A Revised Structure for Crotaramosmin from *Crotolaria ramosissima*

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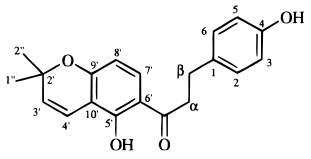
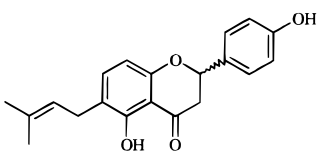
The structure of crotaramosmin has been reassigned to 1-(5-hydroxy-2,2-dimethyl-2*H*-chromen-6-yl)-3-(4-hydroxyphenyl)-propanone (**1**) as determined by extensive NMR investigation.

Several years ago, the isolation and structure assignment of crotoramosmin from *Crotolaria ramosissima* Roxb. (Fabaceae) was reported.[1] Due to limited spectroscopic facilities available at that time, this compound was erronously assigned to the flavanone structure **2** with unknown absolute configuration. We have reexamined this compound from the same plant source by modern NMR methods and found that it is rather a novel dihydrochalcone, namely, 1-(5-hydroxy-2,2-dimethyl-2*H*-chromen-6-yl)-3-(4-hydroxyphenyl)-propanone (**1**). Dihydrochalcones are rare natural products, and this is the first report of the isolation of such a compound from *Crotolaria* species.



1



2

The elemental formula of **1** was determined as $C_{20}H_{20}O_4$ by HRMS. The complete ^1H and ^{13}C connectivity was established by extensive use and interpretation of 2D ($^1H-^1H$) COSY, HMQC (one-bond $^{13}C-^1H$ correlation), and HMBC (long-range $^{13}C-^1H$ correlation) NMR spectra.[2] This provided unequivocally the atomic network for **1** (Table 1).

A few structural features are worth mentioning. The existence of a CH_2-CH_2 group was obvious; ^1H NMR signals appeared as triplets, and the corresponding carbons were identified as CH_2 by a DEPT experiment. This group is flanked by a *p*-hydroxylated phenyl group at one end and by a carbonyl at the other. This was confirmed by the carbonyl chemical shift of δ_C 206.1, a value that is much higher than in the carbonyl groups of chalcones but fits nicely in a dihydrochalcone.[3] The second phenyl group was found to be tetrasubstituted with two *ortho*-positioned hydrogens (H-7′ and H-8′). The pyran ring contains a *cis*-configurated double bond, as evidenced by the 10.0-Hz $^1H-^1H$ coupling constant and a dimethyl carbinol group (δ_C 78.8). It is attached to C-10′ as proven by the observation of a long-range correlation between H-4′ and C-5′, whereas the carbonyl group is fixed at C-6′ (H-7′/C=O correlation). The C-5′ hydroxy group is involved in a hydrogen bridge as shown by the ^1H chemical shift (measured in $CDCl_3$; δ_C 13.1).

Table 1. ^1H and ^{13}C NMR Chemical Shifts of **1**, Including $^{13}C-^1H$ Long-Range Correlations[a]

position	^1H	^{13}C	HMBC C → H
1		133.2	
2	7.02	130.5	4, 6, *β*
3	6.69	116.4	1, 4, 5
4		156.8	
5	6.69	116.4	1, 3, 4
6	7.02	130.5	2, 4, *β*
α	3.11	41.0	*β*, 1, C=O
β	2.86	30.9	α, 1, 2/6, C=O
C=O		206.1	
2′		78.8	
3′	5.59[b]	129.5	2′, 10′
4′	6.63[b]	116.7	2′, 5′
5′		160.9	
6′		114.7	
7′	7.54	132.7	5′, 9′, C=O
8′	6.25	109.4	6′, 10′
9′		160.6	
10′		110.3	
1″	1.39	28.7	2′, 3′, 2″
2″	1.39	28.7	2′, 3′, 1″
5′-OH[c]	13.1		

[a] HMBC, optimized to 7 Hz; solvent, CD_3OD. [b] Vicinal $^1H-^1H$ coupling constant $J = 10.0$ Hz. [c] Taken from $CDCl_3$ solution.

Experimental Section

General Experimental Procedures. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker DRX-500 spectrometer, and standard Bruker software for the 2D NMR experiments was used. The HRMS spectrum was obtained with a Varian MAT CH-5 mass spectrometer using electron impact.

Plant Material. As described previously.[1]

Extraction and Isolation. As described previously.[1]

Compound 1: ^1H and ^{13}C NMR data, see Table 1; EIMS *m/z* 324 (M^+, 20), 309 (100), 291 (5), 203 (29), 187 (9), 185 (9), 161 (4), 160 (5), 107 (17), 91 (3), 77 (7). HRMS, *m/z* (M^+), calcd for $C_{20}H_{20}O_4$, 324.13615; found 324.13557.

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References and Notes

(1) Khalilullah, M.; Sharma, V. M.; Rao, P. S.; Raju, K. R. *J. Nat. Prod.* **1992**, *55*, 229−231.
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