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A PRENYLATED CHALCONE FROM *CROTALARIA MEDICAGINEA*

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Key Word Index—*Crotalaria medicaginea*; Leguminosae; roots; 3',5'-di-isopentenyl; 2',4',4-trihydroxy chalcone.

Abstract—A new prenylated chalcone has been characterized from the root of *Crotalaria medicaginea*.

INTRODUCTION

In view of its importance in Indian medicine [1] and as camel fodder [2], *Crotalaria medicaginea* has been the subject of chemical examination [3] by researchers working on medicinal plants belonging to the Leguminosae. These investigations led to isolation of a hydrocarbon, a phytosterol and various fatty acids [1] and some pyrrolizidine alkaloids [4, 5]. This report deals with the characterization of a new prenylated chalcone, one of the many colouring principles present in the plant species and represents an area which is hitherto unexplored in *Crotalaria* species of Indian origin.

RESULTS AND DISCUSSION

The new chalcone [**1**, $C_{25}H_{28}O_4$, mp 118–119°; UV λ_{max}^{MeOH} nm (log ε): 230(3.95) 370(4.03): IR ν_{max}^{nujol} cm^{-1}: 3330 (OH), 1630 (C=O) 1610 (aromatic), 1510, 1375, 1270] gave a dark brown ferric reaction and a red colouration when dissolved in concentrated sulphuric acid which turned yellow upon addition of nitric acid. Treatment of the compound with concentrated sulphuric acid and acetic anhydride gave an orange red colour. These properties suggested it was hydroxy chalcone. Oxidation of chalcone with alkaline potassium permanganate gave *p*-hydroxy benzoic acid indicating the presence of a 4-hydroxy substituted B-ring in the chalcone.

The ^{1}H NMR spectrum showed the presence of two dimethyl allyl groups and confirmed the 2'-hydroxy chalcone skeleton for the compound. The upfield signals at δ1.77 (12H, *s*, 2 × –C(CH$_3$)$_2$), 3.3 (2H, *d*, J = 3 Hz, –CH$_2$–Ar), 3.45 (2H, *d*, J = 3 Hz, –CH$_2$–Ar), 5.2–5.4 (2H, *m*, 2 × –CH$_2$–CH) corresponded to two C-prenyl functions attached to a phenyl ring thus ruling out the possibility of their linkage to hydroxy groups [6]. Two absorptions of A_2B_2 pattern at δ6.85 (2H, *d*, J = 9 Hz, H-3 and H-5) and 7.25 (2H, *d*, J = 9 Hz, H-2 and H-6 confirmed the presence of a *para* substituted B-ring in the chalcone. While hydrogens attached to the chalcone double bond appeared as two doublets at δ 7.55 (1H, *d*, J = 14 Hz, H-α) and 7.8 (1H, *d*, J = 14 Hz, H-β), the absorptions due to hydroxylic protons showed up as D_2O exchangeable singlets at δ6.2 (1H, *s*, 4'-OH), 7.5 (1H, *s*, 4-OH) and 13.6 (1H, *s*, 2'-OH). Other downfield absorption at δ7.9 was assigned to the only aromatic hydrogen present in the A-ring.

The ^{13}C NMR data supported the proposed structure. The assignments were made on the basis of values of model compounds, [7] and decoupled and off resonance decoupled spectra (Table 1).

Confirmation of the structure was obtained from the high resolution mass spectrum. The mass peaks conformed to the cracking pattern of a 2'-hydroxy chalcone with prenyl functions. Due to the equilibrium existing between a 2'-hydroxyl chalcone and its corresponding flavanone, the spectrum displayed peaks related to both

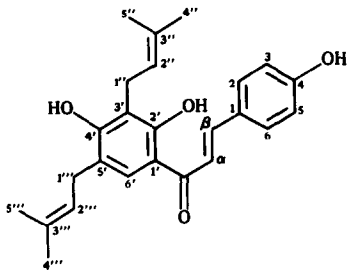

Table 1. ^{13}C NMR spectral data* for compound 1 (25.16 MHz)*

C		C	
C=O	192.1635	-5'', 5'''	17.9307
1'	113.669	-1'''	21.9116‡
2'	159.9386	-1''	22.2437†
3'	107.2951†	-2''	125.5030§
4'	161.9712	-2'''	125.1248§
5'	106.9556†	-3'''	130.7064‖
6'	132.9542	-3'''	130.0891‖
1	121.9579	-4''	25.8081¶
2,6	130.6338	-4'''	25.5537¶
3,5	155.9212		
4	158.0998		
Hα	117.9968		
Hβ	143.8224		

* Decoupled spectrum.
†, ‡, §, ‖, ¶ Assignments interchangeable.

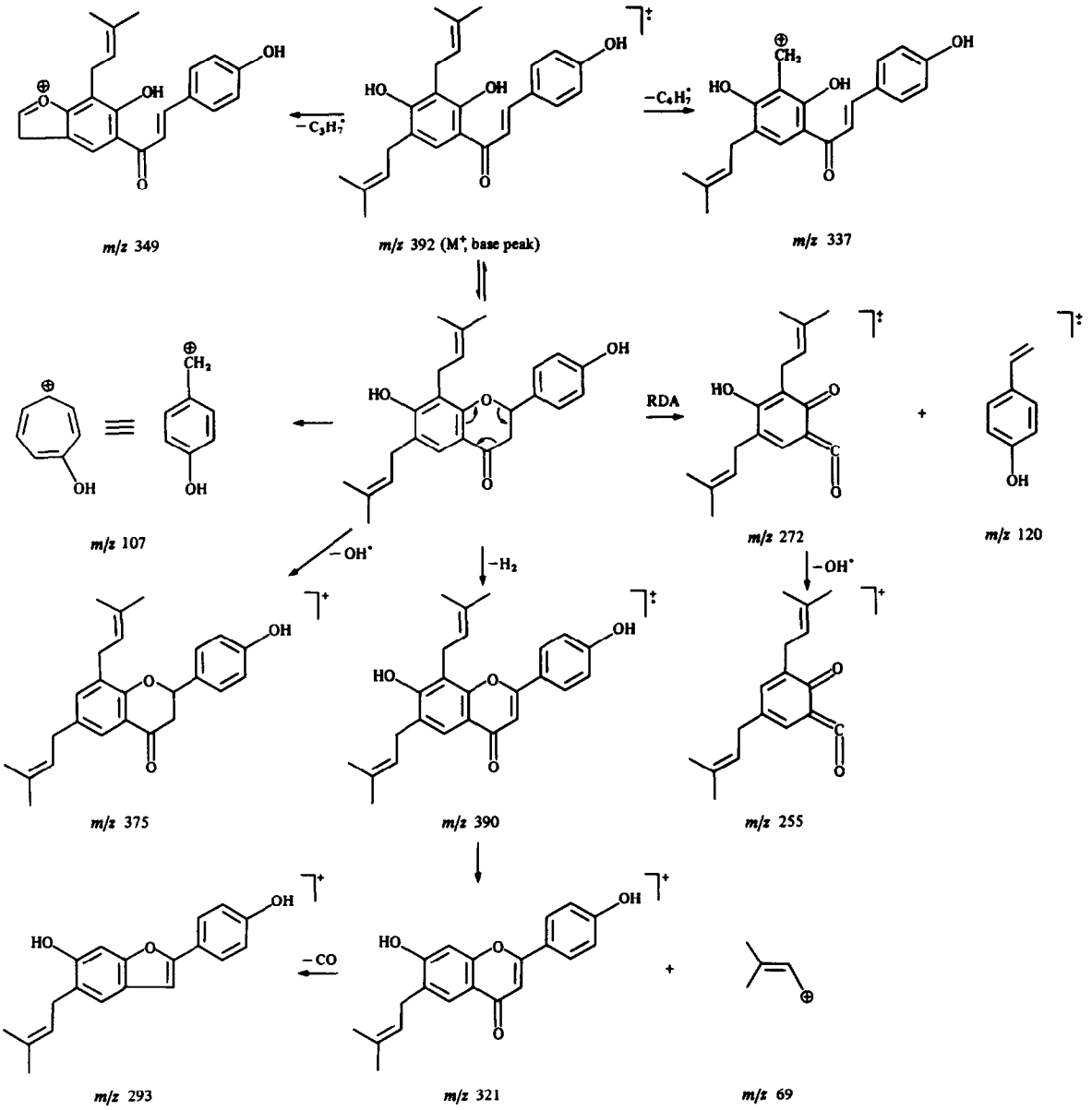

Fig. 1.

the chalcone and the flavanone. A few of the more important fragments are depicted in Fig. 1.

Final proof for the structure (**1**) proposed for the compound came from an unambiguous synthesis involving the condensation 3,5-di-*C*-prenyl, 2,4-dihydroxy acetophenone and *p*-hydroxy benzaldehyde under aqueous alkaline conditions. The substituted acetophenone was prepared by a method reported earlier [8] with slight modification in order to improve yields. Acidification of the reaction mixture followed by column chromatography on silica gel-G using petrol and petrol–benzene (4:1) gave a yellow crystalline material in the latter fractions which was furher purified by recrystallisation from benzene (mp 119°). It was identified as 3′,5′-di-*C*-prenyl, 2′,4′-4-trihydroxy chalcone by chemical and spectral methods. Comparison (mmp, co-TLC, UV, and superimposable IR) with the natural sample established their identity and thus the structural assignment for the new chalcone was proved to be correct beyond doubt.

EXPERIMENTAL

Mp: uncorr.; Microanalysis: Hewlett–Packard 185B Model; IR: nujol; ^{1}H NMR and ^{13}C NMR: 90 MHz and 25.16 MHz respectively, DMSO-d_6, TMS as int. standard.

Isolation. Roots (0.5 kg) of *C. medicaginea* were soaked in petrol (60–80°) for 0.5 hr and the resulting yellow extract was evaporated under vacuum to give a waxy yellow material (500 mg). This was dissolved in MeOH (100 ml) and refrigerated for a couple of days. The solid which separated was filtered off and the process was repeated until no solid was observed after chilling the soln. The methanolic soln was concd under red. pres. to give a yellow crystalline compound (100 mg) which crystallized from C_6H_6 as yellow prisms, mp 119° (**1**) Found: C, 76.4, H, 6.6;

$C_{25}H_{28}O_4$ requires C, 76.5, H, 7.1%.

HRMS: *m/z* (rel. int.): 392.1986 (100%) $[M]^+$ ($C_{25}H_{28}O_4$), 390.1827 (9.24) $[M-H_2]^+$, 375.1609 (18.84), $[M-OH]^+$, 350.1475 (11.78) $[M-C_3H_6]^+$, 349.1447 (51.34) $[M-C_3H_7]^+$, 337.1439 (15.31) $[M-C_4H_7]^+$, 336.1359 (8.46) $[M-C_4H_8]^+$, 321.1126 (17.50) $[M-C_4H_6OH]^+$, 293.0809 (12.54) ($C_{18}H_{13}O_4$), 281.0815 (16.06) ($C_{17}H_{13}O_4$), 272.1409 (12.27) ($C_{17}H_{20}O_3$), 257.1180 (11.15) ($C_{16}H_{17}O_3$), 255.1021 (12.37) ($C_{16}H_{15}O_3$), 244.1464 (10.19) ($C_{16}H_{20}O_2$), 229.0857 (20.85) ($C_{14}H_{13}O_3$), 217.0868 (40.02) ($C_{13}H_{13}O_3$), 216.0788 (13.74) ($C_{13}H_{12}O_3$), 215.0716 (12.94) ($C_{13}H_{11}O_3$), 201.0557 (20.92) ($C_{12}H_9O_3$), 189.0897 (9.28) ($C_{12}H_{13}O_2$), 188.0836 (31.49) ($C_{12}H_{12}O_2$), 173.0606 (11.22) ($C_{11}H_9O_2$), 173.0239 (15.62) ($C_{10}H_5O_3$), 161.0242 (42.28) ($C_9H_5O_3$), 147.0446 (28.85) ($C_9H_7O_2$), 120.0570 (14.52) (C_8H_8O), 119.0499 (15.47) (C_8H_7O), 115.0551 (9.14) (C_9H_7), 107.0494 (8.77) (C_7H_7O), 91.0550 (26.28) (C_7H_7), 77.0385 (10.69) (C_6H_5), 69.0706 (11.74) (C_5H_9), 65.0397 (14.12) (C_5H_5).

Oxidation. The chalcone (30 mg) was taken up in 2% KOH (5 ml) and treated with portions of an aq soln of $KMnO_4$ (2%, 15 ml). The resulting mixture was heated on a water bath for 5–6 hr. It was then satd with SO_2 and extracted with Et_2O (4 × 25 ml). The compound in Et_2O was taken into saturated $NaHCO_3$ (4 × 10 ml), acidified with dil HCl and extracted with Et_2O. Evaporation of the Et_2O extract gave white needles, mp 213–214°, identified as *p*-hydroxy benzoic acid (mmp).

Synthesis. Nuclear prenylation of β-resacetophenone (4 g) was carried out in absolute methanolic KOH (10.2 g, 60 ml) using prenyl bromide (8.5 ml) (mol ratio β-resacetophenone to prenyl bromide, 1:2). The usual work up gave 3,5-di-*C*-prenyl-β-resacetophenone (0.8 g), mp 110°.

3,5-Di-isopentenyl-β-resacetophenone (0.75 g, 2.5 mmol), and *p*-hydroxy benzaldehyde (1.25 g, 0.01 mol), in EtOH (10 ml) were mixed with aq. KOH (7.5 g in 10 ml) and kept at room temp. for 72 hr out of contact with air. Acidification gave a yellow mass which was chromatographed over silica gel-G (30 g) using petrol followed by petrol–C_6H_6 mixtures as eluents. The petrol fractions gave unreacted acetophenone (0.4 g). The fractions collected with benzene–petrol (4:1) gave yellow prisms (0.2 g) mp 119°, [homogenous on TLC: R_f 0.5 Me_2CO–hexane, 1:1), R_f 0.6 (C_6H_6–petrol, 3:2) identical with the natural sample.

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