TABLE 3 – VALUES OF $\Delta\mu_1^{0\#}$ AND $\Delta\mu_2^{0\#}$ IN UREA-WATER AND THIOUREA-WATER AT 303 K

Solvent % (w/w)	$\Delta\mu_1^{0\#}$ kJ mol^{-1}	$\Delta\mu_2^{0\#}$ kJ mol^{-1}
Chromium sulphate in urea-water		
11.52	11.39	46.75
20.31	11.62	54.03
29.64	11.90	53.58
36.83	12.16	59.52
Chromium sulphate in thiourea-water		
3.0	11.38	26.18
6.0	11.42	24.38
9.0	11.46	24.78
12.0	11.48	28.43

solvent compositions in each system. This implies that $\Delta\mu_2^{0\#}$ may be determined by B-coefficient and $(\overline{V}_1^0 - \overline{V}_2^0)$ term. The positive values of $\Delta\mu_2^{0\#}$ in both the systems, suggest that flow rate is not favoured by urea or thiourea content. Moreover, the value of $\Delta\mu_2^{0\#}$ has been found to be greater than that of $\Delta\mu_1^{0\#}$ in both the systems at 303 K, again conforming our conclusions from molar volume and viscosity data that chromium sulphate acts as a structure-maker/promotor in the entire range of solvent composition of urea-water and thiourea-water.

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Auranamide—A Phenylalanine Derivative from *Grangea maderaspatana* Poir.

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IN persuance of our interest in Indian Compositae, we have recently reinvestigated *G. maderaspatana* and reported several clerodane, *nor*-clerodane, *seco*-clerodane, *nor-seco*-clerodane derivatives alongwith phenylalanine, hardwickiic and strictic acid derivatives[1]. The phenylalanine derivative has been identified as auranamide (**1**) by Banerji and Ray[2]. Subsequently, Talapatra *et al.*[3] obtained the same compound and designated it as anabellamide. Previous work on this plant led to the isolation of a number of clerodane derivatives, polyacetylenes, flavones[4,5], chondrillasterol and chondrillasterone[6].

Experimental

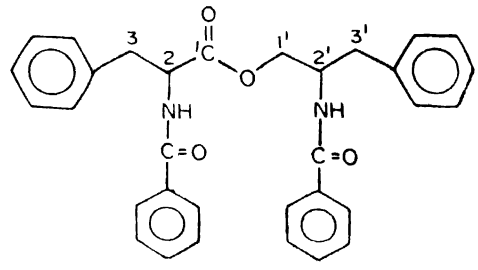
The air dried aerial parts (2 kg) of *G. maderaspatana* (obtained from M/s United Chemicals and Allied Products, Calcutta) were extracted with Et_2O-petrol-MeOH (1 : 1 : 1) mixture for 24 h in cold and the extract was concentrated under reduced pressure giving a greenish mass which was defatted by dissolving in MeOH and leaving overnight at 0°. The concentrated extract was column chromatographed over silica gel (B.D.H.; 60 – 120 mesh) and following four fractions were collected: fraction-1 (petrol), fraction-2 (petrol-Et_2O, 3 : 1). fraction-3 (petrol-Et_2O, 1 : 1) and fraction-4 (Et_2O). Fraction-1 furnished α-humulene (40 mg). Fraction-2 was a complex mixture and separated on PTLC (SiO_2, PF 254) using C_6H_6-CH_2Cl_2 (1 : 1) solvent mixture affording phytol (200 mg), 3-hydroxy-8-acetoxy-pentadeca-1,9,14-trien-4,6-diyne (10 mg), lupeol (40 mg) and a mixture of diterpene acids (400 mg) which on subsequent methylation with ethereal CH_2N_2 and hplc separation (MeOH-H_2O, 9 : 1) over RP 18 (analytical column) gave methyl-10-*epi*-nidoresedoate (30 mg; R_t 11.8 min), methyl strictiate (100 mg; R_t 12.7 min), a mixture of methyl esters of centipedic and nidoresedic acids (170 mg; R_t 15.0 min) and methyl hardwickiate

(100 mg ; R_t16.6 min). Fraction-3 on prep.-tlc (C_6H_6-CH_2Cl_2-Et_2O, 4.5 : 4.5 : 1) yielded 3,8-dihydroxypentadeca-1,9,14-trien-4,6-diyne (6 mg), *p*-hydroxybenzoic acid (14 mg) and a complex mixture of diterpene lactones. The latter was treated with CH_2N and separated by hplc (MeOH-H_2O, 9 : 1) giving 15-methoxy-16-oxo-15,16*H*-strictic acid methyl ester (20 mg ; R_t 6 6 min), 15-methoxy-16-oxo-15,16*H*-hardwickiic acid methyl ester (30 mg ; R_t 7.0 min), 15-methoxy-16-oxonidoresedic acid methyl ester (16 mg ; R_t 7.2 min), methyl *nor*-strictiate 24 mg ; R_t 7.9 min), methyl *nor*-hardwickiate (10 mg ; R_t 9.4 min) and methyl-2α-acetoxyhardwickiate (42 mg ; R_t 12.4 min). Fraction-4 separated on tlc (C_6H_6-CH_2Cl_2-Et_2O, 1 : 1 : 1) yielded 5,3′-dihydroxy-3,6,7,4′,5′-pentamethoxyflavone (130 mg ; R_f 0.33). 16-oxo-15,16*H*-hardwickiic acid (12 mg ; R_f 0.35), 15-methoxy-16-oxo-15,16*H*-strictic acid (20 mg ; R_f 0.30), (−)auranamide (**1**, 14 mg ; R_f 0 40) and 5-hydroxy-3, 6, 7, 3′, 4′, 5′-hexamethoxyflavone (40 mg ; R_f 0 42).

Ir spectra ($CHCl_3$) were recorded on a Perkin-Elmer 337 spectrophotometer, ^{1}H nmr spectra ($CDCl_3$) on a Bruker WM400 (400 MHz) spectrometer and mass spectra on a Varian MAT 711 (70 eV) instrument.

Results and Discussion

Auranamide (**1**) was obtained as a colourless solid, m.p. 203 – 04°, $C_{32}H_{30}O_4N_2$, [M^+] 506.2200 $[\alpha]_D^{24°}$ −35° ($CHCl_3$ 0.05).



1

Its ir spectrum displayed strong carbonyl bands at 1 740 (COOR), 1 40 (CONH) and 1 600 cm^{-1}. The ^{1}H nmr spectrum (400 MHz, $CDCl_3$) was in agreement with the reported data[2]. The mass fragmentation pattern was identical to that reported for auranamide[2]. The identity of physical and spectroscopical properties established that our compound was auranamide (**1**). Since the rotation was negative and similar to that reported for auranamide the configuration at both chiral centres was *S* as established earlier by the synthesis of auranamide[2].

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Fruit Constituents of *Physalis minima* var. *indica* and One-step Conversion of Physalin B to 6-Epiphysalin G Acetate

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In continuation of our search for withasteroids from *Physalis* species[1-3], we now report the chemical constituents of the fruits of *Physalis minima* var. *indica*, an annual weed of this region which differs from *Physalis minima* mainly by its more glabrescent leaves and distinctly five-angular fruiting calyx[4].

Column chromatography of the petroleum ether extract of the fruits of *P. minima* var. *indica* resulted in the isolation of two constituents. The first constituent crystallised from benzene as pale yellow needles, m.p, 173°, and analysed for the molecular formula, $C_{18}H_{16}O_7$ (M^+, m/z 344). It was recognised to be a flavonol from its uv spectral characteristics (vide Experimental). Its ^{1}H nmr spectrum showed the presence of two *meta*-coupled aromatic hydrogens (δ 6.35 and 6.45, 1H, d, *J* 2 Hz each), a 1,2,4-trisubstituted-phenyl nucleus (δ 6 95, 1H, d, *J* 9.1 Hz ; 7.73, 1H, dd, *J* 9 1, 2.2 Hz ; 7.64, 1H, d, *J* 2.2 Hz) and three methoxyl groups (δ 3 87, 6H, s ; 3.99, 3H, s). The compound gave a crystalline diacetate, m.p. 172 – 74°, whose ^{1}H nmr spectrum showed additionally two 3H singlets at δ 2 35 and 2.45 for two acetoxy groupings. The data suggested the isolated flavonol to be a trimethyl ether of quercetin. The locations of the methoxyl groups in the flavone nucleus were considered to be 3, 7 and 4′ from its uv spectral behaviour (vide Experimental) in presence of diagnostic shift