6a,12a-Dehydro- β -toxicarol and Derricarpin, Two New Isoflavonoids, from the Roots of *Derris oblonga* BENTH

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A new dehydrorotenoid, 6a,12a-dehydro- β -toxicarol, and a new pterocarpan, derricarpin, together with a known compound, 6a,12a-dehydro- α -toxicarol, have been isolated from the roots of *Derris oblonga*. Their structures were determined on the basis of spectral and chemical evidence.

Keywords *Derris oblonga*; 6a,12a-dehydro- β -toxicarol; derricarpin; dehydrorotenone; pterocarpan; root

There are only three species of *Derris* (*D.*) indigenous to Taiwan: *D. laxiflora*, *D. oblonga*, and *D. trifoliata*. The chemical constituents of the first¹⁾ and the last²⁾ have been investigated. From other species of *Derris*, many interesting components have been isolated, including flavones, flavonols, chalcones, dihydrochalcones, isoflavones, rotenones, stilbenes, coumarins, auronones, pterocarpanes, coumestans, triterpenes, and glycosides.³⁾

We have now investigated the ethanol extract from the roots of *D. oblonga*, and have isolated two new compounds named 6a,12a-dehydro- β -toxicarol (**1a**) and derricarpin (**2a**), together with a known compound, 6a,12a-dehydro- α -toxicarol (**3**).⁴⁾

6a,12a-Dehydro- β -toxicarol (**1a**) was obtained as yellow needles, mp 195—196 °C. The ultraviolet (UV) spectrum shows absorptions at $\lambda_{\text{max}}^{\text{MeOH}}$ 238 (4.36), 288 (4.49), and 304 (4.41) nm, that is the characteristic absorptions of 6a,12a-dehydrorotenoid.⁵⁾ Elemental analysis gave the molecular formula as $\text{C}_{23}\text{H}_{20}\text{O}_7$, and the mass spectrum (MS) shows fragmentation peaks at 408 (M^+ , 64%), 393 (100%), 363 (13%) and 361 (6%). The infrared (IR) spectrum shows absorptions at 3200—2800 (chelated OH), 1650 (chelated CO), 1620, 1590, and 1505 cm^{-1} (aromatic), and the proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectrum (Table I) shows signals at δ 3.85 and 3.93 (each 3H, s) due to two phenolic methyl ethers. The doublets at δ 5.60 and 6.71 (each 1H, d, $J=10.0$ Hz), and one singlet

at δ 1.45 (6H) are characteristic of the *cis* double bond and *gem*-dimethyl group of 2,2-dimethylchromene.⁶⁾ Signals due to three aromatic protons were discernible at δ 6.27, 6.53 and 8.25 (each 1H, s). The latter signal (δ 8.25) is a characteristic signal for H-1 in dehydrorotenone deshielded by a C-12 carbonyl group.^{4,7)} Two singlets at δ 4.94 (2H) and 13.20 (1H) were assigned to H-6 and chelated phenolic proton, respectively. By comparison of the $^1\text{H-NMR}$ (Table I) and $^{13}\text{C-NMR}$ (Table II) data with those of 6a,12a-dehydro- α -toxicarol (**3**),⁴⁾ compound **1a** can be assigned as an isomer of compound **3**. In compound **3**, the 2,2-dimethylchromene group was fused on C-8 and C-9, and therefore the 2,2-dimethylchromene moiety in compound **1a** must be fused on C-9 and C-10. Further evidence for the fusion of 2,2-dimethylchromene on C-9 and C-10 was obtained as follows. Compound **1a** formed a monoacetate **1b** [with Ac_2O -pyridine at 60 °C, overnight; mp 195—196 °C; $\nu_{\text{max}}^{\text{KBr}}$ 1760 cm^{-1} ; δ CDCl_3 2.49 (3H, s) and 6.47 (1H, d, $J=10.0$ Hz, H-1')]. The result reveals it contains one chelated phenolic hydroxyl group. There was an upfield (0.24 ppm) shift of H-1' in **1b**^{3,8)} compared with **1a**, as well as the presence of a 3.1% nuclear Overhauser effect (NOE) between H-1' and AcO-11 in **1b**.

Derricarpin (**2a**) was obtained as colorless needles, mp 202—204 °C. Elemental analysis gave the molecular formula $\text{C}_{17}\text{H}_{16}\text{O}_6$, and the MS showed peaks at m/z 316 (M^+ , 100%), 301 (48%), 283 (20%), 164 (24%), and 149 (19%).

TABLE I. $^1\text{H-NMR}$ Data^{a)} for **1a**, **2a**, **3**, and **4**^{b)} (300 MHz, CDCl_3)

H	1a	3	2a	4
1	8.25 s	8.26 s	7.03 d (8.7)	7.07 d (9.0)
2			6.65 d (8.7)	6.67 d (9.0)
4	6.53 s	6.51 s		
6	4.94 s	4.95 s	3.68 t (10.9)	3.40—4.40 m
			4.34 dd (5.0, 10.9)	
6a			3.54 m	3.40—4.40 m
7			6.79 s	6.75 s
8	6.27 s	6.25 s		
10			6.49 s	6.45 s
11a			5.40 d (7.0)	5.40 d (7.0)
1'	6.71 d (10.0)	6.62 d (10.0)		
2'	5.60 d (10.0)	5.57 d (10.0)		
4', 5'	1.45 s, 1.45 s	1.46 s, 1.46 s		
OMe	3.85 s, 3.93 s	3.84 s, 3.91 s	3.85 s, 3.95 s	3.92 s
OH	13.20	12.96	5.40 s, 5.60 s	5.49 s

a) Figures in parentheses are coupling constants. b) 60 MHz.

TABLE II. ^{13}C -NMR Data (δ -Value) for **1a**, **2a**, **3**, and **5**

C	1a	3	2a	5
1	110.0 d	110.7 d	133.9 d	132.1 d
2	144.3 s	144.1 s	107.8 d	109.8 d
3	149.6 s	149.2 s	153.8 s	157.1 s
4	100.6 d	101.0 d	146.7 s	104.7 s ^{a)}
4a	146.3 s	146.2 s	147.3 s	156.6 s
6	64.8 t	64.7 t	66.9 t	66.4 t
6a	157.1 s ^{b)}	156.8 s ^{d)}	40.3 d	40.2 d
6b			121.1 d	117.9 d
7			105.4 d	103.7 d ^{a)}
7a	159.4 s ^{b)}	159.2 s ^{d)}		
8	94.8 d	100.5 s	143.2 s	154.2 s
9	162.5 s	162.3 s	141.1 s	148.0 s
10	100.6 s	94.6 d	98.1 d	93.8 d
10a			145.2 s	140.9 s
11	155.9 s ^{b)}	150.8 s ^{d)}		
11a	105.8 s	100.6 s	78.0 d	78.5 d
11b			114.0 s	112.6 s
12	176.2 s	179.2 s		
12a	106.1 s ^{c)}	105.9 s		
12b	109.9 s ^{c)}	109.9 s		
1'	115.5 d	114.3 d		
2'	128.2 d	127.7 d		
3'	78.1 s	78.0 s		
4'	28.3 q	28.2 q		
5'	28.3 q	28.2 q		
OMe	55.9 q	55.9 q	56.3 q	
OMe	56.4 q	56.3 q	56.9 q	
OCH ₂ O				101.3 t

75 MHz in CDCl_3 . Assignments established by off-resonance and DEPT methods. a—d) Assignments may be interchanged.

The UV and IR spectra suggested that it is a phenolic substance devoid of a carbonyl functional group. The ^1H -NMR spectrum (Table I) revealed the presence of the characteristic signals of pterocarpan⁹⁾ at δ 3.54 (1H, m, H-6a), 5.40 (1H, d, $J=7.0$ Hz, H-11a), 3.68 (1H, t, $J=10.9$ Hz, $H_{\text{ax}}-6$), and 4.34 (1H, dd, $J=10.9$, 5.0, $H_{\text{ex}}-6$). Signals due to four aromatic protons were discernible at δ 6.65 and 7.03 (each 1H, d, $J=8.7$ Hz, H-2, H-1), and 6.49 and 6.79 (each 1H, s, H-10, H-7). Derricarpin (**2a**) also contains two phenolic methyl ethers [δ 3.85 and 3.95 (each 3H, s)] and two phenolic hydroxyl groups [δ 5.40 and 5.60 (each 1H, s), disappeared on D_2O addition]. The ^1H -NMR spectrum of **2a** is similar to that of 4-hydroxy-3-methoxy-8,9-methylenedioxypterocarpan (**4**)¹⁰⁾ (Table I). Acetylation of **2a** with acetic anhydride in pyridine at room temperature overnight gave the diacetate **2b** [mp 190—191 °C; $\nu_{\text{max}}^{\text{KBr}}$ 1760 cm^{-1} ; δ CDCl_3 2.28 and 2.33 (each 3H, s)]. The results reveal that it contains two phenolic hydroxyl groups. Based on the above evidence, derricarpin is a 3,4,8,9-tetraoxygenated pterocarpan. Finally, two methoxy groups were assigned to the C-3 and C-8 positions, based on an NOE experiment; in which clear NOE's were observed between H-7 and the methoxy group (δ 3.85) (20.4% enhancement), as well as between H-2 and the methoxy group (δ 3.89) (22.3%, enhancement). The proposed structure was also supported by the ^{13}C -NMR signals [Table II, compare with the data of maackiain (**5**)¹¹⁾].

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 were run on a Bruker

AM 300 at 300 MHz in CDCl_3 solution with tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ -values and coupling constants (J) are given in hertz (Hz). EIMS and UV spectra were taken on a JEOL JMS-100 spectrometer and Hitachi U-3200 spectrophotometer, respectively.

Extraction and Isolation The roots of *Derris oblonga* were crushed into small pieces and dried at 50 °C to give 6.1 kg 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 provided a black viscous mass (270 g), which was subjected to column chromatography on silica gel with hexane- CHCl_3 , CHCl_3 , and CHCl_3 -MeOH gradient solvent systems. The CHCl_3 and 5% MeOH/ CHCl_3 eluates gave 6a,12a-dehydro- α -toxicarol (**3**) (253 mg), and 6a,12a-dehydro- β -toxicarol (**1a**) (12 mg) and derricarpin (**2a**) (18 mg), respectively.

6a,12a-Dehydro- β -toxicarol (1a**)** mp 194—196 °C. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3200—2800, 1650, 1620, 1590, 1505, 1285, 1195, 1150, 1050, 875, 820, 760. ^1H -NMR: Table I. ^{13}C -NMR: Table II. Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_7$: C, 67.64; H, 4.94. Found: C, 67.58; H, 4.99.

Derricarpin (2a**)** mp 202—204 °C. $[\alpha]_{\text{D}}^{20} -144.1^\circ$ ($c=0.5$, CHCl_3). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 300 (3.90). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3480, 1620, 1490, 1210, 1145, 1095, 1010, 880, 855, 775. ^1H -NMR: Table I. ^{13}C -NMR: Table II. Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_6$: C, 64.55; H, 5.10. Found: C, 64.67; H, 5.08.

6a,12a-Dehydro- α -toxicarol (3**)⁴⁾** mp 261—263 °C. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 278 (4.81), 314 (4.39), 331 (4.41). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3400, 1650, 1570, 1510, 1255, 1040, 870, 820, 775. MS m/z (%): 408 (86), 393 (100), 365 (14), 361 (11). ^1H -NMR: Table I. ^{13}C -NMR: Table II.

Acetylation of **1a and **2a** with Acetic Anhydride in Pyridine** Compound **1a** (5 mg) or **2a** (7 mg) was allowed to react with Ac_2O (1.0 ml) in pyridine (1.0 ml) at 60 °C or room temperature overnight, respectively. Usual work-up gave the monoacetate **1b** (5 mg) [mp 195—196 °C. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1760, 1635, 1605, 1500, 1190, 1145, 1040, 830, 790. ^1H -NMR (CDCl_3) δ : 1.47 (6H, s), 2.49, 3.84, 3.92 (each 3H, s), 4.91 (2H, s), 5.75, 6.47 (each 1H, d, $J=10.0$ Hz), 6.51, 6.67, 8.32 (each 1H, s)] or the diacetate **2b** (6 mg) [mp 190—191 °C. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1760, 1620, 1485, 1190, 1100, 1010, 890, 865, 780. ^1H -NMR (CDCl_3) δ : 2.28, 2.33, 3.78, 3.83 (each 3H, s), 3.56 (1H, m, H-6a), 3.67 (1H, t, $J=10.9$ Hz, $H_{\text{ax}}-6$), 4.29 (1H, dd, $J=10.9$, 4.9 Hz, $H_{\text{eq}}-6$), 5.50 (1H, d, $J=7.0$ Hz, H-11a), 6.56, 6.88 (each 1H, s, H-10, H-7), 6.69, 7.35 (each 1H, d, $J=8.7$ Hz, H-2, H-1)], respectively.

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