

## Structure elucidation of some bioactive compounds from a natural source i.e. *Psoralea corylifolia* Linn. by spectral techniques

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### ABSTRACT

Spectral techniques of U.V., I.R., PMR and Mass spectra have been utilized to interpret the structures of three bioactive compounds isolated from the desert variety of *Psoralea corylifolia* Linn. These were identified and an 2',6',4'-trihydroxy-4'-methoxy-3'-(3"-dimethyl allyl chalkone (I), 6-hydroxyl-6", 6"-dimethyl pyrano-(2", 3", 4', 3')-isoflavone (II) and 2',4-dihydroxy-4'-methoxy-5'-(3-methyl-2-butenyl)-chalkone-(III).

**Key words :** *Psoralea corylifolia* Linn, chalkones, isoflavone.

### INTRODUCTION

*Psoralea corylifolia* is a medicinally important plant found throughout the plains of UP, Punjab, Bihar and Rajasthan. The seeds have antipyretic, anthelmintic properties and is useful to cure skin diseases like leucoderma and scabies. The leaves are useful to cure diarrhea while the fruit cures leprosy, is diuretic and an China is prescribed for stomach ache.<sup>2</sup>

Therefore, for the present study this plant was chosen and the bioactive compounds were isolated from the seeds.

### EXPERIMENTAL

The UV spectra was carried out in Shimadzu-1601 spectrometer. FTIR was recorded on Shimadzu-8101 A spectrometer in KBr pellets, NMR was done on Bruker WM 400 Model at 300 MHz with CDCl<sub>3</sub> as the solvent while mass spectra was obtained on JEOL D-300 Model.

### Isolation

Two kg of dried and powdered *Psoralea corylifolia* seeds were successively extracted with hexane and then chloroform. The chloroform extract was treated with hexane and the hexane insoluble part was made into a dry slurry in silica gel. The slurry was fed to a column packed with 680 g of silica-gel G. Mesh size 60-120 and after eluting with hexane. Chloroform (30:70) and concentrating gave compound I. Compound II was obtained by eluting the same column with hexane : Chloroform (10:90) while elution with pure chloroform gave compound III.

### Physical Data

#### Compound I

Orange-coloured flakes on recrystallisation with pure ethanol; m.p. 80°C, yield 1.01 g; R<sub>f</sub> : 0.13 (benzene : methanol, 95.5).

#### Compound II

Creamish white needles; recrystallisation with acetone – ethanol mixture; m.p. 220°C, yield 0.8 g; R<sub>f</sub> : 0.14 (benzene : methanol, 95.5).

**Compound III**

Brown coloured needles, recrystallisation with rectified spirit; m.p. 162°C, yield 2.15 g;  $R_f$  : 0.12 (benzene : methanol, 95.5).

**Spectral data****Compound I**

UV  $\lambda_{\max}^{\text{EtOH}}$  nm (log  $\epsilon$ ) : 250 (1.6), 308 (0.8) and 380 (3.5); UV  $\lambda_{\max}^{\text{EtOH} + \text{NaOH}}$  nm (log  $\epsilon$ ) : 250 (1.6), 304 (0.8) and 466 (3.55); UV  $\lambda_{\max}^{\text{EtOH} + \text{NaOH}}$  nm (log  $\epsilon$ ) : 252 (1.6), 308 (0.9) and 420 (3.52); IR (KBr,  $\nu_{\max}$ )  $\text{cm}^{-1}$  : 3400, 3220, 2960, 2910, 2855, 2635, 1660, 1550, 1510, 1445, 1370, 1320, 1280, 1230, 1170, 1140, 1040, 1010, 970, 860 and 740  $\text{cm}^{-1}$ .

PMR (300 Mz,  $\text{CDCl}_3$ ) :  $\delta$  3.1 (s, 2H, C-2', C-6'-OH protons);  $\delta$  7.8 (d, 1H,  $J=6.5$  Hz, C- $\beta$  protons);  $\delta$  7.45 (d, 1H,  $J=6.5$  Hz, C- $\alpha$  proton);  $\delta$  6.7 (s, 1H, C-5', proton);  $\delta$  6.45 (s, 1H, C-4, OH proton); d 7.6 (d, 2H,  $J=6.5$  Hz, C-2 & C-6 proton);

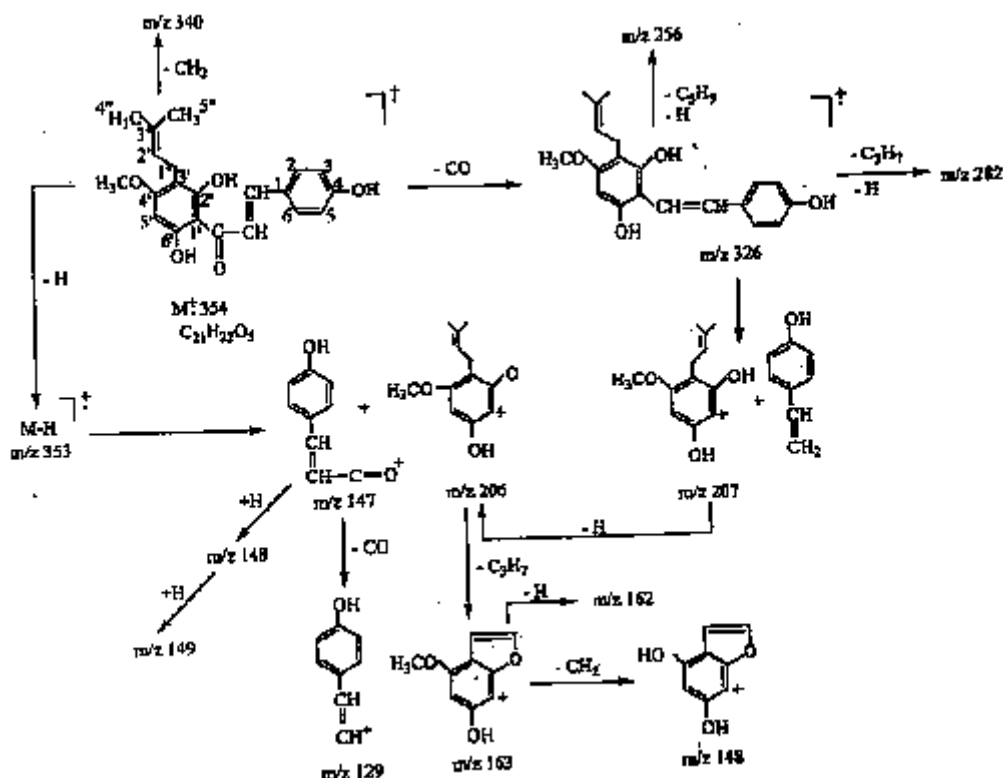
$\delta$  5.2 (t, 1H,  $J=3.5$  Hz, methyne proton at C-2'');  $\delta$  3.9 (s, 3H,  $\text{OCH}_3$  proton);  $\delta$  2.8 (d, 2H,  $J=3.5$  Hz, C-1'' methylene proton);  $\delta$  1.7 (s, 6H, gem dimethyl protons at C-4'' & C-5'').

**Mass spectra**

$M^+$ . 354 (5%);  $m/z$  353 (3.2%);  $m/z$  340 (5.0%);  $m/z$  326 (40.4%);  $m/z$  282 (5.3%);  $m/z$  256 (2.3%);  $m/z$  207 (1.6%);  $m/z$  206 (19.5%);  $m/z$  163 (3.1%);  $m/z$  162 (30.8%);  $m/z$  149 (73.8%);  $m/z$  148 (5.0%);  $m/z$  147 (18.5%);  $m/z$  147 (4.6%);  $m/z$  129 (7.0%).

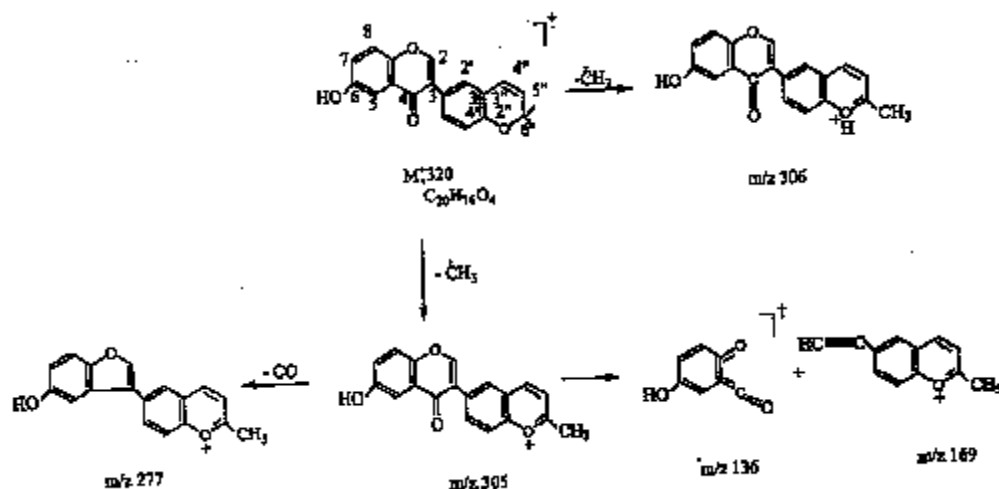
**Compound II**

UV  $\lambda_{\max}^{\text{MeOH}}$  nm (log  $\epsilon$ ) : 247.0 (2.684) and 302 (0.726); UV  $\lambda_{\max}^{\text{MeOH} + \text{NaOH}}$  nm (log  $\epsilon$ ) : 247.0 (2.6664), 327 (0.729) and 205 (2.504); IR (KBr,  $\nu_{\max}$ )  $\text{cm}^{-1}$  : 3400, 3070, 2975, 1640, 1535, 1560, 1500, 1375, 1275, 1265, 1243, 1130, 958, 878, 835 and 723  $\text{cm}^{-1}$ .

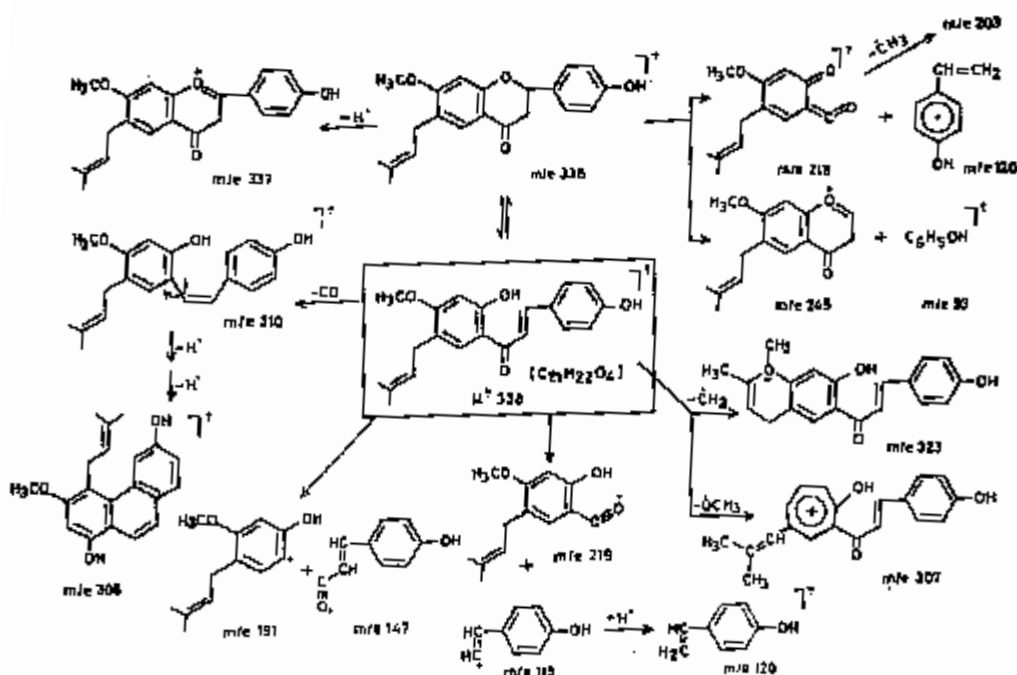


Scheme 1: Mass fragmentation pattern of compound I

PMR (300 Mz, CDCl<sub>3</sub>) : δ 10.64 (s, 1H, C-6-OH); δ 8.18 (s, 1H, C-2); δ 8.057 (δ, 1H, C-5); δ 7.3077 (s, 1H, C-2'); δ 6.985 (d, 1H, C-5'); δ 6.889 (δ, 1H, C-8); δ 6.769 (t, 1H, C-6'); δ 6.43 (δ, 1H, C-4"); δ 5.75 (δ, 1H, C-5"); δ 1.4 (s, 6H, gem-dimethyl).



**Scheme 2: Mass fragmentation pattern of compound II**



**Scheme 3: Mass fragmentation pattern of compound III**

**Mass spectra**

$M^+$ . 320 (70.7%);  $m/z$  306 (70.2%);  $m/z$  305 (100%);  $m/z$  277 (6.5%);  $m/z$  169 (27%);  $m/z$  136 (4.1%).

**Compound III**

UV  $\lambda_{\max}^{\text{EtOH}}$  nm (log  $\epsilon$ ) : 237 (1.67), 308 (1.30), 372 (3.35). IR (KBr,  $\nu_{\max}$ )  $\text{cm}^{-1}$  : 3420, 3298, 3015, 2965, 2910, 2855, 1635, 1560, 1505 – 1520 (broad), 1445, 1370, 1280, 1240, 1200, 1170, 1135, 1000, 975, 838 and 600  $\text{cm}^{-1}$ .

PMR (300 Mz,  $\text{CDCl}_3$ ) :  $\delta$  13.49 (s, 1H, C–2'–OH);  $\delta$  7.83 ( $\delta$ , 1H, C– $\beta$ );  $\delta$  7.57 ( $\delta$ , 2H, C–2 and C–6);  $\delta$  7.43 (d, 1H, C– $\alpha$ );  $\delta$  7.26 (s, 2H, C–5' and C–6');  $\delta$  6.89 (d, 2H, C–3 and C–5);  $\delta$  6.44 (s, 1H, C–4–OH);  $\delta$  5.28 (t, 1H, methane proton of prenyl side chain);  $\delta$  3.87 (s, 3H,  $-\text{OCH}_3$ );  $\delta$  3.26 (s, 2H, methylene protons of prenyl side chain);  $\delta$  1.77 (d, 3H, other methyl group of prenyl side chain);  $\delta$  1.56 (s, 3H, one methyl group of prenyl side chain).

**Mass spectra**

$M^+$ . 338 (100%);  $m/z$  337 (20%);  $m/z$  323 (15.4%);  $m/z$  310 (9.8%);  $m/z$  245 (15.6%);  $m/z$  219 (87.1%);  $m/z$  218 (47.6%);  $m/z$  191 (8.5%);  $m/z$  147 (31.8%);  $m/z$  120 (8.3%);  $m/z$  119 (14.5%).

**RESULTS AND DISCUSSION****Compound I**

The UV–spectrum showed the presence of a less intense band at 250 nm (Band–II), a minor inflection at 308 nm (Band–I), characteristic of a chalcone nucleus.<sup>3–5</sup>

Presence of a sharp band at 3400  $\text{cm}^{-1}$  broad band at 3220  $\text{cm}^{-1}$  in its IR spectrum indicated the presence of at least two hydroxyl groups; one chelated and the other non–chelated.

In its PMR spectra a pair of doublets centered at  $\delta$  7.8 and  $\delta$  7.45 were identified as the C– $\beta$  and C– $\alpha$  protons with respect to the carbonyl carbon, a characteristic feature of chalcones<sup>6,7</sup>. Presence of a doublet centered at  $\delta$  2.8 were the two methylenic protons of the prenyl group while a triplet centered at  $\delta$  5.2 was of the single proton linked to the doubly bonded carbon atom of the allyl side chain. A singlet at  $\delta$  1.7 integrated for six

protons of a gem dimethyl group present in the side chain. A down field singlet at  $\delta$  13.1 was accounted for two protons of the two chelated hydroxyl groups at C–2' and C–6' carbon atoms while another singlet at  $\delta$  6.45 for the unchelated OH group proton at C–4. Another singlet at an upfield value of  $\delta$  3.9 was also observed which integrated for three protons of a methoxy group.

The structure was further supported by the molecular ion peak at  $M^+$ . 354 giving the molecular formula as  $\text{C}_{21}\text{H}_{22}\text{O}_5$ . Other mass fragments at  $m/z$  353 (M–H),  $m/z$  326 (M–CO),  $m/z$  206,  $m/z$  148,  $m/z$  147 etc. strongly support the proposed structure and confirm it to be a chalcone<sup>8,9</sup> (Scheme 1).

Compound II : Its UV–spectrum showed one intense band at 247 nm and other less intense band at 302 nm indicating it to be an isoflavone.<sup>5</sup> The intense band at 247 nm was due to ring 'A' (Band II) and less intense band at 302 nm was due to ring 'B' of isoflavone (Band I). Its UV spectrum in methanolic NaOH solution showed a bathochromic shift of Band I as the peak was observed at 327 nm. The IR spectra showed a strong band at 3400  $\text{cm}^{-1}$ ; indicated the presence of a non–bonded OH group while a characteristic band at 1640  $\text{cm}^{-1}$  indicated the presence of  $\gamma$ . The PMR spectra showed a singlet at  $\delta$  8.18 due to C–2 proton and confirmed it to be an isoflavone as in flavones C–3 proton generally appears as a sharp singlet between  $\delta$  6.3 to 6.8. A strong singlet at  $\delta$  1.4 due to 6 protons indicated a gem–dimethyl group.

A pair of doublet centered at  $\delta$  5.75 and  $\delta$  6.43 indicated the presence of 1 proton each at C–5" and C–4" of the dimethyl pyrano ring. A strong singlet at  $\delta$  7.3 due to C–2' proton and pair of doublets at  $\delta$  6.9 and  $\delta$  6.7 due to C–5' and C–6' protons indicated the unsubstituted C–2' C–5' and C–6' positions of B ring. Presence of two coupled doublets at  $\delta$  6.43 and  $\delta$  5.75 in its NMR spectra were due to the C–4" and C–5" protons further supporting this compound to be an isoflavone with a pyrano nucleus<sup>7</sup>.

Its mass spectrum showed an intense ion peak at  $M^+$ . 320 while a base peak at  $m/z$  305 indicated the loss of methyl group from dimethyl pyrano moiety, thus giving most stable ion. Other

intense peaks at  $m/z$  277 (loss of  $\text{CH}_3$  and CO), at  $m/z$  306 ( $\text{M}-\text{CH}_2$ ), at  $m/z$  169 and at  $m/z$  136 clearly supported the proposed structure of the compound as 6-hydroxy-6"-6"-dimethyl pyrano-(2", 3", 4', 3') -isoflavone (Scheme II).

### Compound III

Its UV spectrum also showed characteristic features of chalcones by showing the presence of a less intense band at 237 nm (Band II), a minor band at 308 nm and a strong band at 372 nm, (Band I). The band at 237 nm corresponded to ring A while band at 373 nm corresponded to ring B of chalcone structure. Presence of two characteristic bands in its IR spectra at  $3420\text{ cm}^{-1}$  and at  $3298\text{ cm}^{-1}$  indicate the presence of a bonded and a non-bonded OH group. A band at  $838\text{ cm}^{-1}$  indicated the presence of para substituted benzene ring.

A pair of doublets at  $\delta$  7.83 and  $\delta$  7.43 ( $J=17\text{ Hz}$ ) in its PMR spectrum due to C-b and C-a protons to the carbonyl carbon a characteristic feature of the chalcone. The two ortho coupled doublets (due to C-3 and C-5 protons and C-2

and C-6 protons) centered at  $\delta$  6.89 and  $\delta$  7.57 for 4 protons of an  $\text{A}_2\text{B}_2$  system indicated a para substituted phenyl ring. The presence of one chelated and other non-chelated hydroxyl group was indicated by the presence of two singlets, one at  $\delta$  13.49 and other at  $\delta$  6.44 respectively. Also the presence of a 3,3-dimethyl allylic side chain was revealed by a singlet at  $\delta$  1.56 due to one methyl group protons and doublet at  $\delta$  1.77 of the gem dimethyl group. The two methylenic protons of the prenyl group was indicated by the presence of a doublet centered at  $\delta$  3.26, and a triplet at  $\delta$  5.28 was due to the single proton linked to a doubly bonded carbon atom of the allyl side chain.

The mass spectra (Scheme III) gave mass fragments at  $m/z$  337 ( $\text{M}-\text{H}$ ),  $m/z$  307 ( $\text{M}-\text{OCH}_3$ ),  $m/z$  310 ( $\text{M}-\text{CO}$ ),  $m/z$  219,  $m/z$  119 etc. which further support the proposed structure with the molecular formula as  $\text{C}_{21}\text{H}_{22}\text{O}_4$ .

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