

Methylation of dihydrosyringetin yielded a pentamethyl ether crystallized from methanol-CH₂Cl₂ m.p. 192° (lit. ampilopsin pentamethyl ether m.p. 194-5°); (Found: C, 61.87, H, 5.56. C₂₀H₂₂O₈ required C, 61.53; H, 5.68); $\nu_{\text{max}}^{\text{KBr}}$ 3450, 3000, 2940, 2840, 1680, 1660, 1620, 1590, 1500, 1460, 1420, 1340, 1245, 1215, 1150, 1100, 980 and 830 cm⁻¹. PMR: C-6 H and C-8 H, 6.15 s; C-2' H and C-6' H, 6.80 s; C-2 H and C-3 H: C-3 H, 4.47 q ($J_{2,3} = 12$ cps; $J_{3,3\text{OH}} = 1.5$ Hz); collapses to doublet on D₂O exchange; C-2 H, 4.97 d ($J_{2,3} = 12$ Hz); 5 O—CH₃, 3.8-4.0. Mass spectrum; m/e 390 (40), 361 (75), 210 (30), 195 (30), 193 (15), 181 (100), 167 (10), 137 (10). Acetate of pentamethylether, m.p. 160°. *Ethylation* yielded triethyl ether m.p. 134°, $\nu_{\text{max}}^{\text{KBr}}$ 3450, 2970, 2930, 2870, 1680, 1610, 1570, 1455, 1430, 1330, 1240, 1200, 1170, 1120 and 800 cm⁻¹. PMR: 2 O—CH₃, 3.9; C-2' H and C-6' H, 6.8 s; C-6 H and C-8 H, 6.12 s; C-3 H, 4.45 d, C-2 H, 4.95 d ($J = 12$ Hz); 9 H, 1.2-1.7 and 6 H, 4.00-4.30 assignable to three ethoxy groups; C-3 OH merged with signal at 4.00. MS. m/e 432 (33), 403 (100), 224 (18), 221 (9), 209 (95), 196 (24), 195 (57), 181 (12), 167 (26), 153 (12).

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Key Word Index—*Soymida fibrifuga*; Meliaceae; obtusifoliol; syringetin; dihydrosyringetin.

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OLEACEAE

BITTER CONSTITUENTS OF *FORSYTHIA VIRIDISSIMA**

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Plant. *Forsythia viridissima* Lindl. *Source.* Botanical Garden of Osaka City University, Osaka, Japan. *Previous work.* Leaves of *F. coreana* Nakai and *F. suspensa* Vahl.¹ Bark and leaves of several *Forsythia* species.²

The fresh leaves, which have a pungent taste, were extracted with hot water and the bitter components were taken into EtOAc. They were separated into five fractions by the partition chromatography on silica gel. The third (15% *n*-BuOH-CHCl₃) and fourth (20% *n*-BuOH-CHCl₃) fractions were responsible for the bitter taste. Further purification by the chromatography on polyamide or neutral alumina afforded arctiin³ and matairesinoside^{2,4} respectively. The corresponding aglycones, arctigenin and matairesinol were

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¹ S. KUNIMINE and S. SUZUKI, *Yakugaku Zasshi* **57**, 902 (1937); **58**, 572 (1938); T. KAKU, H. RI and N. HARA, *ibid.* **59**, 248 (1939). A. SOSA, *Bull. Soc. Chim. Biol.* **29**, 918 (1947); *Chem. Abs.* **42**, 6415 (1948).

² H. THIEM and H. J. WINKLER, *Pharmazie* **23**, 402, 519 (1968); **24**, 117 (1969).

³ M. OMAKI, *Yakugaku Zasshi* **55**, 816 (1935); **56**, 982, 985 (1936); **57**, 269 (1937).

⁴ I. INAGAKI, S. HISADA and S. NISHIBE, *Phytochem.* **10**, 211 (1971).

obtained from the first (5% *n*-BuOH-CHCl₃) and second (7% *n*-BuOH-CHCl₃) fractions respectively. The fifth (MeOH) fraction yielded two flavonol glucosides, isoquercitrin⁵ (quercetin 3-glucoside) and astragalín (kaempferol 3-glucoside).⁶

EXPERIMENTAL

Arctigenin. C₂₁H₂₄O₆. Found: m.p. 99–99.5°; [α]_D –36.7°, CHCl₃; C, 67.7; H, 6.5; methyl ether, m.p. 128.5–129.5°; IR identical to that of authentic arctigenin; m.m.p. Required: m.p. 102°; [α]_D –28.7°, CHCl₃³; C, 67.7; H, 6.5; methyl ether, m.p. 127–128°.⁷

Matairesinol. C₂₆H₂₂O₆. 1/2 C₂H₅OH. Found: m.p. 80–82°; [α]_D^{14.5°} –40.4°, CHCl₃; C, 66.2; H, 6.5; dimethyl ether, m.p. 126–127°; converted to *seco*-isolariciresinol, m.p. 113–114°, [α]_D^{15°} –23.9°, according to the method of Briggs,⁸ which was identified by IR comparison, with that of the authentic sample and m.m.p. Required: m.p. 75°; [α]_D –48.0°, MeOH;⁵ C, 66.1; H, 6.6; dimethyl ether, m.p. 125–127°; *seco*-isolariciresinol, m.p. 112.5–113.5°; [α]_D –35.6°, acetone.⁷

Arctiin. C₂₇H₃₄O₁₁. 1/2 H₂O. Found: m.p. 110–112°; [α]_D^{16°} –51.3°, MeOH; C, 57.8; H, 6.6; hydrolysis with acid or emulsin gave arctigenin and glucose (identified by co-chromatography and formation of the osazone). Required:³ m.p. 112°; [α]_D –38.8°, MeOH; C, 57.8; H, 6.6.

Matairesinoside. Found: amorphous powder (homogeneous on the PPC and TLC with different solvents); [α]_D –39.1°, CHCl₃; pentaacetate C₃₆H₄₂O₁₆, m.p. 95–97°; C, 58.9; H, 5.9; δ_{CDCl₃}, 2.06(6H, s), 2.06(6H, s), 2.33(3H, s), 2.62(4H, broad s), 2.93(2H, broad s), 3.80(6H, s), 3.90(2H, m), 4.23(3H, broad s), 4.80–5.40(4H, m), 6.55–6.80(6H, m); hydrolysis with acid or emulsin produced matairesinol and glucose (identified by co-chromatography and the formation of the osazone); methylation with CH₂N₂ yielded arctiin. Required: amorphous,² m.p. 93°;⁶ [α]_D^{12°} –46.0°, EtOH; pentaacetate, m.p. 86–87°;² C, 59.2; H, 5.8.

Astragalín. C₂₁H₂₀O₁₁. 2H₂O. Found: m.p. 205–206°; λ_{max}^{EtOH} 269 and 360 nm (ε 22 400 and 16 200); C, 52.1; H, 5.2; heptaacetate, m.p. 217–219°; acid hydrolysis gave kaempferol, m.p. 276–278° and glucose (identified by co-chromatography and derivation of the osazone). Required:⁶ m.p. 175–178°; λ_{max} 266, 300 and 350 nm (log ε, 4.30, 4.04 and 4.20); C, 52.1; H, 5.0; heptaacetate, m.p. 218–220°; kaempferol, m.p. 276–278°.

Isoquercitrin. C₂₁H₂₀O₁₂. 2H₂O. Found: m.p. 214–216°; λ_{max}^{EtOH} 260 and 369 nm (ε 24 800 and 17 800); C, 50.0; H, 4.9; octaacetate, m.p. 179–180°; hydrolysis gave quercetin, m.p. > 300° (pentaacetate, m.p. 193–194°) and glucose (identified by co-chromatography and the formation of the osazone). Required:⁵ m.p. 225–227°; λ_{max} 257 and 369 nm; C, 50.0; H, 4.8; quercetin, m.p. 314° (pentaacetate, m.p. 197–198°).

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⁵ S. HATTORI, M. HASEGAWA and K. HAYASHI, *Nippon Kagaku Zasshi* **58**, 844 (1937).

⁶ A. VON WARTBURG and M. KUHN, *Experientia* **21**, 67 (1965).

⁷ R. D. HAWORTH and T. RICHARDSON, *J. Chem. Soc.* 633 (1935).

⁸ L. H. BRIGGS, R. C. CAMBIE and J. L. HOAE, *Tetrahedron* **7**, 262 (1959).

Key Word Index—*Forsythia viridissima*; Oleaceae; arctiin; matairesinoside; bitter lignans; astragalín; isoquercitrin.