[8, 9] or a gossypetone test [10], the negative results jointly suggesting that C-5′ is substituted by the methoxyl group; this was also supported by the MS of **2**. The second OH was placed at C-4′ adjacent to the carbonyl, to explain the solubility of **2** in aq. Na_2CO_3. Consequently, prosogerin-B(**2**) was given constitution 2′,4′-dihydroxy-5′-methoxy-3,4-methylenedioxychalkone (**2**) which was confirmed by the synethesis of its 4′- ethyl ether (**2a**) [7].

EXPERIMENTAL

Prosogerin-A crystallized from EtOH–Me_2CO as light yellow needles, mp 242° (d); gave positive Mg/HCl and Labat (gallic acid/H_2SO_4) tests; UV (MeOH): 270, 350 nm; + NaOAc 270, 350 nm. MS: 312 (M^+), 297, 284, 269, 166, 151 and 146 (Found: C, 65.0; H, 3.7. $C_{17}H_{12}O_6$ requires: C, 65.38; H, 3.87%). Acetylation of **1** with Ac_2O/Py gave **1a**, colourless needles from EtOAc–petrol, mp 226–27° (Found: C, 64.3; H, 3.8. $C_{19}H_{14}O_7$, requires: C, 64.40; H, 3.98%). PMR δ, $CDCl_3$: 2.34 (3H, *s*, —$OCOCH_3$), 3.90 (3H, *s*, —OCH_3), 6.05 (2H, *s*, —O—CH_2—O—), 6.64 (1H, C-3-H), 6.93 (1H, J = 9 Hz, C-5′-H), 7.22 (1H, C-8-H), 7.27 (2H, *m*, C-2′-H and C-6′-H), 7.66 (1H, *s*, C-5-H).Ethylation of **1** with Et_2SO_4 (1 mol)/K_2CO_3 in Me_2CO yielded **1b**, colourless amorphous solid from EtOAc–petrol, mp 227–28° (Found: C, 66.7; H, 5.0. $C_{19}H_{16}O_6$ requires: C, 67.05; H, 4.75%).

Prosogerin-B crystallized from EtOAc–petrol as yellow micro-prisms, mp 186–87°; UV (MeOH): 285, 370 nm; + $AlCl_3$ 300, 395 nm; + $AlCl_3$ + HCl 295, 395 nm. + NaOAc 295, 410 nm. MS: 314 (M^+), 167, 166, 151 and 148 (Found: C, 65.0; H, 4.8. $C_{17}H_{14}O_6$ requires: C, 64.96; H, 4.49%). PMR (δ, $CDCl_3$): 3.89 (3H, *s*, —OCH_3), 5.99 (2H, *s*, —O—CH_2—O—), 6.57 (1H, C-3′-H), 6.88 (2H, *m*, C-5-H and C-α-H), 7.28 (3H, *m*, C-2-H, C-6-H and C-6′-H), 7.35 (1H, C-β-H). Ethylation of **2** with Et_2SO_4 (1 mol)/K_2CO_3 in Me_2CO gave **2a**, yellow prisms from EtOH, mp 219–20°, gave a brown colour with EtOH/$FeCl_3$. (Found: C, 66.3; H, 5.5. $C_{19}H_{18}O_6$ requires: C, 66.66; H, 5.30%).

REFERENCES

1. Chopra, R. N. (1958) *Indigenous Drugs of India*, p. 521. U. N. Dhur, Calcutta.
2. Sharma, R. C., Zaman, A. and Kidwai, A. R. (1964) *Indian J. Chem.* **2**, 83.
3. Chattha, S. M., Mustaq, A., Manzoor, A. and Bhatty, M. K. (1967) *J. Sci. Ind. Res. (Pakistan)* **10**, 248.
4. Jewers, K., Nagler, M. J., Zirvi, K. A., Amir, F. and Cottee, F. H. (1974) *Pahlavi Med. J. (Iran)* **5**, 1.
5. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*, p. 253. Springer, New York.
6. Markham, K. R. and Mabry, T. J. (1975) *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds.) p. 62. Chapman and Hall, London.
7. Sharma, G. C. (1977) Ph.D. Thesis, University of Delhi, Delhi.
8. Gibbs, H. D. (1927) *J. Biol. Chem.* **72**, 649.
9. King, F. E., King, T. J. and Manning, L. C. (1957) *J. Chem. Soc.* 563.
10. Perkin, A. G. (1913) *J. Chem. Soc.* **103**, 650.

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NEW FLAVONOIDS FROM *ANAPHALIS ARANEOSA**

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Key Word Index—*Anaphalis araneosa*; Compositae; 5,7-dihydroxy-3,6,8-trimethoxyflavone; 5,7-dihydroxy-3,6,8,4′-tetramethoxyflavone.

Anaphalis araneosa DC. (tribe: Inuleae) grows in the sub-Himalayan range but does not appear to have been investigated chemically. We now report the isolation of two new flavones, araneol and araneosol, from the petrol extract of this plant and their characterization as 5,7-dihydroxy-3,6,8-trimethoxyflavone (**1**) and 5,7-dihydroxy-3,6,8,4′-tetramethoxyflavone (**2**), respectively.

The aromatic substitution pattern of arneol, $C_{18}H_{16}O_7$ (M^+ 344) and araneosol, $C_{19}H_{18}O_8$ (M^+ 374) was evident from the mass spectral fragmentation [1, 2] of the two compounds. Thus, a strong M-15 peak indicated the presence of a methoxyl group at 6 and/or 8 position(s); the M-43 peak is known to be characteristic of a 3-OMe flavone, while a peak at *m/e* 197 clearly showed that all the four available positions of ring A must be oxygenated, two of which must be methoxyl function. The PMR spectra of the two compounds showed, besides the expected signals for the methoxyl and aromatic protons, two hydroxyl protons one of which could be assigned to the chelated 5-OH group.

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Treatment of araneol with diazomethane (1.5 hr) yielded 5-hydroxy-3,6,7,8-tetramethoxyflavone (**3**), the UV spectra (Table 1) of which showed the characteristic bathochromic shift [3] of the maxima in presence of $AlCl_3$. With MeI/K_2CO_3 in refluxing acetone, **1** yielded the dimethyl ether (**4**), identical in all respects with an authentic specimen of 3,5,6,7,8-pentamethoxyflavone [4]. The position of the second phenolic group in **1** at C-7 was established from the bathochromic shift of the two principal UV maxima in presence of NaOAc [3].

The positions of the two phenolic groups of araneosol (**2**) were similarly established. Treatment of **2** with diazomethane for 1.5 and 24 hr yielded the monomethyl (**5**) and dimethyl (**6**) ethers respectively, the physical constants of which are in good agreement with those reported for calycopterin mono- and dimethyl ethers [5, 6].

EXPERIMENTAL

Flowering plants of *Anaphalis araneosa* collected in December in the Himalayas at an altitude of 1600–2400 m were obtained from United Chemicals and Allied Products, Calcutta and a voucher specimen (No. 1227) is available at the herbarium of the suppliers. The powdered plant material (1.5 kg) was extracted with petrol in a Soxhlet apparatus. The extract was concd and extracted with 5% NaOH soln. From the alkali soluble part, araneol (50 mg) and araneosol (30 mg) was obtained by chromatography over Si gel followed by crystallization from petrol–benzene.

Araneol (**1**). Orange needles, mp 180–81°; IR($CHCl_3$) cm^{-1}: 3510, 3200 br (OH), 1650 (CO), 1585, 1570 (Ar); PMR (80 MHz, $CDCl_3$): δ 3.79, 3.90, 3.95 (3 × OMe), 6.55 (7-OH), 7.45 *m* (3′-H, 4′-H, 5′-H), 8.05 *m* (2′-H, 6′-H), 10.56 (5-OH); MS: *m/e* (rel. intensity) 344 (M^+, 94), 329 (100), 311 (7), 301 (10), 197 (6).

7-O-*Methylaraneol* (**3**). Crystallized from petrol–benzene, mp 98–100° (lit. [4] mp 98–100°); M^+ *m/e* 358.

Dimethylaraneol (**4**). Crystallized from petrol–benzene, mp 86–87°, identical (mmp, UV, PMR) with 3,5,6,7,8-pentamethoxyflavone [4].

Araneosol (**2**). Yellow needles, mp 160–61°; IR($CHCl_3$) cm^{-1}: 3510, 3200 br (OH), 1650 (CO), 1585, 1570 (Ar); PMR (80 MHz, $CDCl_3$): δ 3.79, 3.82, 3.90, 3.95 (4 × OMe), 6.34 (7-OH), 6.95 *d* (*J* = 9.2 Hz, 3′-H, 5′-H), 8.03 *d* (*J* = 9.2 Hz, 2′-H, 6′-H), 10.45 (5-OH); MS: *m/e* (rel. intensity) 374 (M^+, 89), 359 (100), 341 (6), 331 (5), 197 (9).

7-O-*Methylaraneosol* (**5**). Crystallized from petrol–benzene, mp 125–26° (lit. [5, 6] mp 124°; 125–27°); MS: M^+ *m/e* 388.

Dimethylaraneosol (**6**). Crystallized from petrol–benzene, mp 132–33° (lit. [5, 6] mp 131°; 132–34°); MS: M^+ *m/e* 402.

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REFERENCES

1. Bowie, J. W. and Cameron, J. W. (1966) *Aust. J. Chem.* **19**, 1627.
2. Kingston, D. G. I. (1971) *Tetrahedron* **27**, 2691.
3. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*, p. 41. Springer, New York.
4. Hänsel, R., Rimpler, H. and Schwarz, R. (1967) *Tetrahedron Letters* 735.
5. Shah, R. C., Virkar, V. V. and Venkataraman, K. (1942) *J. Indian Chem. Soc.* **19**, 135.
6. Sarin, P. S. and Seshadri, T. R. (1960) *Tetrahedron* **8**, 64.

Table 1. UV maxima (in nm) of araneol, araneosol and their methyl ethers

Compound	MeOH	MeOH/NaOAc	MeOH/NaOH	MeOH/$AlCl_3$
Araneol (**1**)	278, 328, 375sh	282, 385	280, 385	290, 345, 430sh
Monomethylaraneol (**3**)	280, 320, 375sh	280, 320, 375sh	287, 420	300, 350, 440sh
Dimethylaraneol (**4**)	270, 312, 335sh	—	—	—
Araneosol (**2**)	280, 336, 365sh	284, 305sh, 385	286, 305sh, 385	290, 317, 367, 420sh
Monomethylaraneosol (**5**)	281, 335, 365sh	281, 335, 365sh	300, 400	290, 313, 367, 410sh
Dimethylaraneosol (**6**)	270, 332	—	—	—