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MAHOGANIN[1]

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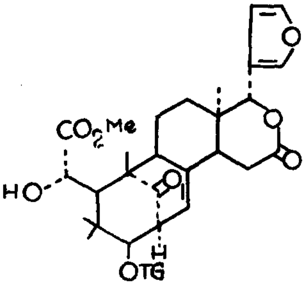
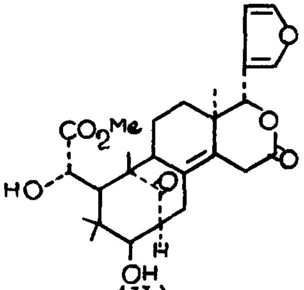
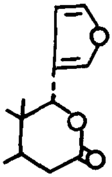
Swietenia macrophylla, one of the two species of the exotic genus Swietenia (Fam. Meliaceae) available in India has been found to yield swietenine[2,3] (I) and swietenolide[4] (II) as major products. From taxonomic considerations, we were interested to examine the seeds of the other species, S. mahagoni from which a bitter constituent[5] and a non-bitter constituent named, mahoganin[6] were reported. We now report the structure of mahoganin.



(I)



(II)



(VI)

Mahoganin, $C_{27}H_{34}O_8$*, $[\alpha]_D^{24^\circ}$ -72° ($CHCl_3$), (M^+ 486), (one OMe) showed uv. max at 207 (logϵ 3.89) and 288 mμ (logϵ 1.88) showing the presence of a β-substituted furan and a saturated cyclic ketone in it. Its ir. spectrum (KBr phase) showed bands at 3570 (hydroxyl), 1505, 875 cm^{-1} (β-substituted furan), and in CCl_4 solution at 1721 (δ-lactone, cyclic ketone), 1739-48 cm^{-1} (hump, ester carbonyl).

Mahoganin furnished a 2:4 DNPH derivative, $C_{33}H_{38}N_4O_{11}$, m.p.260°, a monoxime, $C_{27}H_{35}NO_8$, m.p. 232-4° and a monoacetate, $C_{29}H_{36}O_9$, m.p. 200°, $[\alpha]_D$ -81.2° ($CHCl_3$). On

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*Satisfactory analyses of compounds reported with mol. formulae have been obtained.

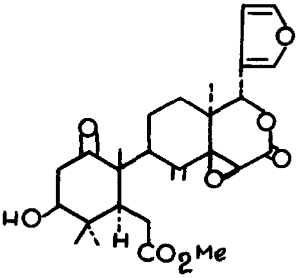
base hydrolysis mahoganin furnished mahoganic acid, $C_{20}H_{32}O_8$ (III), m.p. 246-47°, $[\alpha]_D$ -74.7° ($CHCl_3$). This shows that the methoxyl group in mahoganin is a part of carbomethoxy function. Mahoganin could be hydrogenolysed in Pd/C (acetic acid) to an octahydro acid, $C_{27}H_{42}O_8$ (IV), m.p.102-4° whose methyl ester, $C_{28}H_{44}O_8$, m.p.170°, (two OMe), showed the absence of furan bands in its ir. This shows that mahoganin has the grouping (VI) as is present in many furano-lactones of Meliaceae and Rutaceae.

The following functional hydrogens are readily discernible from the NMR spectrum (60 MHz in $CDCl_3$) of mahoganin: Four quarternary C-methyl (δ 0.87, 0.96, 1.04 and 1.19, 3H each, singlets); one epoxidic proton (δ 3.62), one carbomethoxy group (δ 3.72; 3H singlet), two vinyl protons (δ 4.90, 5.23; 1H each broad singlets), one furfurylic proton (δ 5.69, 1H singlet), one β-furan proton (δ 6.38, 1H broad singlet), two α-furan protons (δ 7.42; 2H, a diffuse multiplet).

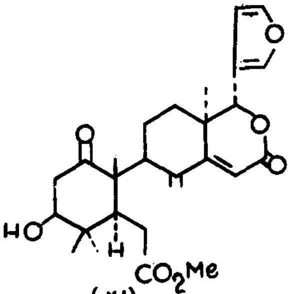
The C_{27} formula, similarity of the functional groups of the compound with those of swietenine, swietenolide, methyl angolensate[7] (VII) and andirobin[8] (VIII) obtained from taxonomically related plants suggest that mahoganin is structurally related to these tetra nor-triterpenoids. The NMR signals at δ 5.69, 6.38 and 7.42 together with the signal at δ 3.62 are consistent with the presence of an $\alpha\beta$-epoxy-δ-furfuryl-δ-lactone system. On Sarret oxidation mahoganin furnished a diketo compound $C_{27}H_{32}O_8$ (IX), m.p.220°, (M^+ 484), $[\alpha]_D$ -37.7° ($CHCl_3$). The compound (IX) was positive to ferric and Zimmermann colour reactions, to which the parent compound was inert. These establish the presence of a keto-methylene group in mahoganin, as evidenced by the NMR signal at δ 2.2. So the hydroxyl and the ketonic groups in mahoganin are at position 3 and 1 respectively. The presence of the broad multiplets for α-hydrogen of the 3β-hydroxyl group[9] at δ 3.2 in the NMR spectrum of mahoganin and mahoganic acid also support these conclusions.

The isolation of a biphenyl derivative (λ_{max} 257.5 mμ) by the zinc dust distillation of the lithium aluminium hydride reduction product of mahoganin establishes the relationship between the ring A and ring C and is in conformity with a B-ring cleaved[10] triterpenoid skeleton in mahoganin. The isolation of formaldehyde (identified as its DNPH derivative by TLC) during ozonolysis of mahoganin confirms the presence of a terminal methylene group in mahoganin. The above evidence together with biogenetic considerations lead to assignment of $\gamma\delta$-location of the vinyl bond with respect to the $\alpha\beta$ epoxy-lactone group.

The ir. data of mahoganic acid show that the ketonic group (ν_{max}^{KBr} 1680 cm^{-1}) is hydrogen bonded. Both mahoganin and mahoganic acid showed a negative cotton effect which means that no drastic change in the conformation of ring A has occurred during base hydrolysis. Consequently the methylene carboxylic acid group located β at C_5 must be in axial position. The negative cotton effect of mahoganin is in conformity with the position of the ketone at 1 position. All these data together with the biogenetic and taxonomic considerations lead to the formulation of mahoganin as (X), the stereochemistry of the compound being assumed on the basis of other furanolactones of the genus Swietenia.



(X)



(XI)

It is obvious that deoxymahoganin (XI) may be obtained by reduction of (X) or as an incomplete epoxidation product[11] during the biosynthesis of (X). The occurrence of the compounds (I), (II) and (X) in the same genus Swietenia gives further credence to the idea of formation of bicyclonoanolides through hypothetical precursor like [2] (XI) as suggested by Connolly et al.

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