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PROSOGERIN-D, A NEW FLAVONE FROM *PROSOPIS SPICIGERA* SEEDS

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Key Word Index—*Prosopis spicigera*; Leguminosae; prosogerin-D; 6,3′,4′,5′-tetramethoxy-7-hydroxyflavone.

Prosopis spicigera, a moderate-sized thorny tree having medicinal properties [1], has already been examined for its chemical constituents [2–6]. This paper reports the isolation and characterization of a new flavone from this plant herein named prosogerin-D.

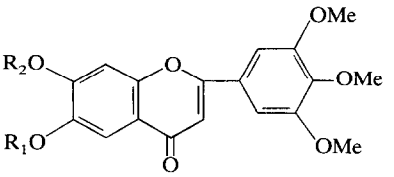
Air-dried seeds (10 kg) of *P. spicigera* were extracted with petrol and then C_6H_6. The C_6H_6 extract was then chromatographed on a Si gel column. Elution with C_6H_6 and C_6H_6–EtOAc (19:1, 9:1 and 17:3) gave prosogerin-C (**1a**) [6] and with C_6H_6–EtOAc (7:3, 3:2 and 1:1) yielded prosogerin-D which was characterized as 6,3′,4′,5′-tetramethoxy-7-hydroxyflavone (**1**).

Prosogerin-D (**1**)

$C_{19}H_{18}O_7$, colour reactions and spectral data indicated the compound to be a flavone. It yielded a mono Me ether (**1a**), monoacetate (**1b**) and a mono Et ether (**1c**) showing it to be monohydroxytetramethoxyflavone. Alkali fission gave tri-*O*-methylgallic acid indicating that the three —OMe substituents were at the C-3′, C-4′ and C-5′ positions. Based on the physical properties and spectral data, prosogerin-D Me ether was identified as 6,7,3′,4′,5′-pentamethoxyflavone (prosogerin-C) (**1a**) [6] showing a 6,7,3′,4′,5′-pentaoxygenation pattern in **1**. Solubility of **1** in aq. Na_2CO_3 (10%) indicated the probable occurrence of an OH at C-7 and thereby the fourth OMe was placed at C-6. Prosogerin-D was thus considered to be 6,3′,4′,5′-tetramethoxy-7-hydroxyflavone which was also supported by the MS of its acetate. The ^{1}H NMR spectrum of the acetate (**1b**) had signals for MeCO (3H, δ 2.29), OMe (12H, δ 3.9) and also for 5 aromatic protons. Furthermore, the signal at δ 6.7 (1H) was considered to be due to an aromatic proton at C-3 as observed for flavones [7]. The signal at δ 7.65 (1H) from the aromatic proton at C-5 was a singlet showing a substituent at C-6. Since the signal (δ 7.35) due to the C-8 proton in the acetate (**1b**) was shifted downfield as compared to that in case of the Me ether (**1a**) (δ 7.0), the acetoxyl function was considered to be at C-7. Consequently the OMe function was placed at C-6 and prosogerin-D must be 6,3′,4′,5′-tetramethoxy-7-hydroxyflavone (**1**).

Since prosogerin-D Et ether on direct comparison was identical with the synthetic 6,3′,4′,5′-tetramethoxy-7-ethoxyflavone (**1c**) and not with 6-ethoxy-7,3′,4′,5′-tetramethoxyflavone (**1d**), the constitutions assigned to prosogerin-D and its Et ether as **1** and **1c**, respectively, were unequivocally confirmed.

1c and **1d** were synthesized by the cyclodehydration of 2-hydroxy-4-ethoxy-5,3′,4′,5′-tetramethoxydibenzoylmethane and 2-hydroxy-4,3′,4′,5′-tetramethoxy-5-ethoxydibenzoylmethane respectively, obtained from the corresponding 2-(3′,4′,5′-trimethoxy)-benzoyloxy-4-ethoxy-5-methoxyacetophenone and 2-(3′,4′,5′-trimethoxy)benzoyloxy-4-methoxy-5-ethoxyacetophenone.



1 R_1 = Me; R_2 = H
1a R_1 = R_2 = Me
1b R_1 = Me; R_2 = COMe
1c R_1 = Me; R_2 = Et
1d R_1 = Et; R_2 = Me

EXPERIMENTAL

Prosogerin-D crystallized from EtOAc–petrol as colourless needles, mp 234–235°; gave a positive Mg–HCl test and dissolved in aq. Na_2CO_3 (10%); UV (MeOH) nm: 270, 280, 330; +NaOAc: 270, 280, 330 (Found: C, 64.0; H, 5.5. $C_{19}H_{18}O_7$ requires: C, 63.68; H, 5.06%).

1a. Methylation of **1** with Me_2SO_4–K_2CO_3 in Me_2CO gave colourless needles from C_6H_6–petrol, mp 233–234°. (Found: C, 64.70; H, 5.70. $C_{20}H_{20}O_7$ requires: C, 64.51; H, 5.41%). ^{1}H NMR ($CDCl_3$): δ 3.9–4.0 (15H, *m*, 5×—OMe), 6.7 (1H, *s*, C-3 H), 7.0 (1H, *s*, C-8 H), 7.1 (2H, *s*, C-2′ H and C-6′ H), 7.55 (1H, *s*, C-5 H).

1b. Acetylation of **1** with Ac_2O–Py gave colourless needles from $CHCl_3$–petrol, mp 220–221° (Found: C, 62.60; H, 4.80. $C_{21}H_{20}O_8$ requires: C, 62.99; H, 5.04%). MS *m/e*: 400 (M^+), 358, 356, 343, 342, 330, 315, 192, 177, 167 and 166. ^{1}H NMR ($CDCl_3$): δ 2.29 (3H, *s*, —OAc), 3.9 (12H, *s*, 4×—OMe), 6.7 (1H, *s*, C-3 H), 7.05 (2H, *s*, C-2′ H and C-6′ H), 7.35 (1H, *s*, C-8 H), 7.65 (1H, *s*, C-5 H).

1c. Ethylation of **1** with Et_2SO_4–K_2CO_3 in Me_2CO gave colourless needles from $CHCl_3$–petrol, mp 239–240° (Found: C, 65.6; H, 6.1. $C_{21}H_{22}O_7$ requires: C, 65.27; H, 5.74%). ^{1}H NMR ($CDCl_3$): δ 1.57 (3H, *t*, —$OCH_2\underline{CH_3}$), 3.95 (12H, *s*, 4×—OMe), 4.20–4.29 (2H, *m*, —$\underline{OCH_2}CH_3$), 6.7 (1H, *s*, C-3 H), 6.98 (1H, *s*, C-8 H), 7.09 (2H, *s*, C-2′ H and C-6′ H), 7.55 (1H, *s*, C-5 H).

6-Ethoxy-7,3′,4′,5′-tetramethoxyflavone (**1d**). 2-Hydroxy-

4-methoxy-5-ethoxyacetophenone [8] (2 g) with tri-*O*-methylgalloyl chloride (2.5 g) in Py (15 ml) gave 2-(3′,4′,5′-trimethoxy)benzoyloxy-4-methoxy-5-ethoxyacetophenone, colourless needles from EtOAc–petrol (2.8 g), mp 177° (Found: C, 62.8; H, 6.3. $C_{21}H_{24}O_8$ requires: C, 62.37; H, 5.98%). This ester (2.5 g) and KOH (2 g) in Py (15 ml) on heating at 40° gave 2-hydroxy-4,3′,4′,5′-tetramethoxy-5-ethoxydibenzoylmethane, bright yellow needles from EtOAc–petrol (1.5 g), mp 151°; green ferric reaction. (Found: C, 62.5; H, 6.0. $C_{21}H_{24}O_8$ requires: C, 62.37; H, 5.98%). On refluxing with HOAc–NaOAc for 3 hr, the dibenzoylmethane (1 g) gave **1d**, colourless needles (0.85 g) from $CHCl_3$–petrol, mp 213–214° (Found: C, 64.9; H, 5.5. $C_{21}H_{22}O_7$ requires: C, 65.27; H, 5.74%). Synthetic **1d** was different from prosogerin-D Et ether.

6,3′,4′,5′-*Tetramethoxy-7-ethoxyflavone* (**1c**). Esterification of 2-hydroxy-4-ethoxy-5-methoxyacetophenone [8] (2 g) with tri-*O*-methylgalloyl chloride (2.5 g) in Py (15 ml) gave 2-(3′,4′,5′-trimethoxy)benzoyloxy-4-ethoxy-5-methoxyacetophenone, colourless needles from EtOAc–petrol (2.7 g), mp 139–140° (Found: C, 62.2; H, 6.0. $C_{21}H_{24}O_8$ requires: C, 62.37; H, 5.98%). This ester (2.5 g) and KOH (2 g) in Py (15 ml) gave 2-hydroxy-4-ethoxy-5,3′,4′,5′-tetramethoxydibenzoylmethane, bright yellow needles from EtOAc–petrol (1.5 g), mp 165° (Found: C, 62.1; H, 6.1. $C_{21}H_{24}O_8$ requires: C, 62.37; H, 5.98%). Dehydrocyclization of the dibenzoylmethane (1 g) with NaOAc (1 g) in HOAc (20 ml) gave 6,3′,4′,5′-tetramethoxy-7-ethoxyflavone (**1c**), colourless needles (0.8 g) from $CHCl_3$–petrol, mp 239–240°, identical with prosogerin-D Et ether.

REFERENCES

1. Chopra, R. N. (1958) *Indigenous Drugs of India*, p. 521. Dhur, Calcutta.
2. Sharma, R. C., Zaman, A. and Kidwai, A. R. (1964) *Indian J. Chem.* **2,** 83.
3. Chatta, 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, P. H. (1974) *Pahlavi Med. J. (Iran)* **5,** 1.
5. Bhardwaj, D. K., Bisht, M. S., Mehta, C. K. and Sharma, G. C. (1979) *Phytochemistry* **18,** 355.
6. Bhardwaj, D. K., Jain, R. K., Mehta, C. K. and Sharma, G. C. (1978) *Indian J. Chem.* **16,** 1133.
7. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*, p. 253. Springer, New York.
8. Sharma, G. C. (1977) Ph.D. Thesis, University of Delhi.

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HILL ACTIVITY AND ANTHOCYANIN LEVELS IN *MANGIFERA INDICA*

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Key Word Index—*Mangifera indica*; Anacardiaceae; chlorophyll; anthocyanin; Hill activity.

Abstract—Anthocyanin composition and the rates of Hill activities were compared in the leaves of *Mangifera indica*. The important feature is the higher rate of Hill activity in anthocyanin-containing leaves as compared to the green leaves.

We have recently demonstrated that the Hill activity in anthocyanin-containing bracts of *Euphorbia pulcherrima* is higher than in the green leaves [1]. However, these studies were done in different foliage types. Therefore, it was of interest to undertake similar studies also in the plants of same foliage type varying in anthocyanin content. In *Mangifera indica*, the newly formed twigs, bear three different fully expanded leaf types, reddish, reddish-green and green leaves varying in anthocyanin and chlorophyll contents. Comparative studies on pigment composition and rates of Hill activities of these leaf types were undertaken. Interestingly enough, the anthocyanin-containing leaves not only show Hill activity but also at rates higher than the