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STRUCTURAL STUDIES OF CHEMICAL CONSTITUENTS FROM BARK OF PTEROCARPUS MARSUPIUM

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ABSTRACT

Pterocarpus marsupium is the Indian Kino tree. It is used to cure many diseases as diarrhoea, elephantiasis, inflammations, leprosy, skin disease, leucoderma, erysipelas urethrorrhoea, diabetes, rectalgia, rectitis, opthalmopathy, dysentery, cough, asthma, greyness of hair and fractures bruises etc. A new compound 5, 7, 4'-trihydroxy-3-(3'-methyl butyl) flavone has been isolated from the bark of Pterocarpus marsupium. The structure of new isolated compound has been studied with the help of UV, ^{1} H NMR, MS, ^{13} C NMR, IR, synthesis and Chemical degradation.

Keywords: Bark, Benzene, extraction.

I. INTRODUCTION

Pterocarpus marsupium is multipurpose forest tree which gives excellent timber for the international trade market. Its wood is used for making furniture. It's called by different names depending upon the name of region as, Malbar Kino tree (English), Venga (Malyalam), Vengi (Tamil) and Bijasal (Hindi) etc. The powdered bark is mixed with Schleichera oleosa and taken with cold water to treat dysentery (Mohanta) [1]. Tribal people residing in the Jodhalal forest of Karnataka use stem bark to treat the wounds, fever, stomachache, diabetes and elephantiasis (Mankani et al.) [2]. the juice of the bark is applied in the mouth (Prusti and Behera) [3].Bark is useful in urinary discharge and piles. The gum Kino is externally applied to leucorrhoea (Pullaiah) [4].Gum Kino is used in the treatment of polyurea. Flowers are bitter, sweet, cooling, appetizing and febrifuge (Warrier) [5]. Bruised leaves are useful in boils sores, skin diseases, stomachic and cholera (Jain) [6]. Leaf juice is given in purulent discharges from ear, plant is useful in snakebite and scorpion sting. Fruit cures biliousness and kapha (Kirtikar and Basu) [7]. According to Grover et al., increase in glycogen content in renal and decrease in glycogen content in hepatic and skeletal muscle was partly prevented by aqueous extract of Pterocarpus treatment [8]. Zaid et al. reported that lowered activities of erythrocytic membrane Ca+ + -ATpase leads to cardiomyopathy indicated by reduction in contractibility, relaxation, cardiac work and diastolic complications in Type-2 diabetes mellitus. When the normal and diabetic type -2 patients treated with 1mm (-) epicatechin, the Ca++-ATpase activity increased both in normal and diabetic type-2 patients [9]. Apart from this many other researchers proved the antidiabetic nature of the Pterocarpus marsupium (Sharma and Kumar) [10]. Srikrishna and Mathew synthesized a dimethyl ether of marsupin [11]. Rajalakshmi et al. studied the antioxidant activity of

P. marsupium on isolated frog heart and found that the plant extract protected the cardiac muscles from oxidative stress induced by H_2O_2. While, the cardiac arrest time was prolonged by 14 minutes in the presence of plant extract than control, indicating the antioxidant activity of the methanolic extract of marsupium bark [12].

II. EXPERIMENTAL PROCEDURE: It has following steps:

2.1 Extraction and Purity:

The plant material was collected from forest of M.P., India and was identified by the botanical survey of India, Central zone Allahabad. The Bark shaving *P. marsupium* were extracted in ethanol at reflux temperature. The extract was concentrated under pressure and the concentrated extract 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 A. Purity of the compound was checked by TLC.

2.2 Instrumentation:

The collected fractions were analyzed by UV, IR Spectral, H^1NMR and C^{13} NMR, Synthesis and Chemical degradation. UV spectra were recorded in EtOH on Hitachi 2205 spectrophotometer. IR spectra were run as KBr disk on perkin-Elmer 577. ^{1}H 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 C_5D_5N solution with TMS employing the FT mode.

2.3 Melting point: 350 ^{0}C

2.4 Molecular Formula:

$C_{21}H_{20}O_5$. 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 %.

2.5 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.

2.6 IR ^{KBr} cm^{-1}:

3445, 2910, 2820, 1750, 1600, 1500, 1300.

max

2.7 ^{1}H 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, $(CH_3)_2CH$), 1.41 (3H $(CH_3)_2$ $CHCH_2$) and 2.83 (2H, d, J=8 Hz, Benzylic CH_2) ppm.

2.8 Mass (70 eV) direct inlet:

m/z 340, 153, 162, 131, 124, 123, 121.

III. RESULT AND DISCUSSION

Compound (Z) showed M^+ in the mass spectrum at m/z 352 in agreement with the formula $C_{12}H_{20}O_5$. 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 ^{1}H NMR of compound A displayed signals at 0.95 (6H, d, J= 6 Hz, $(CH_3)_2$ CH); 1.42 (3H, (CH_3) $CHCH_2$) 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 (Z) on alkylation degradation with 50 % aqueous potassium hydroxide afforded p-hydroxy benzoic acid strongly supporting the presence of hydroxyl group at 4' position.

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 ^{1}H NMR.

Thus compound (Z) is 5, 7, 4'-trihydroxy-3-(3'-methyl butyl) flavone (fig 1).

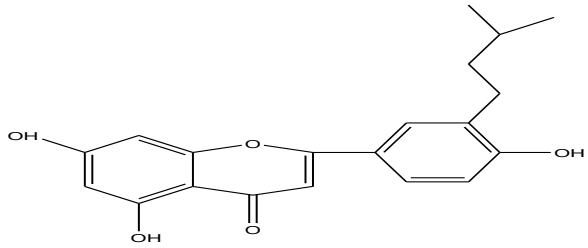

Fig. 1 (5, 7, 4'-trihydroxy-3-(3'-methyl butyl) flavones)

IV. CONCLUSION

The Bark of *Pterocarpus marsupium* has medicinally properties. Compound 5, 7, 4'-trihydroxy-3-(3'-methyl butyl) flavones has been isolated from *Pterocarpus marsupium* first time. Medicinally properties of this compound will be checked for further studies.

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