

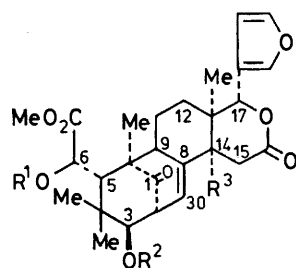
## Tetranortriterpenoids and Related Compounds. Part 24.<sup>1</sup> The Interrelation of Swietenine and Swietenolide, the Major Tetranortriterpenoids from the Seeds of *Swietenia macrophylla* (Meliaceae)

By Joseph D. Connolly\* and Cecilia Labbé, Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

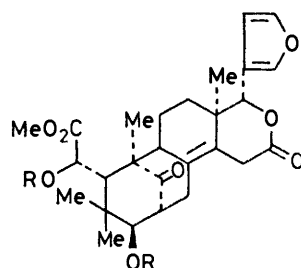
Swietenine (1) has been converted into swietenolide diacetate (10) via 14 $\alpha$ -hydroxyswietenine (5) and the diene (8).

The structures of swietenine (1)<sup>2</sup> and swietenolide (2)<sup>3,4</sup> the major constituents of the seeds of *Swietenia macrophylla*, have been known for more than a decade. They are both bicyclo-nonanolides but differ in the position of the residual double bond. During the course of the structural work on swietenine<sup>2</sup> extensive efforts were

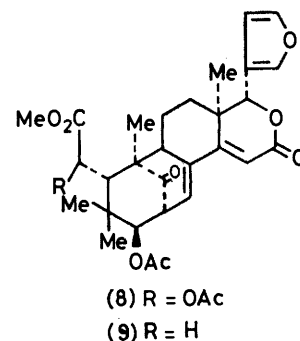
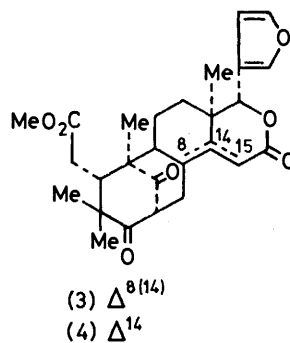
spectroscopic properties compared well with those of angustidienolide (9)<sup>7</sup> [ $\lambda_{\max}$  283 nm;  $\delta_{\text{H}}$  6.23 (s, H-15) and 6.31 (dd,  $J$  5.5, 3.5 Hz, H-30)]. Hydrogenation of the diene (8) over 10% Pd-C in ethyl acetate resulted in 1,4-addition to the *cisoid* diene system with formation of swietenolide diacetate (10)<sup>3</sup> identical (<sup>1</sup>H n.m.r., t.l.c., m.p., m.s.), with an authentic specimen. Thus the interrelation of swietenine and swietenolide was achieved. A second product of the hydrogenation was the  $\Delta^{14}$ -derivative (11) [ $\delta_{\text{H}}$  5.85 (s, H-15)]. Hydrogenation of



- (1)  $R^1=R^3=H$ ;  $R^2$ = tiglate  
 (5)  $R^1=H$ ;  $R^2$ = tiglate;  $R^3=OH$   
 (6)  $R^1=R^2=H$ ;  $R^3=OH$   
 (7)  $R^1=R^2=Ac$ ;  $R^3=OH$



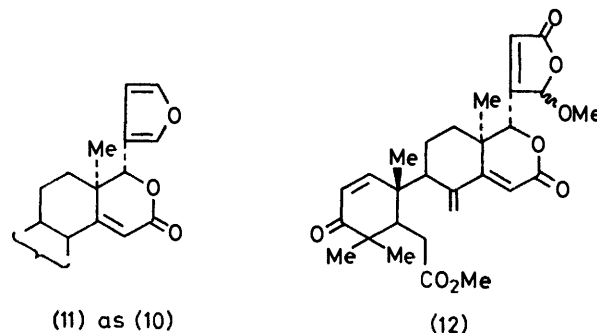
- (2)  $R=H$   
 (10)  $R=Ac$



made to oxidise or migrate the  $\Delta^{8(30)}$  double bond but without success. The singular lack of reactivity of this double bond thwarted previous efforts to interrelate swietenine (1) and swietenolide (2). We now report a simple conversion of swietenine into swietenolide diacetate (10).

### RESULTS AND DISCUSSION

Selenium dioxide oxidation of mexicanolide (3) or carapin (4) has been reported<sup>5</sup> to result in the introduction of a *t*-hydroxy-group at C-8. On treatment with selenium dioxide swietenine (1) was smoothly converted into hydroxyswietenine (5). The new tertiary hydroxy-group is placed at C-14 rather than C-9, since hydroxyswietenine was transformed into the *cisoid* diene-lactone (8) on dehydration (see below) and is assigned the  $\alpha$  configuration by inspection of models, since this can better account for the observed downfield shift (0.25 p.p.m.) of H-30 in the <sup>1</sup>H n.m.r. spectrum of (5) relative to swietenine (1). Kupchan cleavage<sup>6</sup> ( $OsO_4-NaIO_4-HCO_3^-$ ) of the tiglate ester afforded the triol (6) which was converted into the diacetate (7) in the usual manner. Reaction of (7) with thionyl chloride in pyridine at 0 °C yielded the diene (8) [ $\lambda_{\max}$  281 nm;  $\delta_{\text{H}}$  6.19 (s, H-15), 6.26 (dd,  $J$  6, 3 Hz, H-30)] whose



angustidienolide<sup>7</sup> and the deoxyandirobin derivative (12)<sup>8</sup> has been reported to give similar results.

### EXPERIMENTAL

For general experimental details see reference 8.

*Allylic Oxidation of Swietenine.*—Swietenine (1) (650 mg) was refluxed in aqueous acetic acid (10 ml) with selenium dioxide (280 mg) for 1 h. The solution was allowed to cool to room temperature and then poured into an excess of water. Extraction with chloroform, and removal of the solvent *in vacuo*, afforded a gum which was chromatographed over Grade IV alumina in light petroleum. Elu-

tion with ether gave the crystalline 14-hydroxyswietenine (5) (200 mg), m.p. 255–258 °C (from ether–methanol);  $m/e$  584;  $\delta_H$  0.89, 0.94, 1.09 and 1.44 (C-Me), 3.73 (3 H, CO<sub>2</sub>Me), 3.50 (dd,  $J$  9, 6 Hz, H-2), 3.47 (br s, H-5), 4.54 (br s, H-6), 4.65 (d,  $J$  9 Hz, H-3), 5.52 (s, H-17), 5.57 (d,  $J$  6 Hz, H-30), 2.90 and 2.25 (OH, exchangeable with D<sub>2</sub>O), 1.68 and 1.76 (6 H, m, tiglate Me), 6.83 (m, tiglate vinyl-H), and 7.59, 7.44 and 6.42 (furan) (Found:  $m/e$  584.262 30. C<sub>32</sub>H<sub>40</sub>O<sub>10</sub> requires  $M$ , 584.262 43).

**Diacetate (7).**—14-Hydroxyswietenine (5) (147 mg) and osmium tetroxide (65 mg) were kept in ether (1 ml) and pyridine (1 ml) in the dark for 16 h. A saturated solution of sodium metabisulphite in water (10 ml) was added and the mixture stirred for 2 h. The resulting mixture of tetrols was dissolved in methanol and treated with an excess of aqueous sodium metaperiodate solution overnight. The crude pyruvate ester, obtained by dilution with water and extraction into chloroform, was hydrolysed with aqueous sodium hydrogencarbonate solution at room temperature for 5 min. The reaction product was acetylated with acetic anhydride in pyridine for 4 h over a steam-bath. Analytical t.l.c. of the crude product indicated the presence of a main product which was identified as the 3,6-diacetate (7) by a study of its <sup>1</sup>H n.m.r. spectrum;  $\delta_H$  0.80, 1.00, 1.05, and 1.15 (C-Me), 2.04 and 2.17 (acetates), 3.72 (CO<sub>2</sub>Me), 3.50 (dd,  $J$  9, 6 Hz, H-2), 5.55 (s, H-6), 4.64 (d,  $J$  9 Hz, H-3), 5.61 (s, H-17), 5.60 (d,  $J$  6 Hz, H-30), and 6.47, 7.43 and 7.73 (furan) (Found:  $m/e$  586.241 28. C<sub>31</sub>H<sub>38</sub>O<sub>11</sub> requires 586.241 38).

**Diene (8).**—The diacetate (7) in pyridine was treated with thionyl chloride (10 drops) at 0 °C for 5 min. Addition of water and extraction with chloroform afforded a crude product which was purified by column chromatography over Grade IV alumina in light petroleum–ether (9 : 1). The fractions eluted with ether afforded the non-crystalline diene (8) (60 mg);  $m/e$  568;  $\delta_H$  0.92, 1.04, 1.07, and 1.20 (C-Me), 2.16 and 2.18 (OAc), 3.74 (3 H, s, CO<sub>2</sub>Me), 3.46 (s, H-5), 3.64 (obscured m, H-2), 4.75 (d,  $J$  9 Hz, H-3), 5.13

(s, H-17), 5.40 (br s, H-6), 6.26 (dd,  $J$  6 3 Hz, H-30), and 7.53, 7.43 and 6.48 (furan) (Found:  $m/e$  568.230 78. C<sub>31</sub>H<sub>38</sub>O<sub>10</sub> requires  $M$ , 568.230 82).

**Catalytic Hydrogenation of the Diene.**—The diene (8) (47 mg) was dissolved in ethyl acetate (10 ml) and stirred with 10% Pd–C (30 mg) in a hydrogen atmosphere. The reaction was stopped after 2 min when 3 ml of hydrogen had been consumed. Preparative t.l.c. of the product afforded swietenolide diacetate (10) (34.2 mg), m.p. 220–225 °C (from ether–light petroleum) (lit.<sup>4</sup> 225–228 °C);  $m/e$  570;  $\delta_H$  0.86, 1.04, 1.07, and 1.16 (C-Me), 2.16 (6 H, OAc), 3.74 (3 H, s, CO<sub>2</sub>Me), 3.41 (br s, H-5), 3.15 (m, H-2), 4.87 (d,  $J$  10 Hz, H-3), 5.60 (s, H-17), 5.47 (s, H-6), and 6.46, 7.42 and 7.52 (furan). Extraction of the minor band in the plate afforded the non-crystalline 3,6-diacetoxylidihydrocarapin (11) (12.9 mg);  $m/e$  570;  $\delta_H$  0.96, 0.98, 1.16, and 1.20 (C-Me), 2.09 and 2.14 (OAc), 3.73 (3 H, s, CO<sub>2</sub>Me), 2.94 (br s, H-5), 3.17 (m, H-2), 5.10 (s, H-17), 5.58 (s, H-6), 5.45 (d,  $J$  10 Hz, H-3), 5.85 (s, H-15), 7.43 (2 H, m), and 6.4 (furan) (Found:  $m/e$  570.246 32. C<sub>31</sub>H<sub>38</sub>O<sub>10</sub> requires  $M$ , 570.246 47).

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