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THE NEUTRAL VOLATILES OF *BOENNINGHAUSENIA ALBIFLORA*

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Plant. *Boenninghausenia albiflora* Reichb. (Rutaceae). *Source*. India. *Uses*. Flea repellent [1]. *Previous work*. On dictamnin [2], bergapten [2], rutin [3], coumarin [4], and matsukaze lactone [5] from an EtOH extract of the leaves and stems and on an essential oil from the leaves [6,7].

Present work. The leaves and stems of *B. albiflora* were steam-distilled and the volatile oil obtained was chromatographed on silica gel with *n*-hexane, with gradually increasing EtOAc as eluant. Individual constituents were then further purified by preparative TLC and subjected to co-GLC, IR, UV, NMR and MS. The volatile oil was found to be composed of β-myrcene (1·4%), (estimated from the peak area on GLC), α-phellandrene (0·8), β-caryophyllene (3·8), cadinene (13·9), cadalene (3·2), caryophyllene oxide (16·3), spathulenol (11·3), 7-methoxy-2,2-dimethylchromene (4·0), and 6,7-dimethoxy-2,2-dimethylchromene (ageratochromene) (5·5).

β-Myrcene. $C_{10}H_{16}$; δ_{ppm} ($CDCl_3$) 1·57 and 1·67 (each *s*, 6H, C=C(Me)$_2$, 2·16 (*m*, 4H, C=C–CH$_2$), 4·92 (*s*, 2H, =CH$_2$), 5·0–6·4 (*m*, 3H, vinyl group). β-Caryophyllene. $C_{15}H_{24}$; δ_{ppm} ($CDCl_3$) 0·96, 0·98 (each *s*, 6H, gem-dimethyl), 1·57 (*s*, 3H, C=C–Me). IR spectrum was identical with that of an authentic sample. Cadalene. $C_{15}H_{18}$; ν_{max} (liq.) 1604, 1512, 873, 812, 748 (aromatic ring), 1382 cm^{-1} (isopropyl); λ_{max} (EtOH) 229 nm (ϵ 45000), 282 (4500), 324 (490); δ_{ppm} ($CDCl_3$) 1·37 (*d*, *J* 7 Hz, 6H, –CH(Me)$_2$, 2·48 (*s*, 3H, phenyl–Me), 2·61 (*s*, 3H, phenyl–Me), 7·0–8·0 (*m*, 5H, aromatic ring H); picrate, m.p. 116–117° (lit. [8] 116°). α-Phellandrene and cadinene were identified by co-GLC. Caryophyllene oxide. $C_{15}H_{24}O$; *m/e* 220 (M$^+$); ν_{max} (liq.), 1618, 890 (end-methylene), 1376, 1360 (gem-dimethyl), 3021, 1255, 865, 755 cm^{-1} (oxirane ring); δ_{ppm} ($CDCl_3$) 0·96 [*s*, 6H, C(Me)$_2$], 1·17 [*s*, 3H, C(–O–)CMe–] 4·85, 4·95 (*m*, 2H, =CH$_2$). Spathulenol. $C_{15}H_{24}O$; *m/e* 220 (M$^+$); ν_{max} (liq.) 3420 (OH), 3080, 1638, 890 cm^{-1} (end-methylene); δ_{ppm} ($CDCl_3$) 0·6 (*m*, 2H, cyclopropane ring H), 1·08 [*s*, 6H, –C(Me)$_2$–], 1·27 [–C(OH)C$\underline{H}_3$–), 4·68 (*m*, 2H, =CH$_2$). The 3,5-dinitrobenzoate [9], m.p. and mixed m.p. 145–146°. 7-Methoxy-2,2-dimethylchromene. $C_{12}H_{14}O_2$; *m/e* 190 (M$^+$); ν_{max} (neat) 1640 (C=C), 1615, 1570, 1500 (benzene ring), 1025 cm^{-1} (methoxyl); λ_{max} (EtOH) 279 nm (ϵ 5670), 304 (4630); δ_{ppm} ($CDCl_3$) 1·43 [*s*, 6H, O–C(Me)$_2$–], 3·82 (*s*, 3H, O–Me), 5·50 (*d*, *J* 10 Hz, 1H, 3-H), 6·30 (*d*, *J* 10 Hz, 1H, 4-H), 6·4–7·0 (*m*, 3H, benzene ring H). The physical data were identical with those of 7-methoxy-2,2-dimethylchromene isolated from the essential oil of *Ageratum houstonianum* [10]. 6,7-Dimethoxy-2,2-dimethylchromene (ageratochromene). $C_{13}H_{16}O_3$; *m/e* 220 (M$^+$); ν_{max} (neat) 1640 (C=C), 1613, 1575, 1502, 750 (benzene ring), 1380, 1360 (gem-dimethyl), 1010 cm^{-1} (methoxyl); λ_{max} (EtOH) 278 nm (ϵ 3580), 322 (6750); δ_{ppm} ($CDCl_3$) 1·40 [*s*, 6H, O–C(Me)$_2$–C], 3·78 (*s*, 6H, two O–Me), 5·45 (*d*, *J* 10 Hz, 1H, 3-H), 6·21 (*d*, *J* 10 Hz, 1H, 4-H), 6·40, 6·51 (each *s*, 2H, benzene ring H). Catalytic hydrogenation on PtO_2 gave a dihydro-derivative, m.p. 50–60°; δ_{ppm} ($CDCl_3$) 1·32 [*s*, 6H, O–C(Me)$_2$–C], 1·75 (*t*, *J* 7 Hz, 2H, 3-CH$_2$), 2·70 (*t*, *J* 7 Hz, 2H, 4-CH$_2$), 3·80 (*s*, 6H, two O–Me), 6·38, 6·55 (each *s*, 2H, benzene ring H). These data were identical with those of the chromene isolated from *Ageratum mexicanum* Sims. and *A. conyzoides* L. [11].

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METHOXYLATED FLAVONES OF *FORTUNELLA JAPONICA*

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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 auratium* [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; λ_{max}^{EtOH} 332 nm (log ϵ 4·27), 272 (4·01), 250 (4·04); IR: ν_{max}^{KBr} 1653 cm^{-1} (γ-pyrone C=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, M^+–Me from 6–OMe), 240 (1·2, M^+–162, RDA of γ-pyrone ring) [8], 225 (11·2, 240–Me), 197 (23·3, 225–CO), 162 (9·3%, M^+–240). Found: C, 62·50; H, 5·51. $C_{21}H_{22}O_8$ 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° lit^3. 145°); IR: ν_{max}^{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