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THE FLAVONOIDS OF *UVARIA RUFAS*

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Abstract

*Tectochrysin (1), 7-*O*-methylwogonine (2) and 6,7-*O,O*-dimethylbaicalein (3) have been isolated from* Uvaria rufas *Blume. (Annonaceae)*

The genus *Uvaria* comprises 150 species which are distributed throughout tropical Africa, Madagascar, Indomalaya and Australia[1]. Fourteen species have been found in Thailand[2]. *U. rufas* or *U. ridleyi* is commonly encountered in Songkla province and is known locally as นมควาย ("Nom Kwai"). This species does not appear to be used in Thai folk remedies but one *Uvaria* species *(U. acuminata)* has been found to contain 3'-benzylhydrochalcones having inhibitory activity toward the P-388 (3 PS) lymphocytic leukemia test system[3], and another species *(U. chammae)* has been shown to contain *C*-benzylflavones which are cytotoxic principles[4].

Since the bark of *U. rufas* gave a faint positive field test for alkaloids[5], it was decided to investigate the bark of this species in the hope of obtaining the bases. The conventional extraction procedure yielded crude bases which consisted of several components. Due to the small quantity of the crude bases. the non-basic portion of the extract was investigated instead.

Extraction of the non-basic material gave a mixture which consisted of three compounds. These were separated neatly by chromatography. From the physical data and spectroscopic evidence, the three compounds were identified to be tectochrysin[6] (1) 7-*O*-methylwogonin[7] (2) and 6,7-*O*,*O*-dimethylbaicalein[7] (3) by comparison

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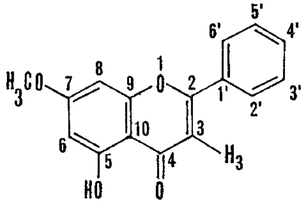
of the physical properties of these compounds and their derivatives with those previously reported.



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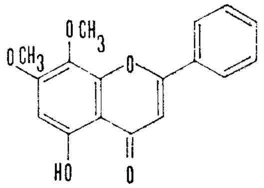

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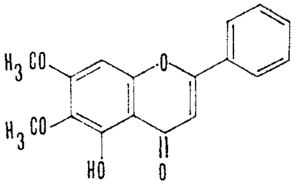

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Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Nuclear magnetic resonance (n.m.r.) spectra were obtained with a Hitachi Perkin-Elmer R-20A instrument operating at 60 MHz. The low resolution mass spectra were measured with a Dupont 490 F GC-MS instrument by direct insertion.

A voucher specimen of the plant material (PS 241) has been deposited in the Herbarium of the Biology Department at the Prince of Songkla University, Hat Yai, Thailand.

Milled air dried barks (2.7 kg.) of *Uvaria rufas* collected at Ban Chalung, Songkla, Thailand were extracted with methanol-acetic acid (95:5) at room temperature until portion of the evaporated extract gave only a faint Mayer's test. The extract was concentrated under reduced pressure to a brown tar which was poured in a thin stream, with vigorous stirring, into 5.1 of 5% sulphuric acid. The dark brown precipitate was filtered and dried to give non-alkaloidal material (1.2 kg). The filtrate was basified with ammonia to precipitate the alkaloids, which were then taken up in chloroform. The chloroform extract was evaporated under reduced pressure to yield the crude alkaloids as a brown gum (0.3 g). Thin layer chromatography indicated that this alkaloidal material was a mixture of several components. Due to the small quantity, this fraction was not further investigated.

A portion (20 g) of the non-alkaloidal material was extracted with light petroleum in a Soxhlet extractor. Yellow crystals (8 g) were collected by filtration. This was chromatographed on a column of silica gel (240 g) which was eluted with benzene. The first series of fractions collected contained mainly one component which crystallized from benzene. Recrystallization from benzene gave yellowish rhombic crystals (4.5 g, 56.25% of the crude crystals) of tectochrysin[6](1), m.p. 163–164°C [Lit.[6] m.p. 165–166°C], λ_{max}(MeOH)269, 310 nm, ε 29944, 12913. λ_{max}(MeOH+$AlCl_3$) 283, 327 nm, ε 29195, 14233. ν_{max}(nujol) 1665 cm^{-1}(C=O). N.m.r.($CDCl_3$) δ 3.90 (s, 3H, OCH_3), 6.38(d, 1H, ArH, J = 2), 6.54(d, 1H, ArH, J = 2), 6.66(s, 1H, H_3), 7.44–7.66 (m, 3H, ArH), 7.84–8.01(m, 2H, ArH), 12.69(s, 1H, OH). ^{13}C n.m.r.(CD_3SOCD_3) δ 55.7(C–methoxyl), 92.6(C–8), 97.8(C–6), 105.2(C–3 and C–10), 126.0(C–2' or C–6'), 126.3(C–6' or C–2'), 128.7(C–3' or C–5'), 129.0(C–5' or C–3'), 130.6(C–1' or C–4'), 131.5(C–4' or C–1'). 157.2(C–5 and C–9), 163.3(C–2), 165.2(C–7). 181.5(C–4). Mass spectrum (230°/70ev) m/e 268(100%), 238(25), 225(13), 138(13), 105(10), 102(10), 95(20), 77(20), 69(25). M.p. of the acetate 155–156°C[Lit[6]. 155–156°C].

The second series of fractions gave yellow needles which were recrystallized from benzene to give yellow needles (1.3 g, 16.25% of the crude crytals) of 7-0-methylwogonine(2), m.p. 181–182°C[Lit[7]. 181–182°C] λ_{max}(MeOH) 277, 315 nm, ε 36847, 7651. λ_{max}(MeOH+$AlCl_3$)298, 330 nm, ε 32216, 11074. ν_{max}(nujol) 1665 cm^{-1} (C=0). N.m.r.($CDCl_3$) δ 3.90(s, 6H, 2xOCH_3), 6.35(s, 1H, ArH), 6.58(s, 1H, H_3), 7.42–7.60(m, 3H, ArH), 7.82–8.0(m. 2H, ArH), 12.53(s, 1H, OH). ^{13}C n.m.r.($CDCl_3$) δ 56.2(C–methoxyl), 61.6(C–methoxyl), 95.7(C–6), 104.7(C–3 or C–10), 105.1(C–10 or C–3). 126.1(C–2' and C–6'), 128.9(C–8, C–3' and C–5'), 131.2(C–1' or C–4'), 131.7 (C–4' or C–1'), 157.4(C–5 and C–9), 158.6(C–7), 163.6(C–2), 182.4(C–4). Mass spectrum (260°/70ev) m/e 298(60%), 283(100), 181(15), 153(30), 125(10), 102(10), 77 (10), 69(19). M.p. of the *O*-methyl ether 167–168°C[Lit[7]. 167–168°C].

The third series of fractions gave yellow needles which were recrystallized from benzene to give yellow needles (1.7 g, 21.25% of the crude crystals) of 6,7–*O*, *O*-dimethylbaicalein[7](3), m.p. 157–158°C[Lit[7]. 156–157°C] λ_{max}(MeOH)274, 315 nm, ε 35710, 20933. λ_{max}(meOH + $AlCl_3$) 284, 337 nm, ε 25488, 23396. N.m.r. ($CDCl_3$) δ 3.94(s, 6H, 2xOCH_3), 6.55(s, 1H, ArH), 6.64(s, 1H, ArH), 7.47–7.65(m, 3H, ArH), 7.81–7.97(m, 2H, ArH), 12.69(s, 1H, OH). ^{13}C n.m.r.($CDCl_3$) δ 56.2(C-methoxyl), 60.6(C-methoxyl), 90.5(C–8), 105.2(C–3 or C–10), 106.0(C–10 or C–3), 126.0(C–2' and C–6'), 128.9(C–3' and C–5'), 130.9(C–1' or C–4'), 131.6(C–4' or C–1'), 132.5 (C–6), 152.8(C–5 or C–9), 153.0(C–9 or C–5), 158.7(C–7), 163.7(C–2), 182.3(C–4). Mass spectrum (235°/70ev)m/e 298(100%), 283(17), 269(18), 255(41), 252(16), 181(13), 153(57), 103(18), 102(19), 77(31), 69(71). M.p. of the *O*-methyl ether 168–169°C[Lit[7]. 168–160°C].

Acknowledgements

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บทคัดย่อ

จากการสกัดและตรวจหาโครงสร้างของสารในต้น *Uvaria rufas* Blume. **พบว่ามีฟลาโวนอยด์ 3 สาร คือ** Tectochrysin (1) 7–*O*–methylwogonine (2) **และ** 6,7–*O*,*O*–dimethylbaicalein (3)