

TWO NEW COUMARONOCROMONE DERIVATIVES, OBLONGIN AND
OBLONGINOL FROM THE ROOTS OF *DERRIS OBLONGA* BENTH

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Abstract----- Two new coumaronochromone derivatives, oblongin and oblonginol, have been isolated from the roots of *Derris oblonga*. Their structures have been elucidated by spectroscopic and chemical methods.

Flavonoids, rotenones, stilbenes, coumarins, aurones, pterocarpanes, coumestanes, triterpenes, and glycosides have been identified as constituents of the species of *Derris* (*D.*).¹ These species of genus *Derris* (Leguminosae) are indigenous to Taiwan: *D. trifoliata*, *D. laxiflora* and *D. oblonga*. The chemical studies of the former have been investigated.² The roots of these plants have been reported to possess insecticidal and piscicidal activities.¹ In connection with our interest in flavonoids and in view of the biological activity of their roots, the chemical studies on the roots of *D. laxiflora* were undertaken.³

Now we have investigated the ethanol extract from the roots of *D. oblonga*. Two new coumaronochromone derivatives, oblongin (**1a**) and oblonginol (**2a**), were isolated, and the structural elucidation of oblongin and oblonginol was based on the following evidence.

Oblongin (**1a**), mp 285-288°C, red needles from ethanol, was formulated as C₁₆H₁₀O₆ on the basis of elementary analysis and the mass spectrum (M⁺ at m/z 298) and gave positive Mg-HCl test. Its ir spectrum revealed the presence of hydroxy (3510 cm⁻¹), conjugated carbonyl (1630 cm⁻¹), and aromatic (1600, 1590, and 1510 cm⁻¹) groups. The ultraviolet absorption bands at $\lambda_{\text{max}}^{\text{MeOH}}$ (log ϵ) 257 (4.41), 288 (4.30), and 323 sh (3.90) nm indicated the similar characteristic

absorption bands of isoflavone.^{4,5} The addition of AlCl_3 or $\text{AlCl}_3\text{-HCl}$ caused no bathochromic shift in the uv spectrum. The evidence suggests no chelated phenolic hydroxyl group. The ^1H nmr spectrum (Table 1) of **1a** exhibited signals for methoxy [δ 3.87 (3H, s)], an ABX system of aromatic protons [δ 8.05 (d, $J=8.4$ Hz), 7.02 (d, $J=2.0$ Hz), and 7.00 (dd, $J=8.4$ Hz, 2.0 Hz)], and two singlet aromatic protons [δ 7.42 and 7.16 (each 1H)]. Two phenolic hydroxy groups are discernible at δ 9.45 and 10.86 (each 1H, s). The compound formed a diacetate (**1b**) [mp 224-226°C; $\nu_{\text{cm}^{-1}}$ 1760, 1745, and 1650; δ 2.36 and 2.35 (each 3H, s)] on reaction with Ac_2O and pyridine at room temperature. Comparison of ^1H nmr data between **1a** and 7-hydroxy-2', 4', 5'-trihydroxyisoflavone (**3**),⁶ we can found that the chemical shift and pattern of ABX system of ring A in **3** [δ 8.19 (d, $J=6.9$ Hz), 6.90 (dd, $J=6.9$, 3.0 Hz), and 6.86 (d, $J=3.0$ Hz)] are very similar to **1a**. But **1a** is not an isoflavone derivative due to absent of singlet signal at δ 7.9-8.3 (a characteristic peak of H-2 in isoflavone).⁶⁻⁸ The ^1H nmr spectral data of **1a** is also similar to those of its isomer 8-methoxycoumestrol (**4**)⁹ [mp > 300°C; red needles; $\nu_{\text{cm}^{-1}}$ 1710; δ 7.69 (1H, d, $J=9.0$ Hz), 6.82 (1H, d, $J=2.0$ Hz), 6.81 (1H, dd, $J=9.0$, 2.0 Hz), 3.88 (3H, s), 7.31 (1H, s, H-7), and 7.10 (1H, s, H-10); the compound was also isolated on same source]. **1a** is not a coumestan derivative ascribing to the carbonyl absorption is far lower than 1700 cm^{-1} and different uv absorption data.⁹ The structure of **1a** can be assigned as a derivative of coumaronochromone, and the signal at low field δ 7.42 will be assigned to H-6' because it received the

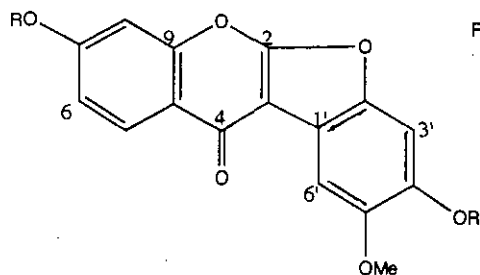
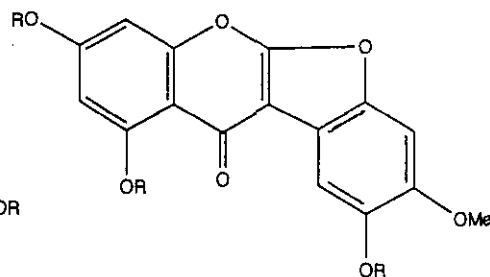
**1a** R=H**b** R=Ac**2a** R=H**b** R=Ac

Table 1 ^1H nmr data (δ -values) for **1a** and **2a** (300 MHz, DMSO- d_6 , TMS as internal standard)

H	1a	2a	H	1a	2a
5	8.05 d (8.4)*		6'	7.42 s	7.31 s
6	7.00 dd (8.4, 2.0)	6.25 br s	-OMe	3.87 s	3.85 s
			-OH	9.45 s	9.50 s
8	7.02 d (2.0)	6.51 br s		10.86 s	10.85 s
3'	7.16 s	7.14 s			12.87 s

* Figures in parenthese are coupling constants in Hz.

Table 2 ^{13}C nmr data (δ -values) for **1a** and **2a** (75 MHz, DMSO- d_6 , TMS as internal standard)

C	1a	2a	C	1a	2a
2	163.7 s	164.0 s	10	102.9 s	102.8 s
3	115.2 s	112.5 s	1'	115.0 s	112.5 s
4	172.4 s	178.1 s	2'	143.0 s	143.3 s
5	126.8 d	162.2 s	3'	98.3 *d	99.2 d
6	113.3 d	97.4 d	4'	145.6 s	146.8 s
7	163.6 s	163.6 s	5'	146.5 s	145.9 s
8	99.2 *d	94.9 d	6'	103.1 d	99.8 d
9	154.5 s	154.6 s	OMe	56.2 q	56.2 q

* Assignment may be interchangeable.

Assignments established by off-resonance and DEPT methods

deshield effect from carbonyl group. The signal of H-6' in lupinalbin A (**5**)¹⁰ expresses at lower field δ 7.81. From the above evidence, **1a** was elucidated as coumaronochromone skeleton with

three oxygenated at C-7, C-4', and C-5'. Finally, the methoxy was assigned to locate at C-5' due to H-6' (δ 7.42) and methoxy group having 23.5 % of NOE. The proposed structure 7, 4'-dihydroxy-5-methoxycoumaronochromone, was also supported by ms fragmentation [m/z (%) 289 (M^+ , 100), 283 ($M^+ - CH_3$, 93), and 255 ($M^+ - CH_3 - CO$, 23) and ^{13}C nmr data (Table 2)]. Oblonginol (**2a**), mp > 300°C, red needles from methanol, had the molecular formula $C_{16}H_{10}O_7$ on the basis of elemental analysis and the mass spectrum (M^+ at m/z 314) and gave positive Mg-HCl test. Its ir spectrum shows the presence of hydroxyl (3400 cm^{-1}), conjugated carbonyl (1660 cm^{-1}) and aromatic (1620, 1605, and 1515 cm^{-1}) groups. The uv absorption bands at λ_{max}^{MeOH} (log ϵ): 257 (4.54), 284 (4.26), 306 (4.10), and 339 (4.19) nm are similar to those of **1a**. The presence of a bathchromic shift (22 nm) with $AlCl_3$, which did not undergo any change with the addition of HCl, showed the presence of chelated OH group with carbonyl. The 1H nmr at δ 9.50, 10.85, and 12.87 for three phenolic hydroxy groups. The latter data is discernible to chelated hydroxy proton. The compound formed a triacetate (**2b**) (Ac_2O/Py ; 60 °C overnight) [mp 255-257°C; $\nu_{cm^{-1}}$ 1770, and 1650; δ 2.34, 2.35, and 2.49 (each 3H, s)]. The presence of a methoxyl group [δ 3.85 (3H, s)], a pair with meta coupling of aromatic protons [δ 6.51 and 6.26 (each 1H, d, $J=2.4$ Hz)], and two singlet aromatic protons (δ 7.31 and 7.14) was revealed from its 1H nmr spectrum. The structure of **2a** was suggested to be a derivative of **1a** by the similarity of its 1H nmr spectral pattern to that of **1a**, except for an extra hydroxyl group which would be assigned to locate at C-5 position due to the presence of a pair of aromatic protons with meta coupling constant and chelated hydroxy proton. The ^{13}C nmr data (Table 2) and ms fragmentation [m/z (%) 314 (M^+ , 100), 299 ($M^+ - CH_3$, 78), and 271 ($M^+ - CH_3 - CO$, 16)] supported the proposed structure. From the above evidence, oblonginol (**2a**) can be assigned as 5,7,5'-trihydroxy-4'-methoxycoumaronochromone based on the following evidence. The NOE was evidently observed between methoxy and H-3' (δ 7.14) (12.8% enhance). According to Dewick's report,¹¹

the natural occurring derivatives of coumaronochromone are scarce.

EXPERIMENTAL

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Ir spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^1H and ^{13}C nmr spectra run on a Bruker AM 300 at 300 MHz in CDCl_3 or $\text{DMSO}-d_6$ solution with tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ -values and coupling constants (J) are given in hertz (Hz). Elms and uv spectra were taken on a JEOL-JMS-100 spectrometer and Hitachi U-3200 spectrophotometer, respectively.

Extraction and Isolation

The roots (6.1 kg) of *Derris oblonga* were crushed into small pieces and dried at 50°C to give 279 g of raw material, which was extracted with 95% ethanol (80 l) three times (8 h, each time) at 60°C . The combined extracts were evaporated *in vacuo* to give a residue (293 g), which was subsequently subjected to partition with ether and H_2O (each 1 l). The upper layer left a black viscous mass (270 g) which was followed to column chromatography on silica gel with hexane- CHCl_3 , CHCl_3 , and CHCl_3 -MeOH gradient solvent system. The 5% MeOH in CHCl_3 eluent was repeatedly chromatographed over Sephadex LH-20 (50% CHCl_3 in MeOH) and silica gel column (CHCl_3 -5% MeOH in CHCl_3), and then oblongin (18 mg) and oblonginol (35 mg) were isolated. Oblongin (**1a**): mp $285\text{--}288^\circ\text{C}$; ir (KBr) ($\nu_{\text{cm}^{-1}}$) 3510, 3120, 1630, 1600, 1590, 1510, 1280, 1095, 1025, 960, 840, 770; Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{O}_8$: C, 64.43; H, 3.38. Found C, 64.56; H, 3.32; ^1H nmr: Table 1; ^{13}C nmr: Table 2. Oblonginol (**2a**): mp $> 300^\circ\text{C}$; $\lambda_{\text{max}}^{\text{MeOH} + \text{AlCl}_3}$ (log ϵ) 235 (4.26), 271 (4.45), 292 (4.39), 308 (4.11), and 378 (4.12) nm. $\lambda_{\text{max}}^{\text{MeOH} + \text{AlCl}_3 + \text{HCl}}$ (log ϵ) 235 (4.26), 271 (4.46), 291 (4.37), 308 (4.08), and 377 (4.13); ir (KBr) ($\nu_{\text{cm}^{-1}}$) 3400, 1660, 1620, 1605, 1515, 1360, 1275, 1205, 1125, 1035, 820, 785; Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{O}_7$: C, 61.15; H, 3.14.

Found C, 61.04; H, 3.20; ^1H nmr : Table 1; ^{13}C nmr: Table 2.

Acetylation of 1a and 2a with Acetic Anhydride and Pyridine

Oblongin (1a) (8 mg, 0.027 mmol) or oblonginol (8 mg, 0.025 mmol) was allowed to react with Ac_2O (0.5 ml, 5.3 mmol) and pyridine (0.5 ml) at room temperature or 60°C overnight, respectively. Usual work-up gave diacetate (1b) (7 mg, 67%) [mp $224\text{--}226^\circ\text{C}$; ir (KBr) ($\nu_{\text{cm}^{-1}}$) 1760, 1745, 1650, 1605, 1505, 1195, 1090, 960, 905, 785; ^1H nmr (CDCl_3) δ 8.40 (1H, d, $J=8.4$ Hz, H-5), 7.44 (1H, d, $J=2.0$ Hz, H-8), 7.28 (1H, dd, $J=8.4, 2.0$ Hz, H-6), 7.74 (1H, s, H-6'), 7.30 (1H, s, H-3'), and 3.94, 2.35, and 2.36 (each 3H, s)] and triacetate (2b) (8 mg, 73 %) [mp $255\text{--}258^\circ\text{C}$; ir (KBr) ($\nu_{\text{cm}^{-1}}$) 1770, 1650, 1610, 1495, 1200, 1110, 1030, 975, 900; ^1H nmr (CDCl_3) δ 7.68 and 7.28 (each 1H, s , H-6', H-3'), 7.38 and 6.95 (each 1H, d, $J=2.0$ Hz, H-8, H-6), and 3.92, 2.34, 2.35, and 2.49 (each 3H, s)], respectively.

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