

## **A Novel 12-Deoxorotenone, 12-Deoxy-12#-acetoyelliptone, from the Roots of *Derris oblonga***

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## A NOVEL 12-DEOXOROTENONE, 12-DEOXO-12 $\alpha$ -ACETOXYELLIPTONE, FROM THE ROOTS OF *DERRIS OBLONGA*

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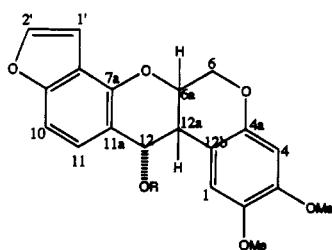
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**ABSTRACT.**—The structure of 12-deoxo-12 $\alpha$ -acetoxyelliptone [**1**], a novel 12-deoxorotenone isolated from *Derris oblonga* (Leguminosae), has been determined on the basis of its spectral and chemical data.

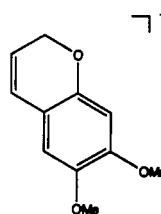
The roots of species of *Derris* (Leguminosae) have been reported to possess insecticidal and piscicidal activities due to interesting compounds including flavonoids, rotenones, pterocarpanes, coumestans, auronones, coumarins, and stilbenes (1–6). Only three species of *Derris* are indigenous to Taiwan. *Derris trifoliata* was investigated and yielded two flavonoid glycosides (7). Chemical studies on the roots of *Derris laxiflora* in our laboratory revealed seven new flavonoids [3'-methoxylupinifolin, laxifolin, isolaxifolin, laxichalcone, derrichalcone, derriflavanone, and epiderriflavanone] together with five known compounds (8–10). We have investigated an EtOH extract of the roots of *Derris oblonga* Benth. and isolated a new compound, 12-deoxo-12 $\alpha$ -acetoxyelliptone [**1**] [a novel 12-

deoxorotenone (11)]. The structural elucidation of this novel compound is based on the following evidence.

12-Deoxo-12 $\alpha$ -acetoxyelliptone [**1**] was obtained as colorless needles, mp 150–152°. Elemental analysis indicated a molecular formula of C<sub>22</sub>H<sub>20</sub>O<sub>7</sub>. Eims fragmentation peaks occurred at  $m/z$  [M]<sup>+</sup> 396 (17%), 337 (4%), 192 (100%) (structure **3** via RDA), 191 (74%), and 177 (39%). Analysis of the ir spectrum suggested acetoxy (1725, 1220, 1090, and 1040 cm<sup>-1</sup>) and aromatic (1600 and 1505 cm<sup>-1</sup>) groups. The <sup>1</sup>H-nmr spectrum of **1** exhibited three singlet Me groups [two MeO and one acetyl group ( $\delta$  3.83, 3.83, and 1.73)] and four aromatic protons [two ortho protons ( $\delta$  7.09 and 7.19), and two singlet protons ( $\delta$  6.40 and 6.67)]. It also exhibited the following signals due



- 1** R=Ac  
**2** R=H



**3**

to protons on carbon atoms bearing oxygen atoms:  $\delta$  4.33 (H-6 $\beta$ ), 4.51 (H-6 $\alpha$ ), 4.98 (H-6a), and 6.42 (H-12). In addition, the characteristic signals of two benzofuranic protons [ $\delta$  6.85 and 7.55] and a triplet proton ( $\delta$  3.67, H-12a) were observed. The  $^1\text{H}$ -nmr spectrum of **1** is similar to that of elliptone (**12**) except for an acetoxy group in place of the ketone group. The structure of **1** was further supported by the  $^{13}\text{C}$ -nmr spectral data. Signals for the acetoxy appeared at  $\delta$  170.1 and 20.8, respectively. The  $^{13}\text{C}$ -nmr spectrum of elliptone (**13**) was also compared. The chemical correlation between 12-deoxo-12 $\alpha$ -acetoxyelliptone [**1**] and elliptone and the configuration of the acetoxy group were achieved as follows.

Hydrolysis occurred as **1** was heated in MeOH under reflux for 4 h without any base to yield alcohol **2** [amorphous;  $\text{ir } \nu$  max (KBr)  $\text{cm}^{-1}$  3450, 1615, 1595, and 1500 (absence of acetoxy absorption bands);  $^1\text{H}$  nmr  $\delta$  5.04 (H-12) and 3.49 (H-12a)]. Compound **2** was oxidized with pcc and molecular sieve (**14**) in dry  $\text{CH}_2\text{Cl}_2$  to give a product which was identical with elliptone (**15**). Finally, the aliphatic acetoxy Me protons in **1**, seen at high field ( $\delta$  1.73), indicated that the acetoxy group must be located at C-12 with  $\alpha$ -axial orientation (**10**). The further proof was that no  $n\text{Oe}$  effect between the acetoxy Me protons and H-12a was observed. From the above-mentioned evidence the structure of **1** as 12-deoxo-12 $\alpha$ -acetoxyelliptone was concluded. This is the first reported isolation of 12-deoxorotenone.

## EXPERIMENTAL

**GENERAL EXPERIMENTAL PROCEDURES.**—Mp's were determined with a Yanagimoto micromelting point apparatus and are uncorrected. Ir spectra were recorded on a Perkin-Elmer 781 spectrophotometer.  $^1\text{H}$ -nmr and  $^{13}\text{C}$ -nmr spectra were run on a Bruker AM 300 spectrometer. Eims and uv spectra were taken on a JEOL-JMS-100 spectrometer and Hitachi U-3200 spectrophotometer, respectively.

**PLANT MATERIAL.**—*D. oblonga* (identified by Mr. Gau Muh-Tsuen) roots were collected at Lanyu

Island, in October 1989. A voucher specimen has been deposited in the herbarium of the Department of Botany of National Taiwan University.

**EXTRACTION AND ISOLATION.**—The roots were crushed into small pieces and dried at  $50^\circ$  to give 6.1 kg of raw material, which was extracted with 95% EtOH (80 liters) three times (8 h each time) at  $60^\circ$ . The combined extracts were evaporated in vacuo to give a residue (293 g), which was subsequently partitioned with  $\text{Et}_2\text{O}$  and  $\text{H}_2\text{O}$  (1:1) (1 liter). The upper layer left a black viscous mass (270 g), which was separated by cc on Si gel with hexane/ $\text{CHCl}_3$ ,  $\text{CHCl}_3$ , and  $\text{CHCl}_3/\text{MeOH}$  gradient solvent systems. The  $\text{CHCl}_3$  eluent gave 12-deoxo-12 $\alpha$ -acetoxyelliptone [**1**] (18 mg) after repeated chromatography on Si gel.

**12-Deoxo-12 $\alpha$ -acetoxyelliptone** [**1**].—Colorless needles from MeOH: mp  $150\text{--}152^\circ$ ;  $[\alpha]_D^{20} -304^\circ$  ( $c=0.5$ ,  $\text{CHCl}_3$ );  $\text{ir } \nu$  max (KBr) 1725, 1600, 1505, 1220, 1190, 1145, 1090, 1040, 980, 940, 855,  $700\text{ cm}^{-1}$ ; uv max (MeOH) ( $\log \epsilon$ ) 238 (4.39), 248 (4.46), 255 (4.45), 283 (4.07), 291 (3.79) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ )  $\delta$  1.73 (3H, s, OAc), 3.67 (1H, t,  $J=5.3$  Hz, H-12a), 3.83 (6H, s, OMe), 4.33 (1H, dd,  $J=11.2, 5.3$  Hz, H-6 $\beta$ ), 4.51 (1H, t,  $J=11.2$ , H-6 $\alpha$ ), 4.98 (1H, m, H-6a), 6.40 (1H, s, H-4), 6.42 (1H, d,  $J=5.3$  Hz, H-12), 6.67 (1H, s, H-1), 6.85 (1H, d,  $J=2.4$  Hz, H-1'), 7.09 (1H, d,  $J=8.5$  Hz, H-10), 7.19 (1H, d,  $J=8.5$  Hz, H-11), 7.55 (1H, d,  $J=2.4$  Hz, H-2');  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ )  $\delta$  20.8 (q,  $\text{COCH}_3$ ), 36.6 (d, C-12a), 55.9 (q, OMe), 56.5 (q, OMe), 64.3 (t, C-6), 69.1 (d, C-6a), 69.1 (d, C-12), 100.2 (d, C-4), 103.9 (d, C-1'), 105.2 (d, C-10), 108.5 (s, C-12b), 111.3 (s, C-8), 111.9 (d, C-1), 117.0 (s, C-11a), 126.8 (d, C-11), 143.5 (s, C-2), 144.3 (d, C-2'), 148.6 (s, C-4a), 149.5 (s, C-3), 156.8 (s, C-7a), 159.9 (s, C-9), 170.1 (s,  $\text{COCH}_3$ ). *Anal.* calcd for  $\text{C}_{22}\text{H}_{20}\text{O}_7$ : C 66.66, H 5.09 (found C 66.75, H 5.01).

**Hydrolysis of 1.**—12-Deoxo-12 $\alpha$ -acetoxyelliptone [**1**] (7 mg) was heated in 5 ml of MeOH for 4 h. After removal of solvent, the reaction mixture gave the alcohol [**2**] (6 mg) [amorphous;  $\text{ir } \nu$  max (KBr) 3450, 1615, 1595, 1500, 1210, 1190, 1070, 1040, 970, 860, 773,  $730\text{ cm}^{-1}$ ; eims  $m/z$  [ $\text{M}-18$ ] $^+$  336 (100%);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ )  $\delta$  7.54 and 6.84 (each 1H, d,  $J=2.0$  Hz, H-2', H-1'), 7.18 and 7.12 (each 1H, d,  $J=8.4$  Hz, H-10, H-11), 6.72 and 6.48 (each 1H, s, H-1, H-4), 5.04 (1H, d,  $J=4.8$  Hz, H-12), 4.94 (1H, m, H-6a), 4.66 (1H, t,  $J=11.4$  Hz, H-6 $\alpha$ ), 4.28 (1H, dd,  $J=5.3, 11.4$  Hz, H-6 $\beta$ ), 3.86 and 3.84 (each 3H, s, -OMe), 3.48 (1H, t,  $J=4.8$  Hz, H-12 $\alpha$ ).

**Oxidation of 1 with pyridium chlorochromate in  $\text{CH}_2\text{Cl}_2$ .**—12-Deoxo-12 $\alpha$ -acetoxyelliptone [**1**] (5 mg) was dissolved in 10 ml  $\text{CH}_2\text{Cl}_2$ , and pyridinium chlorochromate (50 mg) and powdered molecular sieve 4 A (E. Merck, 100 mg) were added. The

reaction mixture was stirred under room temperature for 2 h, and 60 ml of Et<sub>2</sub>O was poured into the reaction mixture. The suspension solution was filtered with celite, and the filtrate gave elliptone (4 mg, mp 177–178°).

#### ACKNOWLEDGMENTS

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