

The Flavanones of *Agonis spathulata* (Myrtaceae)

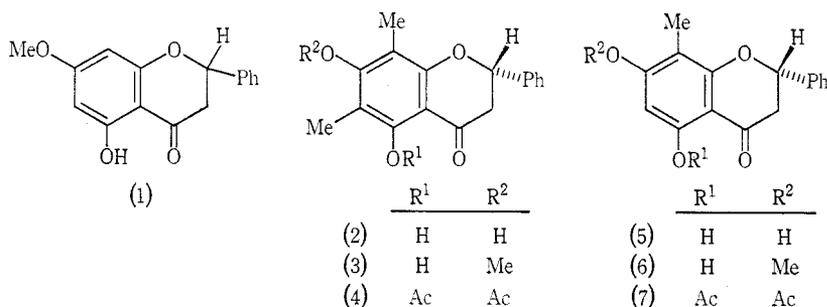
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Abstract

The flavanones (\pm)-pinostrobin (1), (-)-demethoxymatteucinol (2), and (-)-cryptostrobin (5) have been isolated from *Agonis spathulata* Schau.

The genus *Agonis* belongs to the family Myrtaceae and comprises eleven¹ or twelve² species which are endemic to the south western floristic province of Western Australia. The four Queensland species formerly included in *Agonis* have now been transferred to other genera.² Previous work on the Western Australian species appears to have been restricted to examinations of the oil of *Agonis flexuosa*.^{3,4}



A. spathulata Schau. is a straggling shrub which is common near the Stirling Range. In the present work, fractionation of an ether extract of this species with alkalis, followed by chromatography of that portion of the extract which is soluble in aqueous sodium hydroxide, has yielded three flavanones. These substances have been identified as (\pm)-pinostrobin (1), (-)-demethoxymatteucinol (2) and (-)-cryptostrobin (5) by comparison with authentic specimens. Both (2) and (5) have been assigned the (2*S*)-configuration by Clark-Lewis.⁵

¹ Beard, J. S., (Ed.) 'West Australian Plants' 2nd Edn (King's Park Board: Perth 1970).

² Burbidge, N. T., 'Dictionary of Australian Plant Genera' (Angus & Robertson: Sydney 1963).

³ Parry, R. E., *Proc. R. Soc. Victoria*, 1914, [II], 26 (n.s.), 367.

⁴ Phillips, L. W., *Proc. R. Soc. W.A.*, 1923, [II], 9, 107.

⁵ Clark-Lewis, J. W., *Rev. Pure Appl. Chem.*, 1962, 12, 96.

Although demethoxymatteucinol has been isolated from *Eugenia javanica* Lam.⁶ it appears that neither pinostrobin nor cryptostrobin has been isolated from a member of the Myrtaceae previously.

Experimental

General experimental procedures have been described previously.⁷ Voucher specimens (JRC 621007) of the plant material have been lodged in the Western Australian Herbarium, Perth.

Extraction of Agonis spathulata

Leaves and twigs were collected from flowering plants growing near the base of the Stirling Range and the milled, air-dried material (8.01 kg) was extracted exhaustively with ether at room temperature. The concentrated extract (c. 3 l.) was washed with sat. aq. NaHCO₃ then shaken with 5% aq. NaOH. The alkaline layer was filtered to remove an insoluble sodium salt of a triterpene acid (29 g) then acidified and re-extracted with ether. After washing with sat. aq. NaHCO₃ and 5% aq. Na₂CO₃ this solution was again extracted with 5% aq. NaOH. The alkaline solution was acidified and re-extracted with ether; evaporation of the solvent then gave a brown gum (32 g). Chromatography of a portion (28.5 g) of this product on a column of silicic acid (450 g) gave the three major fractions described below.

(±)-Pinostrobin (1)

Elution of the column with benzene gave (±)-pinostrobin (1) which crystallized from light petroleum (b.p. 55–65°) as plates (0.4 g), m.p. 98–99°, not depressed on admixture with an authentic specimen (lit.⁸ m.p. 100°). The infrared spectra (KBr disc) of the two samples showed no significant differences, $[\alpha]_D^{25} -0.2^\circ$ (c, 3.0 in acetone) [lit.⁵ $[M]_D -120^\circ$ (in acetone) for (–)-pinostrobin].

(–)-Demethoxymatteucinol (2)

Elution of the above column with benzene/ether (40 : 1) afforded (–)-demethoxymatteucinol (2) which crystallized from ethanol as pale yellow needles (1.2 g), m.p. 202–204°, not depressed on admixture with an authentic specimen; $[\alpha]_D^{25} -48^\circ$ (c, 3.8 in acetone) [lit.⁹ m.p. 202.5°, $[\alpha]_D^{25} -50^\circ$ (c, 3.86 in acetone)]. The infrared spectra (KBr disc) of the two samples showed no significant differences.

Treatment of (–)-demethoxymatteucinol (2) with excess ethereal diazomethane afforded the monomethyl ether (3), which crystallized from methanol as pale yellow needles, m.p. 112–113°, $[\alpha]_D^{25} -23^\circ$ (c, 5.3 in acetone) [lit.⁹ m.p. 112–112.5°, $[\alpha]_D^{25} -22.47^\circ$ (c, 5.3 in acetone)].

Treatment of (–)-demethoxymatteucinol (2) with pyridine and acetic anhydride for 48 h at room temperature yielded (–)-(2*S*)-5,7-diacetoxy-6,8-dimethylflavanone (4) which crystallized from methanol as needles, m.p. 177–178° (lit.⁶ 177–178°), $[\alpha]_D^{25} -64^\circ$ (c, 1.5 in chloroform) (Found: C, 68.5; H, 5.9. Calc. for C₂₁H₂₀O₆: C, 68.5; H, 5.5%). The substance gave a negative test with ferric chloride.

(–)-Cryptostrobin (5)

Elution of the above column with benzene/ether (20 : 1) afforded (–)-cryptostrobin (5) which crystallized from benzene as cream needles (5.1 g), m.p. 203–204°, not depressed on admixture with an authentic specimen, $[\alpha]_D^{25} -34^\circ$ (c, 1.1 in methanol) [lit.¹⁰ m.p. 202–203°, $[\alpha]_D^{25} -33^\circ$ (c, 1.1 in methanol)] (Found: C, 71.4; H, 5.2. Calc. for C₁₆H₁₄O₄: C, 71.1; H, 5.2%).

Treatment of (–)-cryptostrobin (5) with ethereal diazomethane afforded (–)-(2*S*)-5-hydroxy-7-methoxy-8-methylflavanone (6) which crystallized from methanol as needles, m.p. 148–149°,

⁶ Mitscher, L. A., Wu, W.-N., and Beal, J. L., *Lloydia*, 1973, 36, 422.

⁷ Cannon, J. R., Joshi, K. R., Meehan, G. V., and Williams, J. R., *Aust. J. Chem.*, 1969, 22, 221.

⁸ Mongkolsuk, S., and Dean, F. M., *J. Chem. Soc.*, 1964, 4654.

⁹ Fujise, S., and Kubota, T., *Ber. Dtsch. Chem. Ges.*, 1934, 67, 1905.

¹⁰ Alvarez-Nóvoa, J. C., Erdtman, H., and Lindstedt, G., *Acta Chem. Scand.*, 1950, 4, 390.

$[\alpha]_D^{20} -18^\circ$ (*c*, 1.8 in acetone) (lit.¹¹ m.p. 134–136° for the crude product) (Found: C, 71.6; H, 5.6. $C_{17}H_{16}O_4$ requires 71.8; H, 5.7%).

After the method of Fujise and Kubota,⁹ (–)-(2*S*)-5-hydroxy-7-methoxy-8-methylflavanone (6) (50 mg) was dissolved in ethanol (10 ml) and conc. H_2SO_4 (5 ml) was added. The resulting yellow solution was heated on the steam bath for 30 min, then poured over ice and extracted with ether. Evaporation of the ether gave (±)-5-hydroxy-7-methoxy-8-methylflavanone which crystallized from methanol as needles (38 mg), m.p. 143–144° (lit.¹² 142–143°).

Treatment of (–)-cryptostrobin (5) with acetic anhydride and pyridine at room temperature for 48 h gave (–)-(2*S*)-5,7-diacetoxy-8-methylflavanone (7) which crystallized from methanol as needles, m.p. 115–116.5°, $[\alpha]_D^{21} -68^\circ$ (*c*, 1.0 in chloroform) (Found: C, 67.3; H, 5.3. $C_{20}H_{18}O_6$ requires C, 67.8; H, 5.1%). This substance gave a negative test with ferric chloride.

Acknowledgments

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¹¹ Lindstedt, G., and Misiorny, A., *Acta Chem. Scand.*, 1951, **5**, 1.

¹² Chopin, J., *C. R. Acad. Sci.*, 1957, **245**, 2300.

Corrigendum

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Page 1514, lines 6 and 5 from bottom: *for* 2-methylnortricyclene *read* 3-methylnortricyclene, *and for* 2-methylenenortricyclene *read* 3-methylenenortricyclene.