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LIMONOID EXTRACTIVES FROM *SWIETENIA MACROPHYLLA*

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Key Word Index—*Swietenia macrophylla*; Meliaceae; limonoids; swietenine acetate oxide.

Abstract—Re-examination of the seed of *Swietenia macrophylla* has given the known swietenine and swietenolide, together with swietenine acetate, swietenolide tiglate, swietenolide di-acetate, and a new compound which was identified as 8,30 epoxy swietenine acetate.

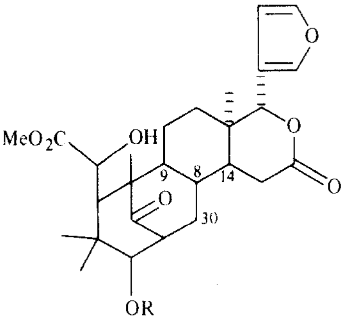
INTRODUCTION

The seed of *Swietenia macrophylla* [1] readily yields swietenine (**1**) [2] and swietenolide (**2**) [3], which were the first of the bicyclononanolide group of limonoids to be discovered. It seemed probable that re-investigation would yield further compounds which might be of interest. This investigation has now been made.

RESULTS AND DISCUSSION

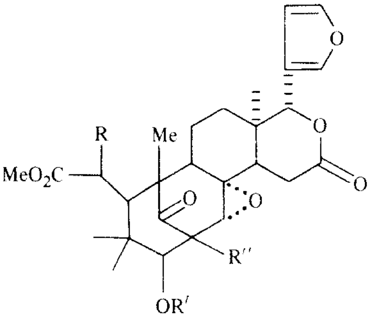
Extraction of the minced seed gave an amorphous solid which was chromatographed on silica. Two main fractions were obtained, crystalline swietenine and non-crystalline swietenolide, identified as the known crystalline diacetate. The mother liquors gave four further pure substances. The first, which remained amorphous, was identical with synthetic swietenine acetate; the second was swietenolide diacetate; the third was swietenolide tiglate which has previously been obtained from *Khaya ivorensis* [4]. The fourth substance was obtained from a silica column as an impure crystalline solid. HPLC then gave a pure substance which remained amorphous. The NMR spectra were similar to those of swietenine, except that the signals for H-30, C-30 and C-8 were missing. In their place, the ^{13}C NMR spectrum contained two signals, 60.3(*s*), and 63.2(*d*), strongly suggesting a three-membered oxide ring. This was confirmed by double irradiation in the ^{1}H NMR spectrum, which revealed H-30 (δ3, *d*, $J = 2.6$ Hz).

These values are very similar to those recorded for xylocarpin (**3**) (δ60.2*s*, 63.3*d*, 3.3*d*, $J = 3$ Hz), and show that the substance is the 8,30α oxide of swietenine acetate (**4**). This is the third 8,30 oxide to be discovered, the other two being the 6-deoxy-3-acetate, xylocarpin [5] from *Xylocarpus granatum* and the 6-deoxy-2-hydroxy-3-butyrate, humilin B (**5**), from *Swietenia humilis* [6]. It is probable that similar oxides are intermediates in the biosynthesis of phragmalin type limonoids [7], production by laboratory oxidation of the appropriate unsaturated compounds has not yet been successful.



1 $\Delta^{8,30}$ R = tigloyl

2 $\Delta^{8,14}$ R = H



3 R = H, R' = Ac, R'' = H

4 R = OAc, R' = tigloyl, R'' = H

5 R = H, R' = isobutyryl, R'' = OH

EXPERIMENTAL

S. macrophylla seed (from British Honduras) (450 g) was minced and percolated with refluxing hexane. The solid which separated (34 g) was filtered off. This (5 g) was separated on a silica column yielding swietenine, swietenolide, swietenine acetate, swietenolide tiglate and swietenolide diacetate (all identical with authentic samples) and an impure solid which after purification by

HPLC gave an amorphous gum. This was identified as 8,30 epoxy swietenine acetate. ^{1}H NMR: δ7.39 (2H, *m*, H-21, 23), 6.3 (*m*, H-22), 5.37 (*s*, H-6), 4.97 (*s*, H-17), 4.77 (*d*, $J = 10$, H-3), 3.70 (3H, *s*, CO_2Me), 3.62 (*q*, $J = 10, 2.6$, H-2), 3.1 (*d*, $J = 2.6$, H-30), 2.07 (3H, *s*, Ac), 1.85 (6H, *m*, tiglate Me), 1.20, 1.02, 1.02, 0.92 (4 × C-Me); ^{13}C NMR: δ213.0*s*, 171.2*s*, 171.0*s*, 169.5*s*, 166.7*s*, 143.1*d*, 140.9*d*, 140.0*d*, 127.7*s*, 120.3*s*, 109.8*d*, 79.5*d*, 78.5*d*, 72.2*d*, 63.3*d*, 60.2*s*, 55.7*d*, 53.2*q*, 48.9*d*, 48.5*s*, 45.3*d*, 45.3*d*, 40.0*s*, 36.1*s*, 34.0*t*, 33.3*t*, 26.5*q*, 23.3*q*, 23.0*q*, 20.9*q*, 20.8*q*, 19.9*t*, 19.7*q*, 15.9*q*.

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ISOLATION AND STRUCTURE OF A QUASSINOID FROM *AILANTHUS GLANDULOSA*[*]

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Key Word Index—*Ailanthus glandulosa*; Simarubaceae; 2-dihydroailanthone; quassinoid.

Abstract—A new quassinoid, 2-dihydroailanthone, has been isolated from the bark of *Ailanthus glandulosa*. Its structure was established on the basis of spectroscopic data and chemical evidence.

Previous studies on the constituents of *Ailanthus glandulosa* Desf. (syn. *Ailanthus altissima* Swingle) bark resulted in isolation of the bitter principles ailanthone **1a** ($C_{20}H_{24}O_7$) [1, 2][||], amarolide ($C_{20}H_{28}O_6$) and acetylamarolide ($C_{22}H_{30}O_7$) [3, 4]. These compounds possess antiamoebic properties, although their rather high toxicity does not favour applications in therapy [5, 6]. On the basis of the reported biological activity and anticancer activities which are generally connected with the bitter principles isolated from the Simaroubaceae [7], we decided to further investigate the alcoholic extract of the plant bark. The search for minor constituents led to the isolation of a new member of the family, for which we have demonstrated the structure **1b**.

Elemental and mass spectral analyses (M^+ at m/z 378) indicated a $C_{20}H_{26}O_7$ molecular formula. By comparison with the previously described compounds from *Ailanthus glandulosa* these data were suggestive of a dihydroailanthone structure. Further confirmation for this structure was provided by IR [ν_{max} cm^{-1}: 3300–3500 (OH), 1715 (C=O)], ^{1}H NMR[¶] (Table 1) and ^{13}C NMR spectra analyses (Table 2).

The lack of conjugation indicated by the UV spectrum (λ_{max} 205 nm) and the appearance of a signal corresponding to the extra oxymethine proton at δ4.59, by comparison to the ^{1}H NMR spectrum of **1a**, suggested the formulation of the structure **1b**. On this basis, the conclusion that the new compound was a 2-dihydroailanthone seems to be straightforward, and the stereochemistry of the new alcoholic function was demonstrated by the coupling constant between the protons on C-1 and C-2 ($J = 8$ Hz).

Unexpectedly, compound **1b** on treatment with acetic anhydride in pyridine gave a triacetate (**2**) [(mp 234–236°, EtOH); $[M - 18]^+$ at m/z 486], whose ^{1}H NMR spectrum clearly demonstrated that the hemiketal function was resistant to acetylation. In order to prove the proposed structure we decided to synthesize **1b** using ailanthone **1a** as starting material since the transform-

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[*] Preliminary results were presented at the International Symposium on Natural Products, Tenerife, Spain, September 1980.

[||] The stereochemistry at C-12 is here displayed according to our original proposal [1] and as recently confirmed by X-ray crystallography [10].

[¶] The 100 MHz proton spectrum was not satisfactorily resolved to enable us to draw a definite conclusion.