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A New Apigenin from *Pterocarpus marsupium*

Anjum Usmani¹, Dr. Jalaj Tripathi Devgan²

Ph. D Student, Faculty: Science and Technology, Shri Venkateshwara University, Gajraula, UP, India¹

Reader, Department of Chemistry, MMH Postgraduate College, Ghaziabad, UP, India²

ABSTRACT: *Pterocarpus marsupium* Roxb. (Fabaceae) commonly known as Indian Kino or Bijasal. It is multipurpose forest tree. *Pterocarpus marsupium* give timber for the international trade market. 3'-methyl butyl apigenin has been isolated from the bark of *Pterocarpus marsupium* and the structure of this new compound has been elucidation by UV, ¹H NMR, MS and ¹³C NMR.

KEYWORDS: Flavone, Bark, MeOH, EtOH.

I. INTRODUCTION

Pterocarpus marsupium is a medium to large deciduous tree. It can grow up to 30 meters height. The plant species is mostly found in India, Nepal and Shri Lanka. Depending upon different region of India, It has different name as Venga (Malyalam), Vengi (Tamil), Malbar Kino tree (English), Bijasal (Hindi) etc. *Pterocarpus marsupium* give tannins that's why it is used as powerful astringent, in treatment of, dysentery, diabetes and diarrhoea. Different parts of *Pterocarpus marsupium* (as bark, roots, flowers and leaves etc) have been believed that they have medicinal properties. It is also used as antibacterial. It estimated to contain about 35 species [1]. The heartwood of *P. marsupium* is astringent, bitter, acrid, anti-inflammatory, anthelmintic and anodyne. It is used for the treatment of elephantiasis, leucoderma, diarrhoea, dysentery, rectalgia, cough and greyness of hair (Gupta R and Gupta RS) [2]. *P. marsupium* is a rich source of polyphenolic compounds including homopterocarpin and Pterocarpin (Amrit Pal Singh Saroya) [3]. The bark and resin decoction of *P. marsupium* is an astringent for severe diarrhea, dysentery, for the treatment of tumors of gland, urethral discharge, used on ringworm of the scalp and chronic ulcer, abortifacient (Basu K.) [4]. In one study it was shown that aqueous extract of *Pterocarpus marsupium* modulates the inflammatory cytokine TNF- alpha in type 2diabetic rats and this has an indirect effect on PPAR-Gamma expression. By decreasing TNF- α , drug can up regulate the PPAR- Gamma and in turn the glucose metabolism (Halagappa et al.) [5]. Compound (I) C₂₂H₂₄O₇, m.p. 129 °C, was found to be a glycoside and on acid hydrolysis with 7% aqueous sulphuric acid gave L-arabinose (cochromatography with authentic sample and osazone derivative) and an aglycone la C₁₇H₁₆O₃, m. p. 179 °C. The aglycone gave positive test with 2, 4-dinitrophenyl hydrazine (C. D. Douglass, Morris, and Wender) [6] and sodium borohydride (R. M. Horowitz) [7] reagents indicating it to be a flavanone which was further confirmed, by its UV and ¹H NMR spectra 279, 311 (sh), JH NMR 5.2) (T. J. Mabry, Markham, and Thomas) [8].

II. RELATED WORK

A series of conventional extraction and separation procedure yielded compound 3'-methyl butyl apigenin (considered as compound (1). Homogeneity and purity of this compound were stabilised by chromatography. Their chemical structures were confirmed by spectral evidences.

Analytical TLC was carried out on silica gel G Merck 7731 with solvent systems unless and otherwise specified as follows:

- CHCl₃: MeOH :: 9:1
- EtOH : Pyridine: Water :: 4:1:5
- Benzene : Methanol :: 8:2

Column chromatography was done on silica gel 60 Merck 7734.

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UV spectra were recorded in EtOH on Hitachi 2205 spectrophotometer. IR spectra were run as KBr disk on perkin-Elmer 577. ^1H NMR spectra were recorded at 90 MHz in CDCl_3 solution on varian CFT 20 unless and otherwise specified using TMS as internal Standard. ^{13}C NMR were taken at 25.05 MHz in $\text{C}_5\text{D}_5\text{N}$ solution with TMS employing the FT mode.

Plant Material: The plant material collected from forest of M.P. (central Province of India) and was identified by the botanical survey of India, Central zone Allahabad. The plant was identified with the help of flowers, leaves and fruits (Reference of family character- Flora of British India by J.D. Hooker, Printed by B.S. Pal Singh Dehradun and periodical experts' 42-D Vivek Vihar, Delhi-32). A Herbarium sheet of the plant material is deposited in Botanical Survey of India (*P. marsupium* No. 43220, Accession No. 50784, collected by R.C. Srivastava Raigarh, M. P.).

Extraction: The Bark shaving 2.5 Kg of *P. marsupium* were extracted in ethanol (4 x 2 litres) at reflux temperature. The extract was concentrated under pressure and the concentrated extract (150 ml) was subject to continuous liquid-liquid extraction employing petroleum ether, hexane, benzene, ethyl acetate and acetone as solvents. The dark brown coloured ethyl acetate extract was concentrated with chromatographed on silica gel column with different solvents and their mixtures to yield the compound 1 (Benzene : Ethyl acetate, 2:8, V/V).

Purity of the compound was checked by PC and TLC.

Compound (1): Melting point 350°C , $\text{C}_{21}\text{H}_{20}\text{O}_5$. Homogeneous on TLC R_f 0.85 (solvent a) and 0.62 (solvent b). Spot appearance (UV) deep purple.

(UV/ NH_3) yellow green (found-C: 71.58%, H: 5.60 % requires C-71.59 %; H-5.68 %).

Λ_{max} (MeOH) nm: 267, 295 (sh), 336; +NaOMe: 275, 320,392; + AlCl_3 : 276, 348, 384; + AlCl_3/HCl : 276, 299,338,331; +NaOAc: 274, 300, 376; +NaOAc/ H_3BO_3 :268,301(Sh), 338.

IR $^{\text{KBr}}$ cm^{-1} : 3445, 2910, 2820, 1750, 1600, 1500, 1300.

^1H NMR 90 MHz, CDCl_3 Values in δ : 6.4 (d, J= 2Hz, 1H, C-8), 6.1 (d, J=2Hz, 1H, C-6), 6.7 (d, J=9Hz, 2H, C-3' 5'), 7.8 (d, J= 9Hz, 2H, C-2'), 0.95 (6H, d, J=6Hz, $(\text{CH}_3)_2\text{CH}$), 1.41 (3H $(\text{CH}_3)_2\text{CHCH}_2$) and 2.83 (2H, d, J=8 Hz, Benzylic CH_2) ppm.

Mass (70 eV) direct inlet: m/z 340, 153, 162, 131, 124, 123, 121.

III. EXPERIMENTAL RESULTS

Compound (1) showed M^+ in the mass spectrum at m/z 352 in agreement with the formula $\text{C}_{21}\text{H}_{20}\text{O}_5$. Its colour reactions indicated that it to be a flavone. A green colour with aqueous Ferric chloride indicated the presence of a hydroxy group at position-5 which was evidenced by UV spectrum exhibiting a bathochromic shift of 45 nm in Band I, in the presence of aluminium chloride-hydrochloric Acid. The presence of 7-hydroxy group was shown by a bathochromic shift of 7 nm in Band II with sodium acetate relative to its methanol spectrum, while the presence of 4'-hydroxy group was confirmed by bathochromic shift of 56 nm and 40 nm in band I with sodium methoxide and sodium acetate respectively.

Thus UV spectrum and diagnostic shift are as Apigenin with free 5, 7 and 4'-hydroxy groups.

The ^1H NMR of compound A displayed signals at 0.95 (6H, d, J= 6 Hz, $(\text{CH}_3)_2\text{CH}$); 1.42 (3H, $(\text{CH}_3)\text{CHCH}_2$) and 2.85 (2H, d, J= 8 Hz benzylic CH_2) for the presence of a 3-methyl butyl side chain. Aromatic protons H-6 and H-8 appeared as doublet J= 2 Hz at 6.7 (d, 2H, J= 9Hz) and 7.8 ppm (d, 2H, J= 9 Hz) were observed for 3', 5' and 2', 6' protons respectively.

Compound (1) on alkylation degradation with 50 % aqueous potassium hydroxide afforded p-hydroxy benzoic acid strongly supporting the presence of hydroxyl group at 4' position.

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It was concluded therefore that 3-methyl butyl side chain must be present at C-3, since no signal due to H-3, could be observed near 6.2-6.3 ppm in its ^1H NMR.

Fig. 1 and Fig 2: Above conclusion was further confirmed by its mass spectrum which exhibited a prominent peak at 131 establishing the structure of ring B and ring C while peak at m/z 152, 153, support the structure of ring A (fig. 1). The Wessely–Moser rearrangement has been an important tool in structure elucidation of flavonoids [9], [10]. Thus compound (1) is 3'-methyl butyl apigenin (fig 2).

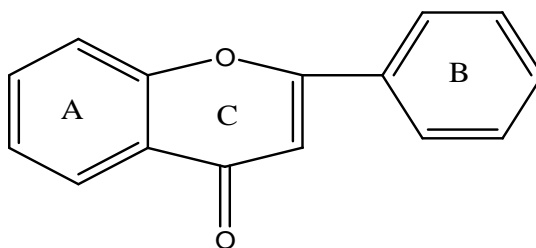


Fig. 1 (Apigenin)

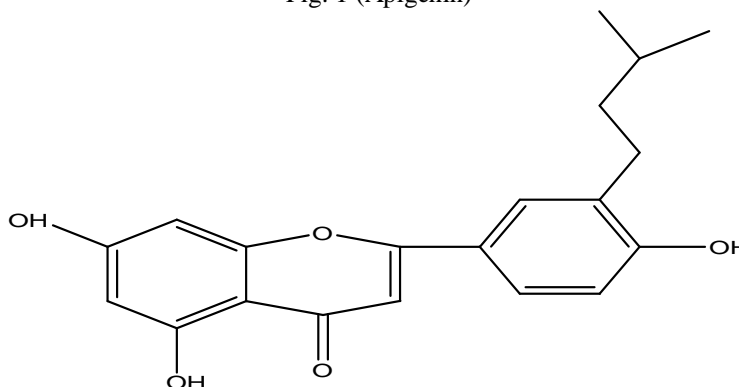


Fig. 2 (3'-methyl butyl apigenin)

IV. CONCLUSION

Pterocarpus marsupium is an important plant which is mostly use to cure many disease as diarrhoea and dysentery etc. especially in rural areas. *Pterocarpus marsupium* has various pharmacological properties .Bark of *Pterocarpus marsupium* has large amount of medicinally important chemicals such as Phenols, alkaloids, terpenoids glycosides and flavone etc. In conclusion this study identified a major compound that is 3'-methyl butyl apigenin from *Pterocarpus marsupium* first time. The compound is isolated from bark of *Pterocarpus marsupium*. Further studies, to characterise the study of isolated compound in detail and explore their potential use in treatment of diseases in human.

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