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MELIACEAE

EXTRACTIVES FROM *SOYMIDA FEBRIFUGA*

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Soymida is a monotypic genus of the order Meliaceae, occurring in Indomalaysia. We have examined the wood and bark of *S. febrifuga* A. Juss for limonoids. The timber of the specimen we examined contained no detectable amount of limonoids, the bark contained approximately 0·1 % of methyl angolensate, identical with an authentic specimen.[1] These results are in agreement with the botanical conclusion[2] that *Soymida* is closely related to the African genus *Khaya* which we have already investigated extensively.[1] Specimens of the plant have been examined anatomically and physically at the Forest Products Laboratory, Princes Risborough, England and found to agree with those in their reference collection.

[1] G. A. ADESIDA, E. K. ADESOGAN, D. A. OKORIE, D. A. H. TAYLOR and B. T. STYLES, *Phytochem.* **10**, 1845 (1971).
[2] Personal communication from Dr. B. T. STYLES.

Key Word Index—Soymida febrifuga; Meliaceae; methyl angolensate.

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OBTUSIFOLIOL, SYRINGETIN AND DIHYDROSYRINGETIN FROM *SOYMIDA FEBRIFUGA*

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Plant. Soymida febrifuga. Source. Kakinada Forest Division, Andhra Pradesh, India. *Previous work.* Methyl angolensate from stem bark.[1]

Petroleum extract of root heartwood yielded sitosterol and a colourless compound, m.p. 144°; positive Liebermann–Burchardt reaction; MW 426, $C_{30}H_{50}O$; yields monoacetate, vinylidene group seen in IR and PMR spectra (see Experimental). This was identified as obtusifoliol,[2] confirmed by direct comparison with authentic material. Further extraction with $CHCl_3$ yielded two flavonoids; syringetin, golden yellow needles, m.p. 288° and dihydrosyringetin, needles m.p. 228°. Syringetin MW 346, $C_{17}H_{14}O_8$, yielded a tetraacetate and a tetraethyl ether mixed with a small quantity of triethyl ether. The oxygenation pattern became clear from the PMR spectrum (see Experimental) of the tetraethyl ether in which appropriate signals corresponding to protons at C-6, C-8, C-2′ and C-6′,

[1] R. Y. AMBAYE, M. A. INDAP and T. B. PANSE, *Current Sci.* 7, 158 (1971).
[2] J. B. BARRERA, J. L. BRETON, J. D. MARTIN and A. G. GONZALIZ, *Anales real soc. espan fis. y. quim.* **63B**, 191 (1967).

could be seen. Signals for two methoxyls and four ethoxyl group protons are also present; since both the methoxyls as also the C-2′ and C-6′ protons are magnetically equivalent, the two methoxyls are placed at C-3′ and C-5′. This was confirmed by the alkaline hydrolysis of the tetraethyl ether which gave 3,5-dimethoxy-4-ethoxybenzoic acid. Complete methylation gave the expected myricetin hexamethyl ether. This is the first isolation of pure syringetin from plants, but it has been obtained earlier, mixed with isorhamnetin, from flowers of *Lathyrus pratensis*.[3]

Dihydrosyringetin is a new plant substance. It gives a triethyl ether; in its PMR spectrum also (see Experimental) the two methoxyls and the C-2′ and C-6′ protons are magnetically equivalent; C-3 and C-2 protons are seen as an AB quartet ($J = 12$ Hz). On oxidation with iodine and potassium acetate, it yields syringetin. Its structure as the dihydro derivative is further confirmed by its complete methylation to ampelopsin pentamethyl ether (MW 390). Its mass fragmentation and that of the triethyl ether supports this structure.

In the mass fragmentation of syringetin tetraacetate, the molecular ion at *m/e* 514 can be seen only in high amplification; one ketene is lost very quickly and the highest *m/e* peak seen in low amplification is at 472. Subsequent losses of ketene lead to the expected fragments of *m/e* 430, 388 and 346. The ethanol extract of this root bark contains methyl esters of *p*-coumaric and caffeic acids.

EXPERIMENTAL

PMR spectra were recorded in $CDCl_3$; chemical shifts are expressed in (δ = ppm) relative to TMS as external standard; MW by MS.

Obtusifoliol. Petrol. extract of root heartwood of *S. febrifuga* yielded sitosterol m.p. 136° and obtusifoliol after chromatography on silica gel column. Obtusifoliol, m.p. 144° from MeOH. (Found: C, 83·40, H, 11·10 $C_{30}H_{50}O$ required: C, 84·44; H, 11·81); ν_{max}^{KBr} 3070, 1640, 885 cm^{-1}; PMR: $=CH_2$ at 4·66 (m); CHOH at 2·9 (b) moves to 4·18 on acetylation. 7 CH_3 0·6 to 1·1.

Syringetin and dihydrosyringetin. Residue extracted with $CHCl_3$; taken into Na_2CO_3, acidified and re-extracted in $CHCl_3$. Solvent evaporated and residue treated with cold EtOAc leaving undissolved solid which on recrystallisation from EtOAc melted at 228° and was dihydrosyringetin ν_{max}^{KBr} 3350, 1630, 1585, 1520, 1455, 1330, 1250, 1150, 1130, 1080 cm^{-1}; MS, *m/e* 348 (51), 319 (37), 196 (79), 167 (76), 153 (100) and 125 (24).

The clear yellow solution decanted and evaporated to a residue, chromatographed over silica gel in EtOAc/HOAc and crystallized from HOAc into bright yellow needles of syringetin m.p. 288°. (Found: C, 59·22; H, 4·29. $C_{17}H_{14}O_8$ required: C, 58·96; H, 4·08.) ν_{max}^{KBr}: 3455, 1650, 1620, 1600, 1500, 1360, 1330, 1250, 1100, 1010, 820 and 800 cm^{-1}. λ_{max}^{EtOH} 253 (4·26), 273 (4·13)sh, 344 (4·19), 378 (4·23); $\lambda_{max}^{(NaOAc)}$ 253 (4·22), 277 (4·12)sh, 335 (4·23), 393 (4·14); $\lambda_{max}^{(AlCl_3)}$ 263 (4·36), 314 (4·19), 434 (4·36); $\lambda_{max}^{(MeOH)}$ ($AlCl_3$) 266 (4·33), 320 (4·03), 438 (4·36); $\lambda_{max}^{(NaOEt)}$ 250 (4·5), 285 (4·3)sh, decomposed. Acetate m.p. 228° from $CHCl_3$/MeOH. (Found: C, 58·10; H, 4·38. $C_{25}H_{22}O_{12}$ required C, 58·35; H, 4·28); ν_{max}^{KBr} 1780, 1640, 1600, 1430, 1340, 1160, 1120 and 1100 cm^{-1}. PMR: 4 CO—CH_3, 2·2–2·5; 2 O—CH_3, 3·85; 2 H (C-2′ and C-6′), 7·0; C-8 H, 7·3 d and C-6 H, 6·8 d ($J = 2$ cps).

Methylation of syringetin with Me_2SO_4–K_2CO_3–Me_2CO for 8 hr gave hexamethylmyricetin m.p. 155° (lit. 155°) from MeOH/petrol. and pentamethylmyricetin m.p. 138° from MeOH (lit. 139°); both identified by comparison with authentic samples. *Ethylation* with EtI/K_2CO_3/Me_2CO followed by chromatography on silica gel in C_6H_6–EtOAc (6:4) yielded a tetraethyl ether m.p. 144° from CH_2Cl_2/petrol. and a triethyl ether, m.p. 104° from MeOH. Tetraethyl ether: ν_{max}^{KBr} 2970, 2930, 2870, 1643, 1600, 1330, 1230, 1190, 1110 and 1020 cm^{-1}. PMR: C-6 H, 6·30 d; C-8 H, 6·41 d ($J = 2·0$ Hz); C-2′ H and C-6′ H, 7·41 s; 2 O—CH_3, 3·91; 12 H, 1·2–1·7 and 8 H, 4·0–4·4 assignable to the four ethoxy groups. Triethyl ether: C-6 H, 6·31 d; C-8 H, 6·41 d ($J = 2·0$ Hz); C-2′ H and C-6′ H, 7·41 s; C-5 OH, 12·5; 9 H, 1·2–1·6 and 6 H, 4·0–4·4 assignable to three ethoxy groups.

Alkaline hydrolysis of syringetin tetraethyl ether (150 mg) by refluxing in 8% alcoholic KOH (8 ml) for 7 hr eventually yielded 4-ethoxy syringic acid, identified by m.m.p. and IR comparison with synthetic sample.

[3] J. B. HARBORNE, *Phytochem.* **4**, 647 (1965).

Methylation of dihydrosyringetin yielded a pentamethyl ether crystallized from methanol–CH_2Cl_2 m.p. 192° (lit. ampilopsin pentamethyl ether m.p. 194–5°); (Found: C, 61·87, H, 5·56. $C_{20}H_{22}O_8$ required C, 61·53; H, 5·68); ν_{max}^{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; $J_{3,3\,OH}$ = 1·5 Hz); collapses to doublet on D_2O exchange; C-2 H, 4·97 d ($J_{2,3}$ = 12 Hz); 5 O—CH_3, 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°, ν_{max}^{KBr} 3450, 2970, 2930, 2870, 1680, 1610, 1570, 1455, 1430, 1330, 1240, 1200, 1170, 1120 and 800 cm^{-1}. PMR: 2 O—CH_3, 3·9; C-2′ H and C-6′ H, 6·8 s; C-6 H and C-8 H, 61·2 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–$CHCl_3$) and fourth (20% *n*-BuOH–$CHCl_3$) fractions were responsible for the bitter taste. Further purification by the chromatography on polyamide or neutral alumina afforded arctiin[3] 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).