

# TRITERPENOIDS AND PHTHALYL ESTERS OF MOGHANIA MACROPHYLLA STEM-BARK

*Moghania macrophylla* Willd (Syn. *Flemingia macrophylla* Willd, *F. congesta* Roxb.; Leguminosae) is an erect shrub occurring at lower elevations throughout India and in Andaman Islands<sup>1</sup>. The earlier work on the mixture of leaves and flowers revealed the presence of several chromenochalkones<sup>2</sup>. The results of an examination of the stem-bark, obtained from Indian Lac Research Institute, Ranchi, Bihar, are described in this note.

The brown coloured, air dried and powdered stem-bark (790 gm) was exhaustively extracted with petrol (60–80°), benzene, acetone and methanol successively in a Soxhlet-extractor. The petroleum ether extract (4.3 gm) yielded an oily concentrate which was subjected to column chromatography over silica gel employing petroleum ether-benzene combinations and the following compounds were obtained in the order of elution and identified by direct comparison with authentic specimens and by the preparation of acetates: lupeol (40 mg),  $\alpha$ -amyrin (30 mg) and sitosterol (50 mg).

Benzene and acetone extracts behaved similarly on T.L.C. and were combined. The oily residue was chromatographed over silica gel. Elution with light petrol-benzene (4 : 1) yielded a pinkish yellow syrupy liquid (1.73 gm) whose infrared spectrum showed absorptions at 1720, 1280, 1120 (aromatic esters), 1600, 1580, 1312, 1280, 1070, 1035 and 740  $\text{cm}^{-1}$  (ortho substituted benzene ring). 60 MHz PMR spectrum ( $\text{CCl}_4$ ) showed a complex but symmetrical multiplet for four protons at  $\delta$  7.58 (characteristic of AA' XX' type), two broad signals each for two protons at  $\delta$  4.20 and 4.30 (methylenes carrying the oxygen function) and aliphatic protons  $\delta$  0.80–1.70. Although it appeared to be homogeneous on TLC system [chloroform-methanol-water, (13 : 7 : 5) lower phase], its mass spectrum showed the presence of two peaks at m/e 278 and m/e 306 in roughly equal intensities. The presence of peaks characteristic of phthalyl esters at m/e 167 and m/e 149 of which the latter was the base peak, coupled with the generation of phthalic acid (m.p., m.m.p., Co-IR) on saponification suggested that the fraction is most likely a 1 : 1 mixture of dibutyl and diamyl phthalates. Further, mass spectra were not indicative of the presence of alkyl chain greater than  $\text{C}_5\text{H}_{11}$  unit.

**Methanol extract:** The brown coloured semi-solid (5.5 gm), obtained on concentrating the methanol extract under reduced pressure, gave positive test for proanthocyanidins and on several repetitions of the process of dissolution in methanol and precipitation by ether afforded light brown

solid. This on hydrolysis with alcoholic 5 N HCl gave cyanidin ( $\lambda_{\text{max}}$  and paper chromatography) indicating the proanthocyanidin to be cyanidin based.

The ether soluble portion on column chromatography over silica gel yielded sitosterol- $\beta$ -D-glucoside in ethyl acetate eluates (45 mg), m.p. 295–303° (d),  $[\alpha]_D - 46.3^\circ$  (pyridine). It gave positive LB, TNM and Molisch tests and the identity was confirmed by direct comparison (mixed m.p., Co-TLC and Co-IR); and by conversion to tetra acetate, m.p. 165–167°,  $[\alpha]_D - 27.6^\circ$  (c, 0.67 in  $\text{CHCl}_3$ ).

The presence of alkyl phthalates has been recorded in some Umbelliferous plants<sup>3,4</sup>, Balanitaceae<sup>5</sup> and Anacardiaceae<sup>6</sup>; this, however, is the first report of their occurrence in Leguminosae. As these compounds are known to be, at times, notorious contaminants from extraneous sources, their presence was confirmed by separate extractions of the bark avoiding contact with plastic and using phthalate free solvents. The presence of phthalyl ester in this species may be of chemotaxonomic significance.

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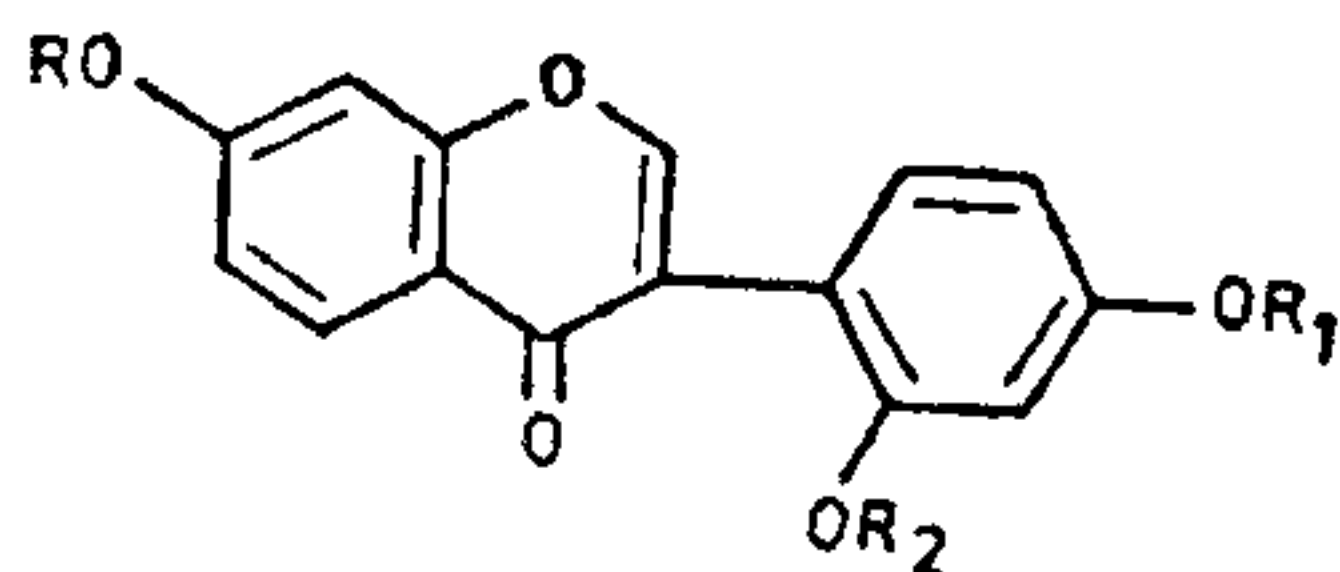
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## SYNTHESIS OF THERALIN

NIKONOV *et al.*<sup>1</sup> have reported the isolation of 7, 4'-dihydroxy-2'-methoxy-isoflavone (theralin) in the grass and groats of *Thermopsis alterniflora*. Its structure is based on degradative and spectral studies. During the course of selective demethylation<sup>2,3</sup> and debenzoylation studies at 2'-position of isoflavones, we have developed a convenient method for the synthesis of 2'-alkoxy isoflavones. The synthesis of theralin has been achieved through this procedure which confirms the above structure,





- (I)  $R = R_1 = R_2 = H$   
 (II)  $R = R_1 = R_2 = CH_2C_6H_5$   
 (III)  $R = R_1 = CH_2C_6H_5, R_2 = H$   
 (IV)  $R = R_1 = CH_2C_6H_5, R_2 = CH_3$   
 (V)  $R = R_1 = H, R_2 = CH_3$

Benzylation of 7, 2', 4'-trihydroxy isoflavone<sup>2</sup> (I), m.p. 284° (d), with benzyl chloride gave the corresponding tribenzyloxy compound (II), m.p. 167° which on selective debenylation at 2'-position using dioxan/HCl afforded 7, 4'-dibenzyloxy-2'-hydroxy isoflavone (III), in good yields, m.p. 175°. Methylation of (III) with dimethyl sulphate in acetone- $K_2CO_3$  yielded 7,4'-dibenzyloxy-2'-methoxy isoflavone (IV), m.p. 133° which on debenylation with Pd/C yielded the required theralin (V) as light yellow needles, m.p. 276° (m.p. of natural theralin, 274–75°<sup>1</sup>). I.R. and U.V. spectra of the synthetic sample are in agreement with those reported for the natural sample.

Details of this work will be published elsewhere.

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#### PAPER CHROMATOGRAPHIC SEPARATION OF POTASSIUM, RUBIDIUM AND CAESIUM IN *n*-AMYL ALCOHOL-HYDROCHLORIC ACID-ETHANOL MIXTURE

THE solvent mixture (HCl-MtOH-BuOH-ketone) reported by Miller and Magee<sup>1</sup> for the paper chromatographic separation of  $K^+$ ,  $Rb^+$  and  $Cs^+$  gives somewhat blurred bands. Phenolic solvents reported by Steel<sup>2</sup> and Magee and Headridge<sup>3</sup>, though give sharp separations yet, attack the paper which

becomes fragile and difficult to handle. Mixture of two of the straight chain aliphatic alcohols, or mixture of an alcohol and an acid has been successfully used for the paper chromatographic separation of  $Li^+$ ,  $Na^+$ ,  $K^+$  and  $NH_4^+$  ions<sup>4-7</sup>. Investigations were therefore undertaken for finding out the possibility of separation of  $K^+$ ,  $Rb^+$  and  $Cs^+$  using a mixture of straight chain aliphatic alcohol and a mineral acid.

#### Experimental

Extra pure *n*-amyl alcohol, freshly distilled absolute alcohol and concentrated hydrochloric acid were used for the preparation of the solvent. Sodium lead cobaltous hexanitrate reagent<sup>3</sup> (fresh) was used as the spraying agent.

**Development of chromatogram.**— One end of 4 × 56.5 cm long strip of Whatman filter paper No. 4 was tailored to 2 cm width. On this tapered end, leaving about 8 cm margin, the requisite volume of the desired solution (0.1%) was applied as a narrow elongated spot (about 2.5 cm × 0.5 cm) and dried. The chromatograms were then developed by descending development till the solvent front moved to the other end of the paper strip. The developed chromatograms were dried in air, hanged upside down and sprayed first with ethanol and then with freshly prepared sodium lead-cobaltous hexanitrate reagent. After about five minutes, the excess of the reagent was washed out with ice-cold distilled water and the position of the bands (Brown for  $K^+$  and  $Rb^+$  and yellowish-brown for  $Cs^+$ ) on the chromatogram was noted (Table I).  $R_f$  values of  $K^+$ ,  $Rb^+$  and  $Cs^+$  in 1 : 2 : 1 AHE solvent determined at 20° ± 1° C are given in Table II.

#### Results and Discussion

In the paper chromatographic separation of  $K^+$ ,  $Rb^+$  and  $Cs^+$ , usually  $Cs^+$  moves faster than the other two and therefore its separation from  $Rb^+$  is comparatively easy. Hence the separation of  $K^+$  and  $Rb^+$  was first tried.

It will be seen from Table I that the best separation of  $K^+$  and  $Rb^+$  could be obtained by the solvent mixture No. 8, although No. 7 also gave clear separation of  $K^+$  and  $Rb^+$  bands with smaller band distance between the two. The  $R_f$  values of all the three alkali metal ions, viz.,  $K^+$ ,  $Rb^+$  and  $Cs^+$  were therefore determined using solvent No. 8. It will be seen from Table II that the chromatogram of individual alkali metal gives higher  $R_f$  values than that of their values obtained from the chromatogram of the mixture of the three alkali metal ions in equal proportion.

Further studies on the separation of  $K^+$ ,  $Rb^+$ ,  $Cs^+$  using 1 : 2 : 1 :: AHE solvent mixture, on 4 cm