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Melianone from *Swietenia mahagoni* Jacq.[1]

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In connection with our studies on *Swietenia mahagoni* Jacq. from which mahoganin[2], 6-hydroxymethyl-angolensate[3], 7-deacetyl-7-oxogedunin[4] and cyclomahogenol[5](16β-hydroxy-24-methylene cycloartenol) have been reported, we now report the isolation of another triterpenoid which has eventually been identified as melianone (I).

The chromatographic fraction (Benzene-chloroform 1 : 1) of the petroleum ether 60-80° extract of the dried leaves of *S. mahagoni* furnished a crystalline compound (I) (methanol) m.p. 225-6° $(\alpha)_D$-48° ($CHCl_3$). The compound was found homogeneous by the thin layer chromatography using ethyl acetate-chloroform (1 : 3) mixture as the developing solvent; (R_f 0.4). From analytical and mass spectral data the molecular formula $C_{30}H_{46}O_4$(M^+ 470) was assigned to the compound. The compound was positive to Liebermann-Burchardt and Ziemmermann colour reactions showing it probably to be a triterpene having a keto group at 3-position.

The uv. spectrum of the compound showed absorption max. at 280mμ(log ϵ 1.79) characteristic for an isolated ketonic system.

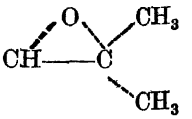
The i.r. spectrum of the compound showed bands at 3440 (hydroxyl function), 1720 (carbonyl group), 1385 (C-methyl and gem-dimethyl) and 1650 (sh) and 885 cm^{-1} (double bond).

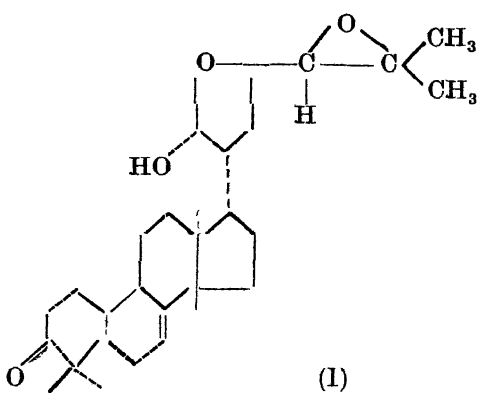
The N.M.R. spectrum of the compound showed bands for 5 C-methyl groups at δ 0.87 (3 protons), 1.08 (9 protons) and 1.15 (3 protons) and 6 protons of deshielded gemdimethyl group at δ 1.33. One hydroxyl proton at δ 3.94; one vinylic proton and one proton adjacent to the hydroxyl group at δ 5.35. One proton signal adjacent to an oxide linkage at δ 2.87.

The compound (I) on acetylation with acetic anhydride and pyridine (at room temperature or heating at 100°) furnished a semisolid acetyl derivative (II) (ν_{max}^{Nujol} 1748 cm^{-1}).

1. Part XIX in the series of chemical taxonomy : Part XVIII. B. K. Chowdhury and D. P. Chakraborty, *Chemistry and Industry*, 1969, 549.
2. D. P. Chakraborty, K. C. Das and C. F. Hammer, *Tetrahedron Letters*, 1968, 5015. Recently D. A. H. Taylor has claimed that mahoganin is a mixture of methyl angolensate and 6-hydroxy methylangolensate (Chemical communication, 1969, 58).
3. K. C. Das, S. P. Basak and D. P. Chakraborty, *Jour. Indian Chem. Soc.*, 1969, **46**, 273.
4. B. K. Chowdhury and D. P. Chakraborty, *Jour. Indian Chem. Soc.*, 1969, **46**, 682.
5. D. P. Chakraborty, S. P. Basak, R. Beugelmans and B. C. Das, Abstract of the Indian Chemical Society Convention, 1967, p. 36 and S. P. Basak, D.Phil. Thesis, Calcutta University, 1968.

On Sarret oxidation, the compound (I) furnished a homogeneous compound (III), m.p. 191-92°. The i.r. spectrum of the Sarret oxidation product the hydroxyl band was replaced by γ-lactone function (ν_{max}^{Nujol} 1780 cm^{-1}). This shows that the hydroxyl group in the triterpene belongs to a γ-lactol function.

On oxidation with chromic acid under condition specified by Spaeth[6], the triterpene (I) gave acetone from the steam volatile fraction of the reaction product. This information together with the signal of the epoxide proton at δ2.90 confirmed the presence of a  system in the compound. It is evident from all these data excepting the m.p. of the γ-lactone (III) (melianone lactone Lit. m.p.[7] 165-66°) and its physical and chemical properties showed that it could be identical with melianone previously isolated[7] from *M. azedirach*. This was confirmed by comparison (m.m.p., t.l.c. and i.r.) with an authentic specimen of melianone kindly supplied by Prof. D. Lavie, Rehovoth, Israel, to whom our thanks are due. This is the second report of the isolation of melianone from a Meliaceous plant.



(I)

The isolation of melianone from a plant elaborating meliacins and cyclomahogenol is interesting from biogenetic considerations.

EXPERIMENTAL

All the m.p.s. reported here are uncorrected. Petroleum ether had the b.p. 60-80°. Samples were analysed after drying over P_2O_5 in vacuo at 80° for 20 hrs.

Isolation of the triterpene (I) :

The neutral fraction of the petroleum ether extract of the leaves of *S. mahagoni* was taken up in benzene and chromatographed over Brockmann's alumina (450 g). The column was successively eluted with pet. ether, pet. ether-benzene (1 : 1), benzene and benzene-chloroform (1 : 1) respectively. Benzene-chloroform eluents (4×300 ml) on distillation furnished

6. E. Spaeth and O. Pesta, *Ber.*, 1934, **66**, 754.
7. D. Lavie, M. K. Jain and I. Kirson, *J. Chem. Soc.*, 1967, 1347.

colourless residue, m.p. 172-85°. These residues on crystallisation from methanol furnished the compound m.p. 225-26°. (Found : C, 76.22; H, 9.73; Calc. for : $C_{30}H_{46}O_4$: C, 76.55; H, 9.85%; $(\alpha)_D$—48°).

Acetylation of the compound (II) : The compound (100 mg) was acetylated with acetic anhydride in presence of pyridine. This on attempted crystallisation from methanol furnished a semisolid mass (i.r. γ_{max}^{Nujol} 1748 cm^{-1}).

Chromic acid-pyridine oxidation of the compound (I) : A solution of the compound (50 mg) in pyridine (1.5 ml) was poured to the chromic acid-pyridine complex (50 mg in 1.5 ml pyridine) at 0-5°. The solution was kept overnight. On working up by the usual procedure a crystalline compound (pet. ether-benzene) was obtained, m.p. 190-91°. (t.l.c., chloroform-acetone, 9 : 1, R_f 0.69).

Chromic acid-acetic acid oxidation of the compound I : To a solution of the compound I (100 mg) in glacial acetic acid (3 ml) was added a solution of chromic acid (100 mg) in acetic acid (50%; 2.5 ml.). The reaction mixture was allowed to stand for 72 hrs. The reaction mixture was then diluted, neutralised and distilled. The distillate (10 ml) was trapped in 2 : 4 dinitrophenyl-hydrazine (0.1%) in H_2SO_4(10%). An immediate flocculent precipitate was obtained. The precipitate was filtered, washed, dried and chromatographed over Brockmann's alumina. Benzene—pet. ether (1 : 1) eluents (3×10 ml) on evaporation furnished a crystalline residue, m.p. 125-26°. This compound was found identical with pure specimen of 2 : 4 DNPH of acetone (m.m.p. and t.l.c., benzene-pet. ether, 2 : 1, R_f 042 in each case).

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