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METHOXYLATED FLAVONES OF *FORTUNELLA JAPONICA*

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Key Word Index—*Fortunella japonica*; Rutaceae; nobiletin; tangeretin; 5,7,8,3',4'-pentamethoxy flavone; sitosterol.

Fortunella is a small genus of evergreen shrubs or small trees, native of South China, cultivated throughout subtropical regions of the world [1]. *F. japonica* (Thumb) Swingle (Syn. *Citrus japonica* Thumb; round or marumi kumquat) and *F. margarita* (Lour) Swingle (Syn. *Citrus margarita* Lour, oval or nagami kumquat) are grown in India as ornamentals and for their fruit which are rich in pectin and excellent for marmalades and jellies [1].

F. japonica has been found to be a rich source of methoxylated flavones. The occurrence of acacetin-7-rhamnoglucoside in the fruits and petals of this plant has been reported earlier [2]. We now describe the isolation of nobiletin (1) [3], tangeretin (2) [4] and 5,7,8,3',4'-pentamethoxy flavone (3) along with sitosterol from the light petrol and CHCl_3 extracts of the leaves and twigs of *F. japonica*. The compounds were characterized from their spectral (UV, IR, PMR, MS) properties and by direct comparison (m.m.p., TLC, IR). Compound (3) was reported earlier from *Citrus aurantium* [5], *C. sinensis* [6] and *C. paradisi* [6]. Nobiletin (1) and tangeretin (2) were converted to the corresponding 5-desmethyl and completely demethylated compounds. The PMR and the mass

spectral characteristics of the above compounds, not reported earlier, are recorded in the Experimental.

EXPERIMENTAL

Extraction. Dried powdered leaves and twigs were Soxhletted with light petrol (60–80°) and CHCl_3 respectively. The neutral fractions were chromatographed over silica gel (g.) and elution with solvent mixtures of increasing polarity yielded in succession sitosterol (mp and $[\alpha]_D$ of compound and acetate), nobiletin (1), tangeretin (2) and 5,7,8,3',4'-pentamethoxy flavone (3). The latter three compounds responded to the Shinoda test [7] for flavones.

The middle C_6H_6 eluates afforded on rechromatography nobiletin (yield 0.12%), in colourless crystals, m.p. 137–138° from light petrol– C_6H_6 mixture; $\lambda_{\text{max}}^{\text{EtOH}}$ 332 nm ($\log \epsilon$ 4.27), 272 (4.01), 250 (4.04); IR: $\nu_{\text{max}}^{\text{KBr}}$ 1653 cm^{-1} (γ -pyrone $\text{C}=\text{O}$); PMR (60 MHz, CDCl_3 , δ): 7.73 (1H, dd, J 8.5 Hz and 2.0 Hz, H-6'), 7.57 (1H, d, J 2.0 Hz, H-2'), 7.13 (1H, d, J 8.5 Hz, H-5'), 6.73 (1H, s, H-3); 4.18 (3H, s), 4.11 (3H, s) and 4.03 (12H, s) for 6 OMe groups; MS m/e (% base peak): 402 (42, M^+), 387 (100, $\text{M}^+ - \text{Me}$ from 6-OMe), 240 (1.2, $\text{M}^+ - 162$, RDA of γ -pyrone ring) [8], 225 (11.2, 240–Me), 197 (23.3, 225–CO), 162 (9.3%, $\text{M}^+ - 240$). Found: C, 62.50; H, 5.51. $\text{C}_{21}\text{H}_{22}\text{O}_8$ requires: C, 62.6; H, 5.47%. Refluxing (1) with Conc. HCl-EtOH (1:1) for 6 hr gave in 60% yield the corresponding 5-desmethyl derivative, m.p. 144–145° lit³, 145°; IR: $\nu_{\text{max}}^{\text{KBr}}$ 1667 cm^{-1} ; PMR (60 MHz, CDCl_3 , δ): 12.58 (1H, s, chelated OH at C-5), 7.59 (1H, dd, J 8.5 Hz and 2.0 Hz, H-6'), 7.43 (1H, d, J 2.0 Hz, H-2') 7.0 (1H, d, J 8.5 Hz, H-5'), 6.6 (1H, s, H-3); 4.12 (3H, s), 3.98 (6H, s) and 3.96 (6H, s) for 5 OMe groups; MS m/e (% base

peak): 388 (83.7, M^+), 373 (100, $M^+ - Me$ from 6-OMe), 226 (0.3, $M^+ - 162$, RDA of γ -pyrone ring), 211 (12.5, 226-Me), 183 (8.1, 211-CO), 162 (2.7, $M^+ - 226$). Nobiletin was fully demethylated [3] to the corresponding hexahydroxy compound, when refluxed with Ac_2O-HI (1:2) for 1 hr, crystallizing from EtOH in yellow needles, m.p. 320° (lit. [3] 310-314°); hexaacetate (M^+ 570), m.p. 220-222° (lit. [3] 226-228°).

The later C_6H_6 and earlier $C_6H_6-CHCl_3$ (1:1) eluates afforded a solid showing single spot in TLC which on exhaustive rechromatography on silica gel yielded a further quantity of nobiletin, and tangeretin (yield 0.04%), crystallized from light petrol- $CHCl_3$ as needles, m.p. 150-151°; IR: ν_{max}^{KBr} 1656 cm^{-1} ; PMR (60 MHz, $CDCl_3$ showed expected signals [9] MS *m/e* (base peak): 372 (37, M^+), 357 (100, $M^+ - Me$), 240 (0.8, $M^+ - 132$, RDA of γ -pyrone ring), 225 (6.7, 240-Me), 197 (12.3, 225-CO), 132 (6.5, $M^+ - 240$). Treatment of (2) with anhydrous $AlCl_3$ in dry Et_2O (R.T., 24 hr) afforded the corresponding 5-desmethyl derivative, m.p. 175° (lit [10] 176°); IR: ν_{max}^{KBr} 1642 cm^{-1} ; PMR (60 MHz, $CDCl_3$, δ): 7.89 *d* and 7.02 *d* (4H, A_2B_2 *q*, *J* 8.5 Hz, H-2', H-3', H-5' and H-6'), 6.58 (1H, *s*, H-3), 4.01 (3H, *s*), 3.96 (6H, *s*) and 3.88 (3H, *s*) for four OMe groups; acetate prepared by Ac_2O -pyridine method had m.p. 161°. The completely demethylated derivative, 5,6,7,8,4'-pentahydroxyflavone, m.p. 320° (lit [9] 316-318°), was prepared by refluxing with Ac_2O-HI for 1 hr. The final $C_6H_6-CHCl_3$ (1:1) and $CHCl_3$ eluted fractions on rechromatography afforded 5,7,8,3',4'-pentamethoxyflavone (3) (yield 0.016%) crystallized from light petrol- $CHCl_3$ as needles, m.p. 200° (lit [6], 197-198°); IR: ν_{max}^{KBr} 1653 cm^{-1} ; PMR (60 MHz, $CDCl_3$, δ) identical with that reported earlier [11] MS *m/e* (100 base peak): 372 (100, M^+), 357 (81, $M^+ - Me$ from 8-OMe), 210 (4, $M^+ - 162$ RDA of γ -pyrone ring), 195 (11.5, 210-Me), 167 (31, 195-CO), 162 (5.5, $M^+ - 210$).

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ALKALOIDS AND TRITERPENES FROM *ZANTHOXYLUM PARVIFOLIOLUM*

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Key Word Index—*Zanthoxylum parvifoliolum*; Rutaceae; alkaloids; chelerythrine; nitidine; triterpenes; lupeol; sitosterol.

Plant. *Zanthoxylum parvifoliolum* A. Chev. (syn. *Fagara parvifoliola* A. Chev. ex Keay) [1]. *Voucher specimens.* Enti 518a and Enti 518b have been deposited with the herbarium of the Royal Botanic Garden, Edinburgh. *Source.* Enti 518a from the Bombiri Forest Reserve, Juasso, Ghana and Enti 518b from the Kade Agricultural Research Station, Ghana. *Previous work.* None on this species. Other species of the *Zanthoxylum/Fagara* complex are

known to yield a wide range of interesting secondary metabolites [2]. *Plant parts.* Stem bark and root bark from Enti 518a and 518b, wood, leaves and cork separated from the root bark of Enti 518b.

Present work. The powdered plant materials were extracted in a Soxhlet apparatus with light petrol (40-60°) and then $CHCl_3$. The light petrol extract from the root bark of Enti 518b (825 g)