J. Indian Chem. Soc.,
Vol. 86, June 2009, pp. 654-656

NOTE

Gangetial, a new pterocarpan from the roots of *Desmodium gangeticum*

Medapati Vijaya Varaprasad[a], Kedike Balakrishna[b], Ethirajan Sukumar[c] and Amarendra Patra[d]*

[a]Sree Vidyaniketan College of Pharmacy, A. Rangampet, Via Tirupathi-517 102, Andhra Pradesh, India

[b]Central Research Institute for Siddha (CCRAS), Arumbakkam, Chennai-600 106, India

[c]Department of Applied Sciences, Higher College of Technology, P.B. 74, P.C. 133, Muscat, Sultanate of Oman

[d]Department of Chemistry, University College of Science, 92, Acharya Prafulla Chandra Road, Kolkata-700 009, India

E-mail : amarendra@sify.com

Manuscript received 17 October 2008, revised 10 February 2009, accepted 11 February 2009

Abstract : A new pterocarpan gangetial (1) has been isolated from the chloroform extract of the roots of the plant *Desmodium gangeticum* together with gangetinin. The structure of the new compound was elucidated as (5b*R*,10b*R*)-5b,10b-dihydro-8-hydroxy-5-methoxy-2,2-dimethyl-2*H*,11*H*-benzo[4,5]furo[2,3-*d*]pyrano[3,2-*g*]chromene-7-carbaldehyde based on the chemical and spectroscopic data.

Keywords : *Desmodium gangeticum*, Leguminosae, pterocarpan, gangetial, (5b*R*,10b*R*)-5b,10b-dihydro-8-hydroxy-5-methoxy-2,2-dimethyl-2*H*,11*H*-benzo[4,5]furo[2,3-*d*]pyrano[3,2-*g*]chromene-7-carbaldehyde.

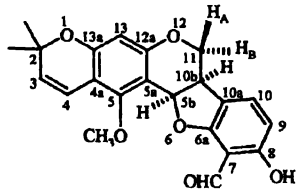
Introduction

Desmodium gangeticum (Linn.) DC. (Syn : *Hedyserum gangeticum* Linn.; Family : Leguminosae) known as *Orilai* in Tamil and *Salaparni* in Sanskrit, is a common shrub, 2–4 ft. high, found throughout India ascending to 5000 ft. in the Himalayas. It grows as undergrowth of the semi-deciduous forests and distributed in tropical Africa, Sri Lanka, South-East Asia, China and Malaysia[1,2]. The root of the plant possesses cardiotonic, diuretic, laxative and nervine properties besides having use in fever, cough, breathing difficulty, dysentery, thirst and vomiting. It is also employed in the treatment of insanity and ulcer[2]. The roots enter into the formulation of the Ayurvedic elixir *Dasamularishtam*[3].

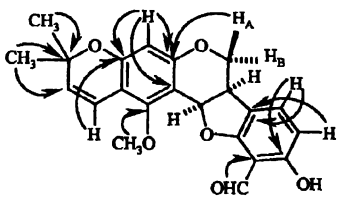
Pharmacological studies on the aqueous extract of the roots showed antiinflammatory, antibacterial, antifungal and diuretic activities besides significant inhibitory effects on isolated frog's heart, relaxant effect on smooth muscles of the intestine of the dog, and on rabbit and rat's uterus[4]. Gangetin, the major pterocarpan present in the roots, exhibited anti-implantation activity in female rats[5] and caused impairment of fertility in male rats[6]. The compound also revealed significant anti-inflammatory and analgesic activities in rats and did not show any toxicity up to 7.0 g/kg body weight[7]. The methanol extract of the plant exhibited antileishmanial activity[8]. Earlier workers have reported the isolation of β-carboline alkaloids, flavonoids, isoflavonoids, pterocarpans, phytosterols, lipids and phospholipids from this plant[9,10] In this communication, the isolation and structure elucidation of a new pterocarpan gangetial (1) from the roots of the plant is reported.

Results and discussion

Gangetial (1), $C_{22}H_{20}O_6$, M^+ 380 responded to colour tests for phenol and aldehyde. It showed UV maxima at 230, 274 and 363 nm, the regions characteristic of pterocarpans[9e] The IR spectrum showed bands at 3400 (chelated phenolic groups), 1640 (aromatic chelated aldehyde), 1600, 1590, 960, 935, 870, 785 (aromatic) cm^{-1}. In the ^1H NMR spectrum, the presence of 2,2-dimethylpyran ring system was shown by two methyl singlets at δ 1.38 and 1.41



1



2

together with double doublets at δ 5.60 and 6.55 (*J* 10 Hz each) corresponding to H-3 and H-4. The aromatic proton H-13 appeared as a singlet at δ 6.24. Two other aromatic protons appeared as *ortho*-coupled doublets at δ 7.33 and 6.44 (*J* 8.3 Hz each) corresponding to H-10 and H-9, respectively. The ^{1}H NMR spectrum further displayed a three-proton singlet at δ 3.97 accounting for the presence of one methoxy group. The C-7 aldehyde proton appeared as a singlet at δ 10.18 while the chelated hydroxyl resonated as a singlet at δ 11.15. The presence of proton signals at δ 3.65 (t, H_A-11) and 4.20 (dd, H_B-11) were in consonance with the presence of a set of non-equivalent methylene protons. The ring junction proton at C-10b resonated as a multiplet at δ 3.45 while H-5b absorbed at δ 5.83 as a one-proton doublet (*J* 7.8 Hz). The ^{1}H NMR data of **1** was similar to that of gangetin reported from the plant earlier, where a prenyl side-chain is present at C-7 instead of the aldehyde group in **1**. The replacement by -CHO caused *para*-hydrogen (H-10) resonance to move downfield to δ 7.33.

The ^{13}C NMR spectrum of **1** showed signals for three methyl groups (two of quaternary carbon at C-2 and another of -OCH_3 group at C-5) and one methylene carbon (C-11) at δ 66.2. The spectrum contained eight CH resonances for one aldehyde, three aromatic, two of the chromene ring and two of the ring junction carbon atoms. In the mass spectrum of **1**, the parent ion peak was observed at *m/z* 380. The ready loss of quaternary methyl at C-2 gave the ion peak at *m/z* 365 (100%). The di-alpha configuration in pterocarpans is usually indicated by the large negative rotation[11,12]. On a similar contention, the stereochemistry at B/C junction for **1** is given as 5b*R*, 10b*R* with both the hydrogens at the ring junction having α-orientation on the basis of the negative rotation observed. Further the 5*bR*, 10*bR* di-alpha configuration has biogenetic support also as all the pterocarpans so far reported from *D. gangeticum* have the same configuration at the B/C ring junction.

The above facts are in favour of the assigned structure for compound **1** as (5b*R*,10b*R*)-5b,10b-dihydro-8-hydroxy-5-methoxy-2,2-dimethyl-2*H*,11*H*-benzo[4,5]furo[2,3-*d*]pyrano[3,2-*g*]chromene-7-carbaldehyde. The 2D-COSY (^{1}H-^{13}C) correlations optimized for one-bond $^1J_{C-H}$ couplings conclusively identified the protonated carbon signals. The long range ^{13}C-^{1}H correlations (optimized for $^3J_{C-H}$ 7 Hz) displayed in structure **2** lent conclusive support to the structure **1** assigned for gangetial.

Experimental

Melting point (°C) is uncorrected. UV and IR spectra were recorded on Shimadzu and Perkin-Elmer spectrophotometers, respectively. ^{1}H and ^{13}C NMR spectra were obtained on Bruker AM 300L instrument operating at 300.13 and 75.47 MHz, respectively. The electron-impact mass spectrum was recorded on a Shimadzu instrument at 70 eV by the direct inlet method.

The roots of *D. gangeticum* were collected in Chennai city in the month of January and authenticated by Dr. S. Usman Ali, Head, Department of Pharmacognosy, Central Research Institute for Siddha (CCRAS), Chennai where a voucher specimen has been deposited.

Shade dried and coarsely powdered roots of the plant (*ca.* 2.0 kg) were exhaustively extracted with chloroform by cold percolation method. After 72 h, the solvent was decanted and distilled over boiling water-bath. Final traces of the solvent were removed *in vacuo* and the extract (12.0 g) was column chromatographed over silica gel (100–200 mesh). The column was eluted with solvents of increasing polarity. Elution of the column with *n*-hexane : benzene (1 : 1) yielded gangetinin (m.p. 136°), previously reported from this plant[10].

The later part of the elution with the above solvent-mixture afforded a pale-yellow amorphous compound

named as gangetial (**1**) which could not be crystallized but gave a single spot on TLC (R_f 0.5 in *n*-hexane : ethyl acetate, 9 : 1) and turned reddish-brown on spraying 1 : 1 H_2SO_4 and on subsequent heating to 100° for 5 min. It had $[\alpha]_D^{25}$ -290° (*c* 0.4, $CHCl_3$) (Found : C, 69.49; H, 5.28. $C_{22}H_{20}O_6$ requires : C, 69.47; H, 5.26%).

Gangetial exhibited UV λ_{max}(MeOH) nm : 230, 274, 312 (sh), 363; (+$AlCl_3$) 230, 286, 435; (+$AlCl_3$ + HCl) 232, 278, 366; IR ν_{max}(KBr) cm^{-1} : 3400, 2905, 2830, 1640, 1600, 1590, 1560, 1470, 1440, 1330, 1310, 1290, 1245, 1185, 1130, 1075, 1050, 960, 935, 870, 785; ^1H NMR ($CDCl_3$) δ ppm : 1.38, 1.41 (3H each, s, 2 × Me), 3.45 (1H, m, H-10b), 3.65 (lH, t, *J* 10 Hz, H_A-11), 3.97 (3H, s, -OMe), 4.20 (lH, dd, *J* 6.0 Hz and 10 Hz, H_B-11), 5.60 (lH, d, *J* 10 Hz, H-3), 5.83 (lH, d, *J* 7.8 Hz, H-5b), 6.24 (lH, s, H-13), 6.44 (lH, d, *J* 8.3 Hz, H-9), 6.55 (lH, d, *J* 10 Hz, H-4), 7.33 (lH, d, *J* 8.3 Hz, H-l0), 10.18 (lH, s, CHO), 11.15 (lH, s, -OH); ^{13}C NMR ($CDCl_3$) δ ppm : 27.6 and 28.1 (2 × CH_3), 38.3 (C-10b), 63.7 (OCH_3), 66.2 (C-11), 76.6 (C-2), 78.0 (C-5b), 101.1 (C-13), 105.8 (C-5a), 107.4 (C-7), 108.7 (C-9), 109.5 (C-4a), 116.5 (C-4), 118.0 (C-10a), 128.7 (C-3), 133.0 (C-10), 155.9 (C-13a), 156.8 (C-12a), 157.1 (C-5), 162.0 (C-8), 163.0 (C-6a), 192.1 (CHO) ; EIMS (*m/z*, % rel. int.) : 380 (M^+, 28), 379 (M-l, 1.5), 365 (M-CH_3, 100), 351 (M-CHO, 1.0), 349 (M-OCH_3, 1.0), 243 (1.0), 228 (2.2), 175 (7.7), 174 (2.4), 162 (1.0), 161 (2.3).

Acknowledgement

The authors are grateful to the Instrumentation Centre, CAS on Natural Products, Department of Chemistry, University of Calcutta for the NMR spectra.

References

1. (a) K. R. Kirtikar and B. D. Basu, "Indian Medicinal Plants", Vol. I, International Book Distributors, Dehra Dun, 1999; (b) "The Wealth of India", Vol. III, Publications and Information Directorate (CSIR), New Delhi, 1952.
2. V. V. Sivarajan and I. Balachandran, "Ayurvedic Drugs and Their Plant Sources", Oxford and IBH Publishing Company Private Limited, New Delhi, 1994.
3. K. M Nadkarni, "Indian Materia Medica", Popular Prakashan, Bombay, 1976.
4. P. Prema, MD Thesis, University of Kerala, Trivandrum, 1968.
5. N. R. Pillai, M. Alam and K. K. Purushothaman *J. Res. Ayur. Siddha*, 1981, **11**, 349.
6. P. Latha, S. Govindasamy and K. Balakrishna, *Phytother. Res.*, 1997, **11**, 372.
7. D. Ghosh and A. Anandakumar, *Indian J Pharmacol.*, 1983, **15**, 391.
8. M. M. Iwu, J. E Jackson, J. D. Tally and D. L. Klayman, *Planta Med.*, 1992, **58**, 436.
9. (a) P. K Banerjee and S. Ghosal, *Aust. J. Chem.*, 1969, **22**, 275; (b) S. Ghosal and P. K. Banerjee, *Aust. J. Chem.*, 1969, **22**, 2029; (c) O. N. Ogbeide and M. Parvez, *J. Liquid Chromatog.*, 1992, **15**, 2989; (d) J. L. Ingham and P. M. Dewick, *Z. Naturforsch.*, 1984, **39C**, 531; (e) K. K. Purushothaman, V. M. Kihore, V. Narayanaswamy and J. D. Connolly, *J. Chem. Soc. (C)*, 1971, 2420; (f) M. Behari and A. Varshney, *Indian Drugs*, 1986, **23**, 434; (g) S. C. Rastogi, G. D. Tiwari, K. C. Srivastava and R. D. Tiwari, *Planta Med.*, 1971, **20**, 131; (h) B. K. Arasathi and J. D. Tiwari, *J. Am. Pharm. Assn.*, 1955, **44**, 625.
10. K. K. Purushothaman, S. Chandrasekaran, K. Balakrishna and J. D. Connolly, *Phytochemistry*, 1975, **14**, 1129.
11. K. G. R. Pachler and W. G. E. Underwood, *Tetrahedron*, 1967, **23**, 1817.
12. A. Pelter and P. I. Amenechi, *J. Chem. Soc.*, 1967, 887.