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

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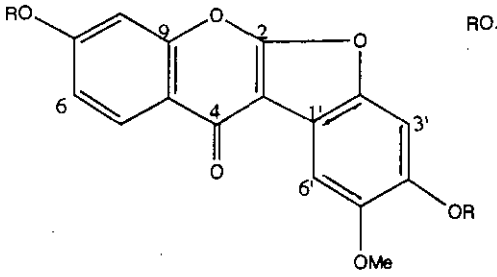
Abstract--------- Two new coumaronochromone derivatives, oblongin and oblonginol, have been isolated from the roots of *Derris oblonga*. Their structures have been elucidated by spectroscopic and chemical methods.

Flavonoids, rotenones, stilbenes, coumarins, aurones, pterocarpans, 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.

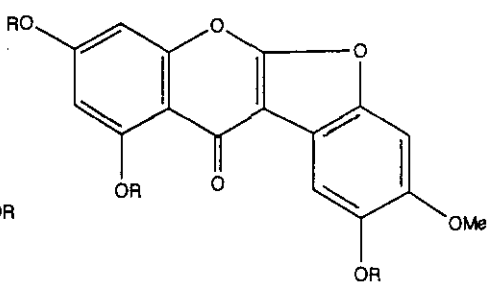
Oblongin (**1a**), mp 285-288°C, red needles from ethanol, was formulated as $C_{16}H_{10}O_6$ on the basis of elementary analysis and the mass spectrum (M^+ at m/z 298) and gave positive Mg-HCl test. Its ir spectrum revealed the presence of hydroxy (3510 cm^{-1}), conjugated carbonyl (1630 cm^{-1}), and aromatic (1600, 1590, and 1510 cm^{-1}) groups. The ultraviolet absorption bands at λ_{max}^{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 $AlCl_3$-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; $\upsilon_{cm^{-1}}$ 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 singnal 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; $\upsilon_{cm^{-1}}$ 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 asceribing 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 ^{1}H 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	6.25 br s	-OMe	3.87 s	3.85 s
	(8.4, 2.0)		-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; υ_{cm}-11770, 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. ^{1}H and ^{13}C nmr spectra run on a Bruker AM 300 at 300 MHz in $CDCl_3$ or 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 285-288°C;ir (KBr) ($\upsilon_{cm^{-1}}$) 3510, 3120, 1630, 1600, 1590, 1510, 1280, 1095, 1025, 960, 840, 770; Anal. Calcd for $C_{16}H_{10}O_6$: C, 64.43; H, 3.38. Found C, 64.56; H, 3.32; ^{1}H nmr: Table 1; ^{13}C nmr: Table 2. Oblonginol (**2a**): mp > 300°C; $\lambda_{max}^{MeOH + AlCl_3}$ (log ε) 235 (4.26), 271 (4.45), 292 (4.39), 308 (4.11), and 378 (4.12)nm. $\lambda_{max}^{MeOH + AlCl_3 + HCl}$ (log ε) 235 (4.26), 271 (4.46), 291 (4.37), 308 (4.08), and 377 (4.13); ir (KBr) ($\upsilon_{cm^{-1}}$) 3400, 1660, 1620, 1605, 1515, 1360, 1275, 1205, 1125, 1035, 820, 785; Anal.Calcd for $C_{16}H_{10}O_7$: C, 61.15; H, 3.14.

Found C, 61.04; H, 3.20; ^{1}H 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 224-226°C; ir (KBr) (υ cm^{-1}) 1760, 1745, 1650, 1605, 1505, 1195, 1090, 960, 905, 785; ^{1}H 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 255-258°C; ir (KBr) (υ cm^{-1}) 1770, 1650, 1610, 1495, 1200, 1110, 1030, 975, 900; ^{1}H 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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