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ISOLATION AND STRUCTURE DETERMINATION OF A NEW 2, 2-DIMETHYL CHROMENO DIHYDRO CHALCONE FROM *CROTALARIA RAMOSISSIMA*

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ABSTRACT

A new 2, 2-dimethyl chromeno dihydro chalcone was isolated from the petroleum ether extract of *crotalaria ramosissima*.

Key words : *Crotalaria ramosissima*, Crotaramin, Dihydrochalcone.

INTRODUCTION

The genus crotalaria belongs to the family leguminasae, sub family papillionaceae is being restricted to tropical and subtropical areas of the world. About 75 species of this genus have been reported to occur in India[1]. Chalcones and dihydrochalcones,, which constitute important sub group of natural products, were known[2] to possess significant biological activity[3]. Earlier phytochemical work on crotalaria species resulted in the isolation of a dihydrochalcone crotaramosmin[4] at our lab. A detailed re-investigation of *crotalaria ramosissima* has resulted in the isolation of another new dimethyl chromeno dihydrochalcone crotaramin **(1),** whose structure elucidation by various 2D spectra is presented in this paper. Also acetyl derivative of **(1)** was prepared and dihydro derivative of crotaramin was synthesized by reducing crotaramin using catalytic hydrogenation transfer method[5],, which offers simple and convenient method developed by Brieger and Nestrick[6] and it is popularized by a review article published by Johnston et al.[6]

EXPERIMENTAL

Crotalaria ramosissima is a weed plant found in the open places mainly at Ranga Reddy and Prakasham districts of Andhra Pradesh. During flowering, a yellow waxy

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exudate appear in its inflorscence. The exudate contains substituted chalcones.

Extraction and isolation

Shade dried aerial roots of *crotalaria ramosissima* were soaked in light petroleum ether for a week and filtered off to remove mechanical impurities. Filterate thus obtained on concentration in vaccum gave a green gummy substance, which was chromatographed over silica gel. The column was eluted with light petroleum ether, pet. ether : ethylacetate mixture, with increasing conc. of ethylacetate. Fractions collected from pet. ether : ethyl acetate (9 : 1) mixture were found to be homogenous on TLC. These fractions were combined and concentrated to give a pale yellow solid,, which on crystallisation from petroleum ether yielded colourless prisms m. p. 62°C.

Crotaramin : m. p. 62°C. yield 0.4% M. F. $C_{21}H_{22}O_4$ M^+ (m/z = 338) ^{1}H NMR and ^{13}CNMR data given in Table 1.

Acetylation of crotarmin

Crotaramin (25 mg), was mixed with acetic anhydride (3 mL) in R. B flask then dry pyridine (1 mL) was added and the mixture was heated on steam bath for 2 hours using guard tube maintaining dry conditions. It was cooled and poured over crushed ice to get crude acetate. The solid obtained was recrystallized from ethanol to get colourless crystals m. p. 82°C.

Dihydrocrotaramin synthesis

A mixture of crotaramin (25 mg), sodium formate (500 mg) and pd/c (10%, 500 mg) were taken in R. B flask and dissolved in methanol (20 mL) and refluxed for 2 hours. The reaction mixture was filtered and the solvent was evaporated. The residue was treated with water and the product was extracted with ether. The ether solution was washed with water, dried over sodium sulphate and solvent removed by evaporation. The residue was pure and does not require crystallization m.p. 64-65°C; yield – 20 mg (90%).

RESULTS AND DISCUSSION

The new dimethyl chremeno dihydrochalcone, crotaramin obtained as pale yellow solid, analysed for $C_{21}H_{22}O_4$ [M^+] m/z = 338. The uv absorption maxima at 266 and 306 nm suggested presence of dihydro chalcone system. The IR bands at 1630 cm^{-1} and 3230 cm^{-1} were attributed to chelated carbonyl and phenolic hydroxyl group. Two doublets at 5.59 δ and 6.63 δ (J=10 Hz) in ^{1}H NMR spectrum corresponds to olefinic hydrogens of

dimethyl chromene ring and a singlet at 13.79 δ at H-5' indicates chelated hydroxyl group. Another set of doublets for orthocoupled hydrogens were observed at 6.25 δ and 7.54 δ for H-8' and H-7', respectively.

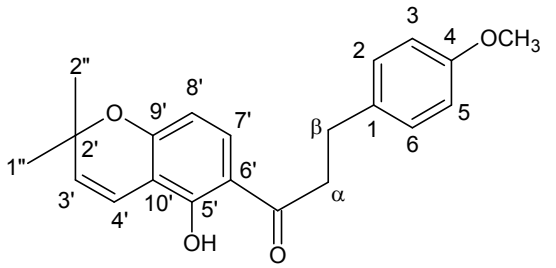
Table 1 : 2D-NMR Spectra data of Crotarmin

^{1}H	^{13}C	HMBC	Assignment
1.46	28.3	28.3; 77.7; 128.2	1", 2"
3.00	29.6	39.8; 129.3; 132.9; 203.9	β
3.19	39.8	29.6; 132.9; 203.9	α
3.80	55.3	158.1	4-OMe
5.59	128.2	77.7; 109.3	3'
6.32	108.3	109.3; 159.6	8'
6.73	115.8	77.7; 159.6; 159.7	4'
6.85	114.0	132.9; 158.1	3, 5
7.16	129.3	29.6; 129.3; 158.1	2, 6
7.53	130.8	159.6; 159.7; 203.9; 109.3	1', 7'

Two doublets with A_2B_2 pattern at 6.69 and 7.02 δ each integrating for two hydrogens indicate presence of monosubstituted B ring. Two upfield triplet signals at 2.26 δ and 3.11 δ correspond to α and β hydrogens as CH_2-CH_2 group. ^{13}C NMR spectrum of crotaramin confirms presence of methoxyl group and dimethyl chromene ring in it. A set of peaks at 128.2 δ and 115.8 δ characteristic of dimethyl chromene ring was observed,, which correspond to double bonded carbons of C-3' and C-4'. A down field signal at 109.3 δ corresponding to C-10' is due to isoprenyl group attached to it and a carbon signal at 203.9 δ is attributed to carbonyl group. Structure of crotaramin was established as a dihydro pyrano chromene from its ^{1}H NMR and ^{13}C NMR spectra. Assignments of signal at each proton and carbon was made by HMQC and HMBC experiments. Spectral data indicated presence of two aromatic rings, one cis double bond, two methyl groups and one methoxyl group and one carbonyl group. chelated hydroxyl group is present in ring-A at C-5' and carbonyl group is attached with C-6' of aromatic ring A and is also attached with 1, 4 substituted aromatic ring B through CH_2- CH_2 group. Proton at C-7' is correlated with C-9' and C-5' and carbonyl carbon as shown by HMBC experiments. Methoxy group located at C-4 (158.1 δ) is correlated with H-2 and H-6 as well as H-3 and H-5 protons as

shown by HMBC.

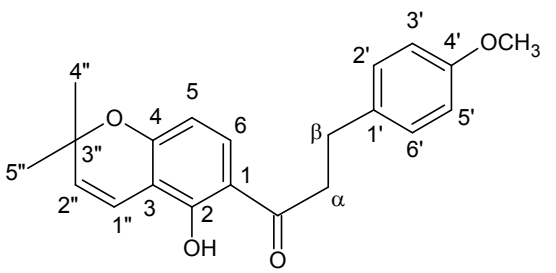
Thus, based on ^{13}C NMR and ^{2}D NMR data support the assignment of structure **(1)** to crotaramin.



Structure (1) : Crotaramin

Crotaramin acetate derivative, was obtained on acetylation of crotaramin, as colourless crystals, m. p. 82°C. It gave no colouration with neutral $FeCl_3$ suggesting the absence of free phenolic group. ^{1}H NMR spectrum of crotaramin acetate showed same data as in crotaramin, except a peak at 2.36 δ as singlet integrating for 3 protons assignable to 5'-acetoxy group.

Dihydro crotaramin obtained on reduction of crotaramin by catalytic hydrogenation transfer method was obtained as pure solid m. p. 65°C, yield 90%, ^{1}H NMR analysis showed four triplets in the upfield region; each integrating for two protons at 3.18 δ, 2.98 δ for α and β protons, 2.68 δ and 1.81 δ for H-1" and H-2". Appearance of additional pair of triplets revealed dehydrogenation of chromene ring of crotaramin. $^{13}CNMR$ data showed upfield signals at 16.3 δ and 31.8 δ for C-1" and C-2" indicating absence of unsaturation. All other carbon signals resonated in the same manner as carbons in crotaramin.



Structure (2) : Dihydrocrotaramin

By above spectral analysis the compound dihydro crotarmin has been assigned

structure **(2)** is analysed for 3", 3"-dimethyl chromano-2-hydroxy-4'-methoxy dihydrochalcone.

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