoxyl-4-hydroxyl type,* and on phytochemical grounds† the lignan can be formulated as (−)-2:3-bis(4′-hydroxy-3′-methoxybenzyl)-butan-1:4-diol (II, R = H).

* Cf. the co-occurring lignans, matairesinol (I, R = H) and α-conidendrin.

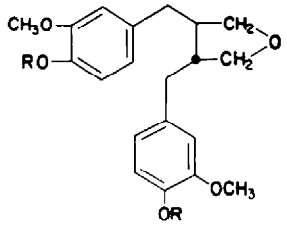
† For reviews of the naturally occurring lignans see W. M. Hearon and W. S. MacGregor, *Chem. Rev.* **55**, 957 (1955); H. Erdtman in *Modern Methods of Plant Analysis* Vol. III, p. 428. Springer-Verlag, Berlin (1955).



I



II



III

The lignan has not been previously isolated from natural sources or prepared synthetically but has been detected by paper chromatography among the hydrogenation products of pinoresinol.[10] To indicate the structural relationship to isolariciresinol, the name seco-isolariciresinol* is proposed for the new lignan. Support for the formulation was obtained by the correspondence of the melting point of the di-O-methyl ether, $C_{22}H_{30}O_6$ m.p. 120–123°, with that recorded by Schrecker and Hartwell for (—)-2:3-diveratryl-butan-1:4-diol (II, R = OCH_3).[11] The di-O-methyl ether, $C_{22}H_{28}O_5$, m.p. 120·5–121°, was obviously the anhydro derivative of the former, formed by ready dehydration of the diol grouping[11] by anhydrous potassium carbonate used during the reaction. The melting-point of the anhydro derivative again showed close agreement with the corresponding synthetic derivative, 3:4-bis(3′:4′-dimethoxybenzyl) tetrahydrofuran (III, R = OCH_3) recorded by the above workers. The infra-red spectra of both the di-O-methyl derivatives of the natural products, however, did not have point for point identity with those recorded for the optically active synthetic derivatives.[11,12]

In order to carry out a direct comparison, 2:3-diveratryl-butan-1:4-diol was prepared from (—)-dimethylmatairesinol (I, R = OCH_3) by Haworth and Wilson's method[13] and it in turn dehydrated to the tetrahydrofuran derivative (III, R = OCH_3).[11,13,14] Each of the di-O-methyl derivatives of the naturally occurring lignan showed no melting point depression when mixed with their corresponding synthetic analogues and their corresponding infra-red spectra were identical.

* The prefix *seco* was originally used in the steroid field [Editorial Report on Nomenclature, *J. Chem. Soc.* 3535 (1957)], to denote ring fission with the addition of two hydrogen atoms to the two terminal groups, but has been extended with the same meaning by workers to other fields, e.g. W. H. Evans, A. McGookin, L. Jurd, A. Robertson and W. R. N. Williamson, *J. Chem. Soc.* 3510 (1957).

[10] K. Freudenberg and L. Knof, *Chem. Ber.* **90**, 2857 (1957).
[11] A. W. Schrecker and J. L. Hartwell, *J. Amer. Chem. Soc.* **77**, 432 (1955).
[12] A. W. Schrecker, *J. Amer. Chem. Soc.* **79**, 3823 (1957).
[13] R. D. Haworth and L. Wilson, *J. Chem. Soc.* 71, (1950).
[14] R. D. Haworth and D. Woodcock, *J. Chem. Soc.* 1054 (1939).

The structure of seco-isolariciresinol was further confirmed by an absolute synthesis from (−)-matairesinol (I, R = H). Reduction by lithium aluminium hydride of the dibenzyl derivative of (−)-matairesinol (I, R = $C_6H_5CH_2$), by Schrecker and Hartwell's method[11] for lactonic lignans, gave the diol (II, R = $C_6H_5CH_2$). Hydrogenolysis of the diol with palladium-charcoal gave 2:3-bis(4′-hydroxy-3′-methoxybenzyl)-butan-1:4-diol (II, R = H), identical in all respects (m.p. and mixed m.p., optical rotation, infra-red spectrum) with seco-isolariciresinol.

The absolute configuration of (−)-matairesinol has been established as 2L, 3D (I, R = H).[15–18] Since the synthesis of seco-isolariciresinol from (—)-matairesinol only involves the reduction of the potential carboxyl group to a primary alcoholic group it follows that the new lignan must have the same absolute configuration, provided the asymmetry at C_2 is preserved. As reduction with lithium aluminium hydride of a carbonyl group adjacent to an asymmetric centre does not affect the symmetry[19] and as benzylation and debenzylation would also not be expected to affect the asymmetry, the synthesis leads to the absolute configuration of seco-isolariciresinol as 2L, 3D (II, R = H).

EXPERIMENTAL

Analyses were by Dr. A. D. Campbell and associates, University of Otago, New Zealand. Infra-red spectra were measured as KBr disks with a Beckmann IR2 instrument and ultra-violet spectra in EtOH solutions with a Beckmann DU instrument. Ultra-violet spectral shifts were measured by the methods of Jurd and co-workers.[20–22] Circular paper chromatography of phenolic constituents was carried out on Whatman's No. 1 paper (24 cm) with the following solvent systems: (A) 60% aqueous acetic acid, (B) phenol saturated with water at 20°. The positions of spots were shown with either 1% alcoholic ferric chloride or diazotized *p*-nitroanaline spray reagents. Light petroleum was of b.p. 50–60°.

Extraction of Podocarpus spicatus *heartwood.* Continuous extraction (Soxhlet) of the finely ground wood (9·3 kg) with 80% aqueous methanol for 56 hr and removal of the solvent *in vacuo* gave a black tar (1·5 kg). After the addition of a little hot methanol the tar was intimately mixed with Celite (1·1 kg) and the friable solid, obtained on drying, successively re-extracted (Soxhlet) with light petroleum, benzene, ether, chloroform, ethyl acetate, butan-1-ol and finally methanol. The residues from each extract, with the exception of the light petroleum and methanol extracts, were purified directly, where possible, by fractional crystallisation from 60% acetic acid. Non-crystalline residues were then fractionated in a suitable solvent between saturated sodium hydrogen carbonate, 10% sodium carbonate, 0·2% sodium hydroxide and 4% sodium hydroxide solutions. Residues from the light petroleum extract were chromatographed directly in benzene on alumina (Brockman, grade III). No crystalline products were isolated from the methanol extract by any purification procedures attempted.

Lignans

Matairesinol. Matairesinol (total yield 210·5 g), m.p. and mixed m.p. 117–118° (identical infra-red spectrum), was isolated by fractional crystallisation of the benzene, ether and chloroform extracts and from the sodium hydroxide fractions from these extracts and the ethyl acetate extract. It was also isolated in trace amount by elution of the light petroleum extract from the column with benzene–ether mixtures.

[15] A. W. Schrecker and J. L. Hartwell, *J. Org. Chem.* **21**, 381 (1956).
[16] A. W. Schrecker and J. L. Hartwell, *J. Amer. Chem. Soc.* **79**, 3827 (1957).
[17] A. W. Schrecker and J. L. Hartwell in *Progress in the Chemistry of Organic Natural Products* Vol. XV, pp. 111–119. Springer-Verlag, Austria (1958).
[18] R. D. Haworth and D. Woodcock, *J. Chem. Soc.* 154 (1939.)
[19] D. S. Noyce and D. B. Denney, *J. Amer. Chem. Soc.* **72**, 5743 (1950).
[20] L. Jurd, *Arch. Biochem and Biophys.* **63**, 376 (1956).
[21] L. Jurd, and T. A. Geissman, *J. Org. Chem.* **21**, 1395 (1956).
[22] L. Jurd, and R. Horowitz, *J. Org. Chem.* **22**, 1618 (1957).

α-Conidendrin. α-Conidendrin, m.p. and mixed m.p. 240–244°* (identical infra-red spectrum), was isolated in small yield (500 mg) from the 4% sodium hydroxide fraction of the chloroform extract by fractional crystallisation from aqueous acetic acid or from ethanol.

seco-isoLariciresinol. Water extraction of the residues from the 0·2% sodium hydroxide fractions of the ether and chloroform extracts and of the sodium carbonate fraction of the chloroform extract gave colourless needles of *seco-isolariciresinol* (1·13 g). After recrystallization from water or dilute alcohol as rods it had m.p. 112·5–113·5°, $[\alpha]^{25}$ −35·6° (*c*, 1·07 in Me_2CO) (Found: C, 66·3; H, 7·2; OMe, 17·0. $C_{20}H_{26}O_6$ requires: C, 66·3; H, 7·2; 20 Me, 17·1%), λ_{max} 209 mμ (log ε 4·5), 229 mμ (log ε 4·3) and 283 mμ (log ε 3·9). Infra-red spectrum: 3436, 3165, 2915, 1608, 1515, 1471, 1458, 1433, 1385, 1359 (Sh.), 1339, 1312, 1272, 1241, 1199, 1189, 1155, 1129, 1120, 1098, 1064, 1050 (Sh.), 1036, 1007, 977, 947, 937, 919, 910, 897, 844, 808, 798 and 744 cm^{-1}.

*seco-iso*Lariciresinol is sparingly soluble in cold water, ether and chloroform but readily soluble in methanol, ethanol and acetone. A concentrated solution gave a green colour with alcoholic ferric chloride.

Tetra-O-acetyl-seco-isolariciresinol. Acetylation of seco-isolariciresinol with acetic anhydride–pyridine (1 hr; 100°) or with acetic anhydride–fused sodium acetate (2 hr; 100°) and isolation of the products by pouring onto crushed ice, in each case gave an oil which could not be obtained as a solid from any of the normal organic solvents. After chromatography in ethyl acetate on neutralized alumina the *tetra-acetate* was obtained as a colourless glass, b.p. 348° (micro method), which could not be induced to crystallize (Found for sample dried at room temp: C, 62·6; H, 6·7; Ac, 29·2. $C_{28}H_{34}O_{10}$ requires: C, 63·4; H, 6·5; 4Ac, 32·5. $C_{28}H_{34}O_{10}\cdot\frac{1}{2}H_2O$ requires: C, 62·3; H, 6·5; 4 Ac, 31·9%).

Tetra-O-benzoyl-seco-isolariciresinol. Benzoylation of seco-isolariciresinol with benzoyl chloride–pyridine (1 hr; 100°) and isolation of the product by pouring onto crushed ice gave the *tetra-benzoate* which was obtained as a colourless microcrystalline mono-hydrate, m.p. 55–57°, from aqueous methanol (Found, for sample dried at room temp; C, 72·3: H, 5·4. $C_{48}H_{42}O_{10}\cdot H_2O$ requires: C, 72·4; H, 5·6%).

Mono-O-3:5-dinitrobenzoyl-seco-isolariciresinol. Treatment of seco-isolariciresinol with 3:5-dinitrobenzol chloride (2 fold excess)-pyridine (1 hr; 100°) and isolation of the product in the usual manner gave a gum from which the *mono-3:5-dinitrobenzoate*, was obtained as a microcrystalline powder, m.p. 115–118°, from aqueous acetic acid (Found: C, 58·4; H, 5·1. $C_{27}H_{28}O_{11}N_2$ requires: C, 58·3; H, 5·2%). The infra-red spectrum showed strong hydroxyl absorption at 3086 cm^{-1}.

Di-O-methyl-seco-isolariciresinol (II, R = OCH_3). Dimethyl sulphate (1 ml) was added dropwise to a solution of seco-isolariciresinol (150 mg) in 2 N sodium hydroxide solution (5 ml) and the mixture heated on the steam-bath for 1 hr. Repeated crystallization of the resulting gum from aqueous methanol gave *di-O-methyl-seco-isolariciresinol* as colourless needles (110 mg), m.p. 59–60°. Further crystallization from chloroform-light petroleum (prisms) raised the melting point to 120–123° (Found: C, 67·4; H, 8·1; OMe, 35·1. $C_{22}H_{30}O_6$ requires: C, 67·8; H, 7·7; 4 OMe, 34·3%). The compound gave a negative ferric chloride reaction and the infra-red spectrum showed strong hydroxyl absorption at 3472 cm^{-1}.

Anhydro-di-O-methyl-seco-isolariciresinol (III, R = OCH_3). Methylation of seco-isolariciresinol (200 mg) with freshly dried potassium carbonate (500 mg) and dimethyl sulphate (1 ml) in boiling acetone (10 ml) for 20 hr gave a gum which crystallized from aqueous methanol as colourless prisms (98 mg), m.p. 120·5–121° (Found (avge. of two determinations): C, 70·75; H, 7·6; OMe, 33·1. $C_{28}H_{28}O_5$ requires: C, 70·9; H, 7·6; 4OMe, 33·3%). The compound gave a negative ferric chloride reaction and the infra-red spectrum showed no hydroxyl absorption. It did not depress the melting point of a sample, m.p. 119–120°, prepared from di-O-methyl-seco-isolariciresinol by dehydration with potassium hydrogen sulphate following the procedure of Schrecker and Hartwell[11] for the preparation of anhydro compounds.

3:4-*Bis*(3′:4′-*dimethoxybenzyl*)-*tetrahydrofuran* (III, R = OCH_3). (−)-Dimethylmatairesinol prepared in 71% yield from (−)-matairesinol by the method of Briggs *et al.*[2] was reduced to 2:3-bis (3′:4′-dimethoxybenzyl)-butan-1:4-diol by Haworth and Wilson's method[13] in 80% yield. The diol crystallised from aqueous methanol as prisms, m.p. 123–124° (lit.[11] m.p. 123–123·7°), undepressed by di-O-methyl-seco-isolariciresinol (identical infra-red spectrum). Dehydration of the diol

* Cf. the melting point recorded by K. Freudenberg and L. Knof,[10] for α-conidendrin.

with potassium hydrogen sulphate[11] and crystallisation of the product (80% yield) from methanol gave 3:4-bis(3′:4′-dimethoxybenzyl)-tetrahydrofuran as prisms, m.p. 119·5 (lit.[11] m.p. 118·4-119·7°), undepressed by anhydro-di-O-methyl-seco-isolariciresinol (identical infra-red spectrum).

Dibenzylmatairesinol (I, R = $C_6H_5CH_2$). (−)-Matairesinol (10 g) and potassium hydroxide (10 g) were heated under reflux with dry acetone (50 ml). Benzyl chloride (13 ml) was added and the mixture heated under reflux for 10 hr after which the solution was decanted from precipitated potassium chloride which was washed well with hot acetone. The combined solutions were concentrated and steam distilled to remove volatile impurities whereupon *dibenzylmatairesinol* was obtained in 95% yield. Four crystallizations from anhydrous ether containing a little dry benzene gave colourless prisms, m.p. 100°, insoluble in dilute alkali and giving a negative ferric chloride test (Found: C, 75·8; H, 6·7. $C_{34}H_{34}O_6$ requires: C, 75·8; H, 6·4%). The infra-red spectrum showed the absence of hydroxyl bands.

2:3-*Bis*(4′-*benzyloxy*-3′-*methoxybenzyl*)-*butan*-1:4-*diol* (II, R = $C_6H_5CH_2$). An ice-cooled solution of dry I (R = $C_6H_5CH_2$) (5 g) in sodium-dried ether (100 ml) was added with stirring over 2·5 hr to a suspension of lithium aluminium hydride (4 g) in dry ether (50 ml). After 3 hr stirring at room temp, excess lithium aluminium hydride was decomposed by addition of ethyl acetate (18 ml) and saturated ammonium chloride solution (17 ml). The precipitate was collected and extracted several times with boiling ethanol, the combined filtrates refiltered to remove precipitated ammonium chloride and the solvent removed *in vacuo*. Further inorganic salts were washed out with water. 2:3-*bis*(4′-*benzyloxy*-3′-*methoxybenzyl*)-*butan*-1:4-*diol* (62% yield) crystallized from methanol as colourless needles, m.p. 116–116·5°. (Found: C, 75·1: H, 6·7. $C_{34}H_{38}O_6$ requires: C, 75·25; H, 7·1%). Infra-red spectrum: 3268 (OH) cm^{-1}.

2:3-*Bis*(4′-*hydroxy*-3′-*methoxybenzyl*)-*butan*-1:4-*diol* (II, R = H). A mixture of II (R = $C_6H_5CH_3$) (0·5 g) and 10% palladium-charcoal (0·4 g) in methanol (25 ml) was shaken under pressure (2·5 atmos) with hydrogen for 4 hr. The catalyst was removed and the filtrate concentrated *in vacuo*. The resulting oil crystallized from dilute methanol to yield 2:3-bis(4′-hydroxy-3′-methoxybenzyl)-butan-1:4-diol (80% yield), m.p. 113·5°, undepressed by seco-isolariciresinol, $[\alpha]_D^{25}$ −36·7° (*c*, 1·16 in Me_2CO), identical infra-red spectrum (Found: C, 66·0; H, 7·0. Calc. for $C_{20}H_{26}O_6$: C, 66·3; H, 7·2%).

isoFlavones

Podospicatin. Podospicatin (11·9 g), m.p. and mixed m.p. 213·5–214°, was isolated by fractional crystallization of the light petroleum, benzene and ether extracts and from the sodium carbonate fractions of the benzene, ether and chloroform extracts. Circular R_f (A) 0·85, (B) 0·90.

Genistein. Genistein (5·1 g), m.p. and mixed m.p. 298–300° (decomp), was isolated by fractional crystallization of the ether extract after removal of quercetin. It was also isolated by fractional crystallization of the sodium carbonate fractions of the ether and chloroform extracts. Circular R_f (A) 0·75, (B) 0·90.

Flavonols

Quercetin. Quercetin (77·7 g), m.p. and mixed m.p. 313–316°, was isolated as the major product by fractional crystallization of the ether extract. It was also detected by paper chromatography in the sodium carbonate fractions of the ether, chloroform and ethyl acetate extracts. Circular R_f (A) 0·48 (B) 0·49.

Kaempferol. Paper chromatographic examination showed that quercetin was accompanied throughout by small amounts of a further yellow pigment, circular R_f (A) 0·58, (B) 0·74, separation of which was achieved by partition chromatography of quercetin mother liquors in 50–60% acetic acid on cellulose powder (Whatman, standard grade). Crystallization from 60% acetic acid and from aqueous ethanol gave kaempferol (200 mg), yellow needles, m.p. and mixed m.p. 280–283° (decomp) (Found: C, 63·2; H, 3·7· Calc. for $C_{15}H_{10}O_6$: C, 62·9; H, 3·5%) (identical infra-red spectrum). λ_{max} 266 mμ (log ε 4·24) and 370 mμ (log ε 4·40). Ultra-violet spectra in the presence of sodium acetate, sodium acetate–boric acid, sodium ethylate and sodium metaborate were identical with those for an authentic sample and also those recorded by Jurd *et al.*[10,21]

Flavononols

(+)-*Taxifolin.* After removal of matairesinol, the acidified aqueous phase of the sodium hydrogen carbonate fraction of the ether extract was extracted with ether and butan-1-ol. The concentrate from

the combined extracts was chromatographed in ethanol–chloroform–water (2 : 8 : 5) on columns of powdered cellulose following the procedure of Brewerton.[23] Crystallization of residues from slower moving fractions from aqueous ethanol gave (+)-taxifolin (180 mg), plates, m.p. and mixed m.p. 240° (decomp) $[\alpha]_D^{25}$ +48° (*c*, 1·0 in Me_2CO–H_2O) (Found: C, 57·8; H, 4·0. Calc. for $C_{15}H_{12}O_7 \cdot H_2O$: C, 57·5; H, 4·2%) (identical infra-red spectrum). λ_{max} 290 mμ (log ε 4·28) and shoulder at 330 mμ (log ε 3·56). Circular R_f (A) 0·77, (B) 0·69. The penta-acetate crystallized from absolute ethanol as needles, m.p. and mixed m.p. 118–120*. (Found: C, 58·1; H,4·45; Ac, 41·6. Calc. for $C_{25}H_{22}O_{12}$: C, 58·4; H, 4·3; 5 Ac, 41·8%).

(+)-*Aromadendrin.* Paper chromatography showed that taxifolin was accompanied by small amounts of a further 3-hydroxyflavanone (positive Pew's test[24]). The circular R_f values (A) 0·88, (B) 0·69 were identical with those of authentic aromadendrin and the ultra-violet spectrum determined by eluting the compound from paper strips by Geissman and Harbone's method[25] was identical with that of aromadendrin. λ_{max} 292 mμ and shoulder at 330 mμ. The compound was isolated in a crude condition by re-chromatography of the faster moving fractions from the partition columns above, in ethanol–chloroform–water (3 : 27 : 10). Acetylation and repeated purification from aqueous methanol gave (+)-aromadendrin tetra-acetate, m.p. 82–84° with shrinking at 60°, undepressed by a sample prepared from authentic (·)-aromadendrin (Found: C, 60·9; H, 4·4; Ac, 36·2. Calc. for $C_{23}H_{20}O_{10}$: C, 60·5; H, 4·4; 4 Ac, 37·7%).

Cyclitol

Sequoyitol. Extraction of the concentrate of the butan-1-ol extract with water, followed by concentration, gave a yellow syrup which on trituration with ethanol and long standing gave yields of optically inactive colourless leaflets. Recrystallization from aqueous methanol gave sequoyitol (840 mg), m.p. 240·5–241·5°, undepressed by an authentic sample (identical infra-red spectrum) (Found: C, 43·3; H, 6·9; OMe, 16·15. Calc. for $C_7H_{14}O_6$: C, 43·3; H, 7·3; 1 OMe, 16·0%). The penta-acetate, needles from benzene–ligroin, had m.p. 194° (lit.[26] m.p. 200°).

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* H. V. Brewerton and R. C. Cambie, *New Zealand J. Sci.* **2**, 95 (1959) have recorded the correct melting points of the optically active and inactive penta- and tetra-acetates of dihydroquercetin.

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