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FURTHER TERPENOID AND PHENOLICS OF *DRYMIS WINTERI**

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Key Word Index—*Drymis winteri*; Magnoliaceae; cryptomeridiol; flavones; flavanonol; tumour inhibitors.

Plant. *Drymis winteri*, collected in the Valdivia region of Chile. **Previous work.** The light petrol. extract of the bark of several *Drymis* species, including *D. winteri*, has been extensively studied and shown to contain a range of sesquiterpenes of the drimane type.¹

Present work. As part of a general screening programme of Chilean flora for anti-tumour compounds* it has been found that the C₆H₆ and EtOAc extracts from the leaves of this plant were active in a test against mouse leukaemia lymphocytes (P388).²

Chromatography of the C₆H₆ extract through alumina afforded one major fraction, eluted with 1:3 CHCl₃–light petrol. This material crystallized, m.p. 132–134°, shown to be identical to cryptomeridiol³ by comparison with an authentic sample. This appears to be the first example of the eudesmane class of sesquiterpenes in the *Drymis* species. This material was inactive in the P388 test.

The EtOAc was removed from the extract with this solvent and the residue macerated with water and re-extracted with CHCl₃ in order to separate the glycosides from the aglycones. Concentration of the chloroform layer afforded crystals of cirsimaritin (5,4'-dihydroxy-6,7-dimethoxyflavone),⁴ identified by direct comparison with an authentic sample and by preparation of its acetate, m.p. 199–201° (MeOH), (Calc. for C₂₁H₂₂O₈: C, 63.31; H, 4.55. Found: C, 63.41; H, 4.48%).

The CHCl₃-insoluble part of the EtOAc extract was subjected to silica gel column chromatography, followed by paper chromatography to give the following compounds; Quercetin,⁵ m.p. 313–314°, identical by direct comparison with authentic material. Taxifolin,⁶ m.p. 228–230° (lit.⁶ m.p. 234°), [α]_D²⁰ +42° (c 1.0, acetone), λ_{max} 290, 330 nm, λ_{max}^{NaOMe} 245, 325 nm, λ_{max}^{AlCl₃} 276 (sh), 312, 375 nm. Acetylation afforded a penta-acetate, m.p. 128–129°, τ 2.78 (3H, *m*, H-2', H-5', H-6'), 3.29–3.45 (2H, *dd*, *J* 2.1 Hz, H-6 and H-8),

* Part III in the series "Anti-tumour compounds from Chilean Plants". For Part II see GNECCO, S., POYSER, J. P., SILVA, M. and SAMMES, P. G. (1973) *Phytochemistry* **12**, 2467. This work was supported by the Organization of American States (Grant PMC-8/1).

¹ APPEL, H. H., BROOKS, C. J. W. and OVERTON, K. G. 1959 *J. Chem. Soc.* 3322; APPEL, H. H., CONNOLLY, J. D., OVERTON, K. H. and BOND, R. P. M. *J. Chem. Soc.* 4658 (1960); BOND, R. P. M. and OVERTON, K. H. (1963) *Tetrahedron* **19**, 635.

² Cytotoxicity (KB) and *in vivo* (P388) tests were carried out at the National Cancer Institute, N.I.H. For procedures see *Cancer Chemother. Rep.* **25**, 1 (1962).

³ SUMIMOTO, M. (1963) *Chem. Ind. (London)* 1356, 1436.

⁴ MORITA, N. and SHIMIZU, M. (1963) *Chem. Abstr.* **59**, 15374.

⁵ BATE-SMITH, E. C. (1962) *J. Linn. Soc. (Bot)* **58**, 39.

⁶ GEISSMAN, T. A. (1960) *J. Am. Chem. Soc.* **62**, 3258; CLARK-LEWIS, J. W. and KARYTNYK, W. (1958) *J. Chem. Soc.* 2367.

4.40–4.64 (2H, *dd*, *J* 12 Hz, H-2 and H-3), 7.68 (3H, *s*), 7.75 (9H, *s*), 8.00 (3H, *s*). The UV values are the same as those reported in the lit.⁷ *Astilbin*,⁸ m.p. 179–180° (lit.⁸ 180°), $[\alpha]_D^{20}$ –18° (*c* 1.0, EtOH), M^+ 450 ($C_{21}H_{22}O_{11}$). Acid hydrolysis under standard conditions afforded rhamnose and taxifolin. *Quercitrin*,⁹ m.p. 185–187°, (lit.⁹ m.p. 182–185°), identical to an authentic sample. It gave an acetate, m.p. 198–199°; acid hydrolysis afforded rhamnose and quercetin.

Anti-tumour properties. Assay of taxifolin against the KB and P388 test systems showed it to be inactive against the KB test but active against the P388 system, with a T/C ratio of 140 at 150 mg/kg and 137 at 100 mg/kg.

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⁷ MABRY, T. J., MARKHAM, K. R. and THOMAS, M. B. (1970) *The Systematic Identification of Flavonoids*, p. 224, Springer, New York.

⁸ HAYASHI, K. and OUCHI, H. (1950) *Misc. Reps. Research Inst. Nat. Resources (Tokyo)* **17–18**, 19; (1952) **26**, 22.

⁹ GEISSMAN, T. A. (ed.) (1962) *The Chemistry of Flavanoid Compounds*, p. 336, Macmillan, New York.

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LACTONIC LIGNANS OF *POLYGALA CHINENSIS*

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Key Word Index—*Polygala chinensis*; Polygalaceae; suchilactone; chisulactone; helioxanthin.

Plant. *Polygala chinensis* L.¹ *Source.* Several parts of India.² *Uses.* As a substitute for *Polygala senega* as an expectorant. *Previous work.* On the whole plant reported to contain saponins,³ but their nature was not determined.

Present work. The dried and powdered whole plant (5.8 kg) was first extracted in a Soxhlet with petrol. (60–80°) followed by EtOH, 16 hr each. Each of these extracts were examined separately.

Petrol. extract. The extractives crystallized from EtOH as needles (4.3 g). *Suchilactone.* The analytical TLC showed two spots and the components were separated by preparative TLC. The major compound, suchilactone, was identified as 2-piperonylidene-3-veratryl-3S-γ-butyrolactone (m.p., $[\alpha]_D$, UV, IR, PMR, MS). It was previously reported as a degradation product of helianthoidin.⁴ The diol, $C_{21}H_{24}O_6$ (M^+ , 372), from the $LiAlH_4$ reduction of suchilactone had m.p. 118°; λ_{max}^{EtOH} 208, 255–260 nm; v_{max} (mineral oil)

¹ SHAH, C. S., VYAS, L. S. and AGHARA, L. P. (1957) *Indian J. Pharm.* **19**, 10.

² The plant material was collected from Varanasi and the identity was confirmed by Dr. C. S. P. Rao, Department of Botany, Banaras Hindu University. A voucher specimen has been preserved at the Department of Pharmaceutics.

³ WAHID, M. and SAMIULLAH, A. (1960) *Pakistan J. Sci. Ind. Res.* **3**, 228; (1963) *Chem. Abstr.* **58**, 1301.

⁴ BURDEN, R. S., CROMBIE, L. and WHITING, D. A. (1969) *J. Chem. Soc. C*, 693.