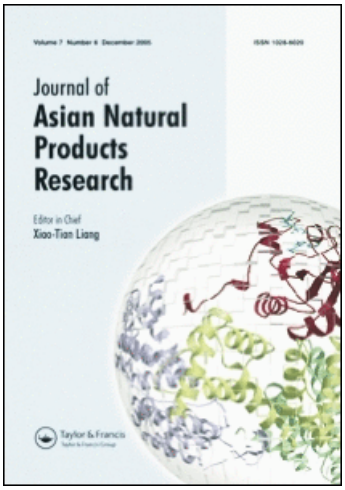

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

A new pregnane steroid from the stems of *Caralluma umbellata*

Kothamasu Suresh Babu[a]; Vidadala Rama Subba Rao[a]; Sriveda Vyasa Radhakrishnan[a]; Janaswami Madhusudana Rao[a]; Sakhamuri Siva Rambabu[a]
[a] Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad, India

To cite this Article Suresh Babu, Kothamasu , Rama Subba Rao, Vidadala , Vyasa Radhakrishnan, Sriveda , Madhusudana Rao, Janaswami and Siva Rambabu, Sakhamuri(2008) 'A new pregnane steroid from the stems of *Caralluma umbellata*', Journal of Asian Natural Products Research, 10: 11, 1013 — 1016
To link to this Article: DOI: 10.1080/10286020802277998
URL: http://dx.doi.org/10.1080/10286020802277998

Journal of Asian Natural Products Research
Vol. 10, No. 11, November 2008, 1013–1016

A new pregnane steroid from the stems of *Caralluma umbellata*

Kothamasu Suresh Babu, Vidadala Rama Subba Rao, Sriveda Vyasa Radhakrishnan, Janaswami Madhusudana Rao and Sakhamuri Siva Rambabu*

Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad, India

(*Received 4 December 2007; final version received 14 May 2008*)

A new pregnane steroid with an unusual formyl group (**1**) was isolated from the stems of *Caralluma umbellata*, together with three known steroid compounds. The structure of **1** was elucidated on the basis of spectral evidence including 2D NMR studies.

Keywords: *Caralluma umbellata*; *Boucerosia*; Asclepiadaceae; pregnane steroid

1. Introduction

Caralluma umbellata (syn. *Boucerosia*) is an erect, branching, succulent perennial herb growing wild in Tirumala forest and surrounding places of Andhra Pradesh, India. It grows to a height of about 1 foot to 2 feet and the roots are fibrous. The plant, belonging to the family Asclepiadaceae, is medicinally important and rich in pregnane glycosides, which may possess different biological activities [1]. In folkloric medicine, as well as in unani and Ayurvedic systems of medicine, the plants of *Caralluma* are being used for the treatment of diabetic patients and rheumatism [2]. The pregnane steroid isolated from *C. umbellata* was shown to possess anti-inflammatory activity. Carumbelloside-I (**3**), isolated from *C. umbellata*, exhibited significant analgesic activity and antimicrobial activity [3]. A survey of the literature revealed that species of the genus *Caralluma* have been investigated on alcoholic extracts and found to be a source of steroids, triterpenes, and steroidal glycosides [4–13]. The isolation and structural elucidation of three pregnane glycosides **2**, **3**, and **4** and one flavanone glycoside luteolin-4-*O*-neohesperidoside were reported from *C. umbellata* [14]. However, very few investigations were carried out on the extracts of non-polar solvents such as hexane and benzene. In order to search for any possible new compounds that could be extracted into non-polar solvents such as hexane and benzene, the present investigation was taken up and the results are reported in this paper.

2. Results and discussion

Compound **1** was isolated as a white powder. The molecular formula was deduced from the HREIMS analysis at *m/z* 365.2082 $[M + Na]^+$, ^{13}C NMR and DEPT experiments as $C_{22}H_{30}O_3$. The IR spectrum indicated two sharp bands at 1738 cm^{-1} (ester carbonyl) and 1707 cm^{-1} (carbonyl). The ^1H NMR spectrum of compound **1** showed one-proton singlet at δ 9.98, suggesting a typical formyl proton. Two doublets at δ 6.31 (H-6, $J = 5.5$ Hz) and 6.90 (H-7, $J = 5.5$ Hz), suggesting two olefinic protons. A multiplet at δ 2.85 indicated the

*Corresponding author. Email: sivarambabu_anu@yahoo.co.in

ISSN 1028-6020 print/ISSN 1477-2213 online

DOI: 10.1080/10286020802277998
http://www.informaworld.com

Table 1. ^{1}H and ^{13}C NMR spectral data of **1**.

No.	^{1}H NMR	^{13}C NMR
1	2.31 (m)	33.7
2	1.91 (m)	21.0
3	2.32 (m)	24.8
4	2.39 (m)	29.7
5	–	134.4
6	6.31 (d, $J = 5.5$ Hz)	119.6
7	6.90 (d, $J = 5.5$ Hz)	139.8
8	–	168.7
9	1.45 (m)	54.3
10	–	44.7
11	1.43 (m)	22.7
12	1.73 (m)	41.9
13	–	50.8
14	–	81.3
15	1.51 (m)	34.1
	1.97 (m)	–
16	1.22 (m)	23.9
17	2.50 (m)	64.4
18	1.01 (s)	16.3
19	0.91 (s)	14.3
20	–	212.8
21	2.51 (s)	28.7
22	9.98 (s)	188.2

presence of H-17, and three sharp singlets integrating each for three protons at δ 2.30, 1.01, and 0.91 indicated the presence of three methyls, suggesting the presence of the pregnane-type nucleus [15] except for the absence of the hydroxyl group at C-3. The ^{13}C NMR spectral data (Table 1) indicated the presence of 22 carbons, which were sorted by DEPT into three methyls, eight methylenes, five methines, and six quaternary carbons. The position of the *O*-formyl group was established by HMBC, where H-22 correlated with C-14 (Figure 2). Other major correlations are H-6 and H-4 with C-5 and H-6, H-7, and H-9 with C-8. The $^{1}H-^{1}H$ COSY correlations (Figure 2) between H-6 and H-7 suggested that the double bonds are in conjugation, and the *J* values clearly indicated the *cis* relationship. On the basis of the above evidence, the structure of **1** was determined as in Figure 1. These results were supported by the HSQC and HMBC experiments (Figure 2).

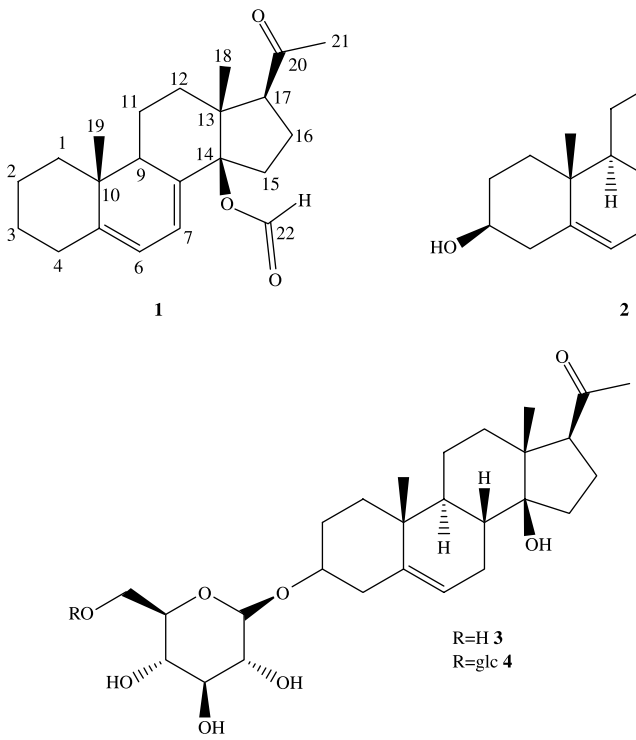

Figure 1. Structures of compounds **1**–**4**.

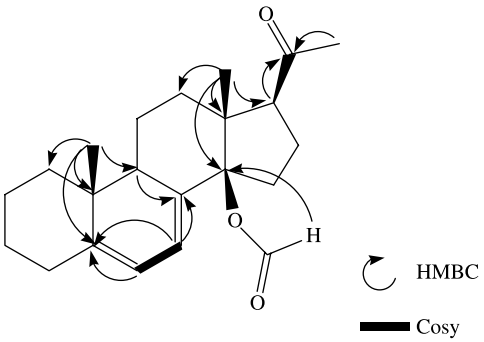

Figure 2. $^{1}H-^{1}H$ COSY correlations (bold lines) and key HMBC correlations (H → C) of **1**.

3. Experimental

3.1 General experimental procedure

Melting point was recorded on a Fisher–John apparatus. The specific rotation was recorded on a Perkin–Elmer precision Model-343. The IR spectra were recorded on an IFS-120H spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker 300 MHz, 75 MHz spectrometer, using TMS as an internal standard. ESIMS was recorded on a ZAB-HS mass spectrometer and HREIMS was recorded on the Agilent Technologies 6510 Q-TOF LC/MS. Column chromatography was performed on silica gel (100–200 mesh). TLC was carried out on coated silica gel G glass plates with a thickness of 1 mm (PF 254, art 7747, Merck). Solvents and reagents were purified according to standard procedures.

3.2 Plant material

The stems of *C. umbellata* (15 kg) were collected from the forests of Tirumala, Andhra Pradesh, India, in January 2007. It was identified by Dr K. Madhava Chetty, Department of Botany, Sri Venkateswara University, Tirupati. A voucher specimen of the plant is deposited in Herbarium, Department of Botany, with the accession number 1553.

3.3 Extraction and isolation

The air-dried stems of *C. umbellata* (50 g) was powdered and extracted with petroleum ether, benzene, chloroform, and methanol successively. The petroleum ether extract was evaporated under reduced pressure to obtain a residue (7.0 g). The residue was adsorbed on silica gel and subjected to column chromatography eluted with benzene and by mixtures containing increasing amounts of EtOAc. The fractions eluted at 2% EtOAc in benzene were collected separately, concentrated, and rechromatographed using silica gel column to obtain compound **1** (10 mg) in pure form.

3.3.1 Compound (*1*)

White powder, m.p. > 200°C, $[\alpha]_D^{20} = -190$ (*c* 0.006, $CHCl_3$); IR ν_{max} (KBr) (cm^{-1}): 1730 (formyl C═O), 1707 (C═O), 1630 (C═C), 1215 (C—O); ^{1}H NMR and ^{13}C NMR spectral data: see Table 1; HREIMS *m/z* 365.2082 $[M + Na]^+$ (calcd for $C_{22}H_{30}O_3Na$, 365.2087); ESIMS *m/z* 365 $[M + Na]^+$.

Acknowledgements

The authors are thankful to CSIR, UGC, New Delhi, and the Director of the IICT, Hyderabad for the financial support.

References

[1] K. Anitha, G. Jayalakshmi, P. Kiranmayee, and S. Siva Rama Babu, *I.C.C.E. Res. J. Chem. Envi.* **2**, 346 (2005).
[2] B.M. Sawant, T.D. Sayad, and S.D. Gayakwad, *J. Shivaji Univ. Sci.* **16**, 43 (1976).
[3] B.M. Sawant and T.D. Sayad, *J. Shivaji Univ. Sci.* **18**, 87 (1978).
[4] V.A. Castro, C. Garcia, A.G. Gonzalez, R. Hernandez, and E. Suarez, *Phytochemistry* **19**, 2210 (1980).
[5] T. Rudolf and M. Guentr, *Tetrahedron Lett.* **15**, 1359 (1967).
[6] A.R. Menon, K.M. Bhatti, and A.N. Menon, *J. Chem. Soc. Pakistan* **6**, 71 (1984).
[7] H. Nikaido, Y. Shimizu, and H. Mitsuhashi, *Chem. Pharm. Bull.* **15**, 725 (1967).
[8] K. Hayashi, I. Iida, Y. Nako, Y. Nakao, and K. Kaneko, *Phytochemistry* **27**, 3919 (1988).
[9] T. Tanaka, S. Tsukamoto, and K. Hayashi, *Phytochemistry* **29**, 229 (1990).
[10] M. Ramesh, Y.N. Rao, M.R. Kumar, and A.V.N. Apparao, *Ethanol Pharm. J.* **68**, 349 (1999).

[11] L.J. Lin, L.Z. Lin, R.R. Gil, G.A. Cordell, M. Ramesh, B. Reddy, and A.V.N. Appa Rao, *Phytochemistry* **35**, 1549 (1994).
[12] S.X. Qiu, L.Z. Lin, G.A. Cordell, M. Ramesh, B. Ravi Kumar, M. Radhakrishna, G.K. Mohan, B.M. Reddy, Y.N. Rao, B. Sirinivas, N.S. Thomas, and A.V.N. Apparao, *Phytochemistry* **46**, 333 (1997).
[13] V.U. Ahmed, K. Usmanghani, and H. Rizwani, *J. Nat. Prod.* **51**, 1092 (1988).
[14] M. Ramesh, Y.N. Rao, M.R. Kumar, G.K. Mohan, B.R. Kumar, A.V.N. Apparao, N.R. Krishna, and B.M. Reddy, *Biochem. Syst. Ecol.* **27**, 85 (1999).
[15] V. Anjaneyulu and B.H. Babu, *Indian J. Chem.* **29B**, 683 (1990).