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GLABONE, A NEW FURANOFLAVONE FROM *PONGAMIA GLABRA*

P. DAS KANUNGO, A. GANGULY, A. GUHA, ANJAN BHATTACHARYYA and N. ADITYACHAUDHURY

Department of Agricultural Chemistry and Soil Science, Bidhan Chandra Krishi Viswavidyalaya, Kalyani-741 235, West Bengal, India

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Key Word Index—*Pongamia glabra*; Leguminosae; flowers; faranoflavone; glabone.

Abstract—A new furanoflavone, glabone, has been isolated and identified as 4′-methoxy-6,7-furanoflavone from the flowers of *Pongamia glabra*.

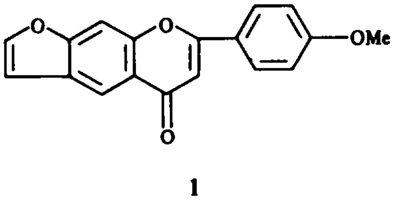
INTRODUCTION

The plant *Pongamia glabra* is reputed to possess medicinal properties [1, 2]. Recent investigations on the oil obtained from the seeds of *P. glabra* indicated that the oil contains some toxic principles which exhibit deleterious effects on chicks [3]. Several furanoflavones, flavones and chalcones have already been isolated from the seeds, flowers and aerial parts of *P. glabra* [4–9]. As a part of our research programme on plants possessing biological activity, we have investigated the flowers of *P. glabra*. In this communication we report the isolation and structure elucidation of a new furanoflavone designated as glabone (**1**).

RESULTS AND DISCUSSION

Glabone (**1**) crystallized from benzene–petrol as pale yellow needles, analysed for $C_{18}H_{12}O_4$ ($[M]^+$ at *m/z* 292), mp 170–171°. The colour reactions (green ferric colour; positive Shinoda test) and UV spectrum (λ_{max}^{EtOH} 215, 268, 305 and 330 nm) together with the appearance of a singlet (H-3, δ6.63) in the 80 MHz ^{1}H NMR spectrum confirmed the presence of a flavone system [5]. The IR spectrum also disclosed the presence of a conjugated carbonyl function (1645 cm^{-1}), a benzofuran ring and a *p*-disubstituted benzene ring (825 cm^{-1}), [4, 5]. Functional group analysis revealed the presence of a methoxy group (δ4.15, 3H, *s*). In angular furanoflavones the H-6 appeared around δ7.55–7.63 as double doublets and the H-5 signals around 7.89–8.20 as doublets [5], whereas in linear furanoflavones the H-5 and H-8 appear at 7.28 and 7.39, respectively, as sharp singlets [4, 10, 11]. The appearance of two sharp singlets at δ7.29 (H-5) and 7.45 (H-8) in the NMR spectrum of glabone provided strong evidence in favour of a linear furanoflavone system.

The mass spectrum showed two important peaks of *m/z* 264 $[M-28]^+$ and 160 $[M-132]^+$ corresponding to the loss of CO and $[CH_3OC_6H_4C\equiv CH]^+$ fragments from the M^+ peak. The loss of the $[CH_3OC_6H_4C\equiv CH]^+$ ion fragment at *m/z* 160 showed the presence of one methoxyl group in the B-ring of glabone. On the basis of the spectral evidence the structure of glabone was assigned as **1**.



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EXPERIMENTAL

The plant material used in this investigation was obtained from the United Chemicals and Allied Products, 10 Clive Row, Calcutta 1, India, where a voucher specimen is preserved.

Dried flowers (2 kg) of *Pongamia glabra* were extracted with petrol (60–80°) and the concd extract chromatographed over silica gel. C_6H_6 eluted a thick oily mass which on rechromatography over silica gel yielded glabone (**1**) (yield: 0.001 %).

Glabone (**1**), mp 170–171°, crystallized from C_6H_6–petrol, analysed for $C_{18}H_{12}O_4$ ($[M]^+$ at *m/z* 292); UV λ_{max}^{EtOH} nm: 215, 268, 305 and 330. IR ν_{max}^{KBr} cm^{-1}: 1645 (conjugated carbonyl), 1610, 1540, 1460, 1370, 1280, 1065 (benzofuran-ring), 825 (*p*-disubstituted benzene ring) and 755. MS *m/z*; 292 $[M]^+$, 264 $[M-CO]^+$, 160 $[M^+-MeOC_6H_4C{=}CH]^+$, 132 $[CH_3OC_6H_4C{\equiv}CH]^+$, and or $[160-CO-]^+$, 117 (132−Me] along with other peaks at 291, 263, 246.

^{1}H NMR (80 MHz, $CDCl_3$): δ4.15 (*s*, 3H, −OMe), 6.63 (*s*, 1H, H-3) 7.01–6.97 (*dd*, 1H, *J* = 2.4 Hz, H-3″), 7.29 (*s*, 1H, H-5), 7.43–7.32 (*m*, 2H, H-5′ and H-3′), 7.45 (*s*, 1H, H-8), 7.56–7.53 (*d*, *J* = 2.4 Hz, H-2″), 7.92–7.79 (*m*, 2H, H-2′ and H-6′).

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PEPTIDE ALKALOIDS FROM *ZIZYPHUS* SPECIES

S. DEVI, V. B. PANDEY, J. P. SINGH* and A. H. SHAH†

Department of Medicinal Chemistry, Institute of Medical Sciences, Banaras Hindu University, Varanasi, India; †Research Centre, College of Pharmacy, King Saud University, Riyadh-11451, Saudi Arabia

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Key Word Index—*Zizyphus nummularia; Z. jujuba; Z. xylopyra;* Rhamnaceae; alkoloids; frangufoline; amphibine-H; nummularine-K; nummularine-R.

Abstract—The isolation of cyclopeptide alkaloids, frangufoline from *Zizyphus jujuba* and *Z. nummularia*, amphibine-H and nummularine-K from *Z. xylopyra* and nummularine-R, a new 13-membered cyclopeptide alkaloid, from *Z. nummularia* is reported. The structure of the new alkaloid was elucidated by spectroscopic methods and by chemical degradation.

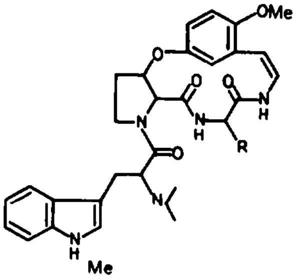
In continuation of our search for peptide alkaloids [1] from *Zizyphus* species we have re-examined the stem bark of, *Z. nummularia*, *Z. jujuba* and *Z. xylopyra*, Repeated CC and prep. TLC of the alkaloidal fraction resulted in the isolation of the cyclopeptide alkaloids, frangufoline [2] from *Z. jujuba* and *Z. nummularia*; amphibine-H [3] and nummularine-K [4] from *Z. xylopyra* and nummularine-R (**1**) a new 13-membered cyclopeptide alkaloid from *Z. nummularia*.

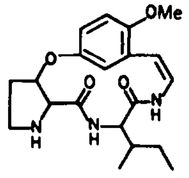
The absorption bands in the IR and UV spectra and the mass fragmentation pattern of nummularine-R (**1**), mp 134–135°, $C_{33}H_{41}N_5O_5$ ($[M]^+$ 587.3116) were exactly same as those reported for sativanine-E (**2**) [5]. The essential difference between the two was observed by acid and alkali hydrolysis. Acid hydrolysis of **1** with 6 N HCl furnished isoleucine whereas sativanine-E gave leucine. Hydrolysis of **1** with $Ba(OH)_2$ gave *N*,*N*-dimethyltryptophan. The attachment of isoleucine bound to the nitrogen of the styrylamine function in **1** was proved by partial hydrolysis after heating with HCl-HOAc-H_2O (1:1:1) when **1** furnished a major compound (**3**) which on further hydrolysis with 6 N HCl gave isoleucine. Based on these findings, the structure of nummularine-R is settled as **1** which differs from that of sativanine-E (**2**) in having a isoleucine unit instead of leucine as the amino acid bound to the nitrogen of the styrylamine function. Nummularine-R is thus a new member in the growing list of peptide alkaloids.

The structure of the known alkaloids was established by spectral evidence, hydrolysis and direct comparison with authentic samples. These alkaloids have not previously been reported from the above species.

EXPERIMENTAL

Plants were collected from Mirzapur District of Uttar Pradesh, India and identified by Prof. S. K. Roy, Dept. of Botany, Banaras Hindu University. The crude alkaloids were extd by usual methods [6]. Extensive chromatography and repeated prep. TLC of the crude bases of *Z. nummularia* (5 kg) with $CHCl_3$–Me_2CO–MeOH (10:6:1) and $CHCl_3$–MeOH (20:1) furnished frangufoline (10 mg), mp 233–235°, and compound **1** (21 mg), mp 134–135°. **1** showed IR $\nu_{max}^{CHCl_3}$ 3385, 3251 (-NH), 2775 (-NMe), 1670 (amide), 1630 (C=C), 1592, 1490 (aromatic), 1040 and 1200 (aryl ether) cm^{-1}; UV λ_{max}^{MeOH} 320, 268 nm^{-1}





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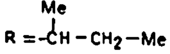

$R = -\overset{Me}{\overset{|}{C}}H-CH_2-Me$

(2) $R = -CH_2-CH-(Me)_2$

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* Present address: Department of Chemistry, S. G. R. (P.G.) College, Dobhi, Jaunpur, India.