

MELIACEAE

LIMONOIDs FROM *SWIETENIA HUMILIS*

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Abstract—Two new limonoids have been isolated from the seed of *Swietenia humilis*. They have been identified as methyl 2-hydroxy-3-isobutyryloxy-meliac-8(30)-enate (present as a mixture with the 3-tiglate) and its 8(30) oxide.

THE GENUS *Swietenia* contains three species, *S. mahogani* (L.) Jacq., *S. macrophylla* King, and *S. humilis* Zuccarini. These are the true Central American mahoganies. It has been shown that the timber of *S. mahogani* and *S. macrophylla* contains cycloecalenol but no limonoids;^{1,2} the seeds of *S. macrophylla* yield swietenine³ (Ia) and swietenolide⁴ (Ib); those of *S. mahogani* yield a complex mixture containing mainly methyl angolensate (II) and methyl 6-hydroxy angolensate.⁵

By the courtesy of Dr. B. T. Styles of the Commonwealth Forestry Institute, we have now been able to examine specimens of *S. humilis* collected by Dr. G. Pennington in Mexico. The timber gave no limonoids; the seed gave two main constituents which were isolated by chromatography on silica gel, though neither was obtained crystalline. One was a mixture, showing a mass peak at 556, with a less intense companion at 568. This suggested a mixture of an isobutyrate and a tiglate. Such mixtures are common in Meliaceae,^{6,7} and are very difficult to separate. The NMR spectrum showed two peaks, one at 84.9, one at 84.88. This is characteristic of H-3 in similar mixtures, the tiglate giving a peak that is slightly further upfield. The characteristic resonance of the tiglate vinyl proton could be seen near 87, it integrated for approximately half a proton. Otherwise, the NMR spectrum was very similar to that of methyl 3 β -isobutyryloxy-meliac-8(30)-enate (Ic),⁷ except that the proton ascribed to H-3 was a singlet instead of a doublet, and that ascribed to H-30 was one multiplet, instead of a pair of multiplets. This suggested that C-2 was fully substituted, and from this and the mass spectral molecular weight, which corresponds to one oxygen atom more than there are in (Ic), we consider the mixture to contain the 3-tiglate and 3-isobutyrate of methyl 2,3-dihydroxy meliac-8(30)-enate (Id). The acetate of the corresponding 8:30-dihydrocompound is already known.⁸

¹ L. AMORÓS-MARÍN, W. I. TORRES and C. F. ASENJO, *J. Org. Chem.* **24**, 411 (1959).

² D. A. H. TAYLOR, unpublished work.

³ J. D. CONNOLLY, R. HENDERSON, R. McCRINDLE, K. H. OVERTON and N. S. BHACCA, *J. Chem. Soc.* 6935 (1965).

⁴ J. D. CONNOLLY, R. McCRINDLE, K. H. OVERTON and W. D. C. WARNOCK, *Tetrahedron Letters* 2937 (1965).

⁵ D. A. H. TAYLOR, *Chem. Commun.* 58 (1969).

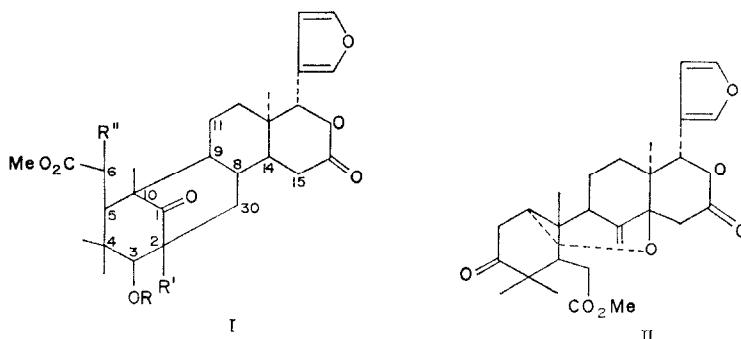
⁶ D. A. H. TAYLOR, *J. Chem. Soc. (C)* 2439 (1969).

⁷ E. K. ADESOGAN and D. A. H. TAYLOR, *J. Chem. Soc. (C)* 1974 (1968).

⁸ D. A. H. TAYLOR, *J. Chem. Soc. (C)* 336 (1970).

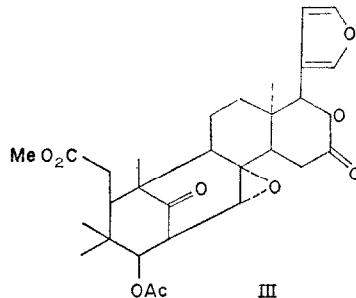
The second compound appeared to be pure, and had a mass spectral molecular weight of 572; 16 more than the isobutyrate (Id). The NMR spectrum was very similar to that of xylocarpin (III),⁹ except that the peaks assigned to H-3 and H-30 were both singlets instead of doublets; and that xylocarpin is an acetate. We considered therefore that this compound was the 8-30 oxide corresponding to (Id). This was confirmed by chromous chloride reduction which gave the isobutyrate (Id); identical with the natural sample in NMR spectrum, except for the absence of the peaks assigned to the tiglate as described above.

Swietenia humilis seed therefore contains a mixture of (Id) and its 8(30) oxide; a mixture of the two corresponding 2-deoxy acetates occurs in *Xylocarpus granatum* (also Meliaceae).⁹



- (a) R = tigloyl, R' = H, R'' = OH, Δ 8-30
- (b) R = R' = H, R'' = OH, Δ 8-14
- (c) R = COPr, R' = R'' = H, Δ 8-30
- (d) R' = OH, R'' = H, Δ 8-30

R = tigloyl or COPr



EXPERIMENTAL

Swietenia humilis seed (8 g) was ground and extracted with refluxing light petrol (b.p. 60–80°). The concentrated extract showed two main spots on TLC. Chromatography on a column of silica gel and elution with ether–light petrol mixtures gave two fractions corresponding to the above main spots. Neither crystallized. The first (50 mg) showed M^+ 556 (satellite 568), and NMR absorptions at 87.81, 7.43 (α -furan protons); 6.48 (β -furan), 5.66 (H-17, satellite at 5.63), 5.38 ($W/2 = 4$ c/s) (H-30), 4.90 (H-3, satellite at 4.91), 3.71 (carbomethoxy) and tertiary methyl groups at 46, 48, 75 and 66 c/s from tetramethyl silane at 60 Mc/sec (calc.¹⁰ 45, 48, 76, 66 c/s).

The second compound (35 mg) showed M^+ 572, and NMR absorptions at δ 7.50, 7.45 (α -furan), 6.45 (β -furan), 5.21 (H-17), 5.11 (H-3), 3.73 (carbomethoxy), 3.55 (H-30) and tertiary methyl groups at 46, 47, 69 and 60 c/s from tetramethyl silane at 60 Mc/sec (calc.¹⁰ 45, 46, 70, 61 c/s). Chromous chloride reduction of this compound (30 mg) as described for xylocarpin,⁹ gave the isobutyrate (Id).

⁹ D. A. OKORIE and D. A. H. TAYLOR, *J. Chem. Soc. (c)* 211 (1970).

¹⁰ N. S. OHOCHUKU and D. A. H. TAYLOR, *J. Chem. Soc. (c)* 864 (1969).