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*Phytochemistry*, 1979, Vol. 18, pp. 355–356. © Pergamon Press Ltd. Printed in England. 0031-9422/79/0201-0355 $02.00/0

# FLAVONOIDS OF *PROSOPIS SPICIGERA* FLOWERS

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(*Received* 1 *May* 1978)

**Key Word Index**—*Prosopis spicigera*; Leguminosae; prosogerin-A; 6-methoxy-7-hydroxy-3′,4′-methylenedioxyflavone; prosogerin-B; 2′,4′-dihydroxy-5′-methoxy-3,4-methylenedioxychalkone.

*Prosopis spicigera*, a moderate-sized thorny tree, is reported to possess medicinal properties [1]. During the course of our work on plants of medicinal interest, *Prosopis spicigera* flowers which had not been systematically studied before, were investigated. Earlier, the isolations of patulitrin [2], sitosterol [3] and spicigerin [4] were reported from this plant. This communication reports the isolations and characterizations of two phenolic compounds, prosogerin-A and B.

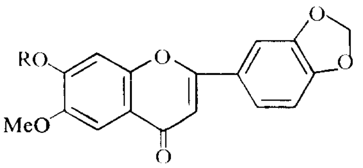
Air-dried flowers (5 kg) of *P. spicigera* were extracted with petrol and then benzene. The benzene extract on preparative TLC (silica gel) using $C_6H_6$–MeOH (9:1) yielded prosogerin-A and B which were characterized as 6-methoxy-7-hydroxy-3′,4′-methylenedioxyflavone (**1**) and 2′,4′-dihydroxy-5′-methoxy-3,4-methylenedioxychalkone (**2**), respectively.

## *Prosogerin-A*

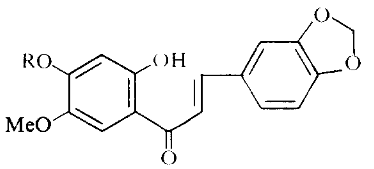
$C_{17}H_{12}O_6$ ($M^+$ 312). Colour reactions and spectral data indicated it to be a flavonoid. Prosogerin-A (**1**) formed a monoacetate (**1a**) and a monoethyl ether (**1b**) showing a free OH. **1** developed a bluish-green colouration with gallic acid–$H_2SO_4$ characteristic for the methylenedioxy group at δ 6.05 besides those for the other trum of its acetate (**1a**) which had a signal for the methylenedioxy group at δ 6.05 besides those for the other substituents: an acetoxyl (3H, δ 2.34) and a methoxyl (3H, δ 3.90). On alkali fission, **1** gave piperonylic acid fixing methylenedioxy group at C-3′ and C-4′ positions in the B-ring. Further, the signal at δ 6.64 (1H) was considered due to an aromatic proton at C-3 as observed for flavonoids having an unsubstituted C-3 position [5,6]. The signal at δ 7.66 (1H) due to the aromatic proton at C-5 was a singlet thereby showing a substituent at C-6. As the signal due to the aromatic proton at C-8 was shifted downfield to δ 7.22, the acetoxyl function was considered at C-7. Consequently the methoxyl function was placed at C-6 and prosogerin-A must be 6-methoxy-7-hydroxy-3′,4′-methylenedioxyflavone (**1**). This structure was fully supported by its mass spectrum and by the synthesis of its 7-*O*-ethyl ether (**2b**) [7].

## *Prosogerin-B*

$C_{17}H_{14}O_6$ ($M^+$ 314). Colour reactions and spectral data showed it to be a chalkone derivative having a methylenedioxy, a methoxyl and hydroxyl (s) as the substituents. Prosogerin B (**2**) yielded a monoethyl ether (**2a**) which dissolved in 10% aq. NaOH and also gave positive ferric reaction indicating that **2** contained a chelated OH at C-2′ besides one more OH function. On alkali fission, **2** yielded piperonylic acid showing the methylenedioxy function at C-3 and C-4. UV spectral shifts with $AlCl_3$ and the colour with alc. $FeCl_3$ confirmed a chelated OH at C-2′, **2** did not give a Gibbs



**1** R = H
**1a** R = COMe
**1b** R = Et



**2** R = H
**2a** R = Et

[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 $\delta$, $CDCl_3$: 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 ($\delta$, $CDCl_3$): 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-$\alpha$-H), 7.28 (3H, *m*, C-2-H, C-6-H and C-6′-H), 7.35 (1H, C-$\beta$-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 %).

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*Phytochemistry*, 1979, Vol. 18, pp. 356–357. © Pergamon Press Ltd. Printed in England. 0031-9422/79/0201-0356 $02.00/0

# NEW FLAVONOIDS FROM *ANAPHALIS ARANEOSA**

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(*Received* 4 *May* 1978)

**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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* Part 49 in the series "Studies on Indian Medicinal Plants". For Part 48 see Pakrashi, S. C., Chakravarty, A. K., Ali, E., Dhar, T. K. and Dan, S. (1979) *J. Indian Chem. Soc.* (in press).

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