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Organic Chemistry

CONSTITUTIONS OF NEW PIGMENTS FROM *Prosopis spicigera*

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Prosogerin-D and -E, two new polyphenolics isolated from the benzene and ethanolic extracts of the seeds of *Prosopis spicigera* were proposed their constitutions as 6,3′,4′,5′-tetramethoxy-7-hydroxyflavone (I) and 6,7-dihydroxy-3′-4′,5′-trimethoxyflavone (II) respectively. However, no direct synthetic supports were provided for these structural assignments. This paper confirms their proposed structures by syntheses and also reports the syntheses of their isomers: isoprosogerin-D and -E.

INTRODUCTION

Prosogerin-D

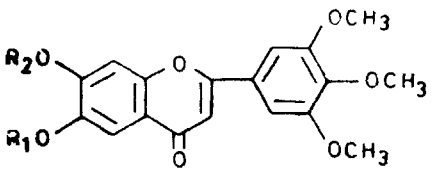
Among the phenolic components isolated (Bhardwaj *et al.*, 1978*a*, 1979*a*, 1980*a*, 1981) from *Prosopis spicigera*, prosogerin-D, a new 6,7,3′,4′,5′-pentaoxygenated flavone, on the basis of the studies of its colour reactions, spectral data and degradation was proposed its constitution as 6,3′,4′,5′-tetramethoxy-7-hydroxyflavone (I). In this connection, it may be mentioned that prosogerin-D has a free hydroxyl function at C_7 position as shown by its solubility in aqueous sodium carbonate (10 per cent) and the N.M.R. spectral data of its acetate. However, on the contrary UV spectrum of prosogerin-D when recorded in the presence of sodium acetate, did not exhibit the usual bathochromic shifts characteristic for the free C_7 hydroxyl of the flavonoids (Geissman, 1962; Mabry *et al.*, 1970; and Harborne *et al.*, 1975) thereby suggesting the methoxyl instead of hydroxyl at C_7. This discrepancy has been now settled by the identity of prosogerin-D with synthetic 6,3′,4′,5′-tetramethoxy-7-hydroxyflavone (I) but not with the isomeric synthetic 6-hydroxy-7,3′4′5′-tetramethoxyflavone (isoprosogerin-D) (V) now obtained as described in this paper.

Syntheses of prosogerin-D (I) and its isomer, isoprosogerin-D (V) have been carried out using 2-hydroxy-4-benzyloxy-5-methoxyacetophenone (Laumas *et al.*, 1957) and 2-hydroxy-4-methoxy-5-benzyloxyacetophenone (Bhardwaj *et al.*, 1979*b*) respectively as the starting compounds. 2-Hydroxy-4-methoxy-5-benzyloxyacetophenone on condensation with tri-0-methylgallaldehyde (Dornow & Petsch, 1951) gave 2′-hydroxy-3,4,5,4′-tetramethoxy-5′-benzyloxychalkone (III) which when treated with selenium dioxide, underwent cyclodehydrogenation (Mahal *et al.*, 1935; Mahal & Venkataraman, 1936; and Bhardwaj *et al.*, 1977, 1978*b*) to give 6-benzyloxy-7,3′,4′,5′-tetramethoxyflavone (IV). Debenzylation of this flavone (IV) yielded 6-hydroxy-7,3′,4′,5′-tetramethoxyflavone (V) which was characterised as its 6-0-acetyl

derivative (VI). Similarly, 2-hydroxy-4-benzyloxy-5-methoxyacetophenone was treated with tri-0-methylgallaldehyde to obtain 6,3',4',5'-tetramethoxy-7-hydroxyflavone (I) and its 7-0-acetyl derivative (IX) through 2'-hydroxy-4'-benzyloxy-3,4,5,5'-tetramethoxychalkone (VII) and the corresponding 6,3',4',5'-tetramethoxy-7-benzyloxyflavone (VIII) (*see* Chart I).

On direct comparisons, prosogerin-D and its acetate agreed with the synthetic flavone (I) and its acetate (IX) respectively but not with the corresponding isomeric synthetic flavone (V) and its acetate (VI).

Chart I



I , $R_1 = CH_3$; $R_2 = H$

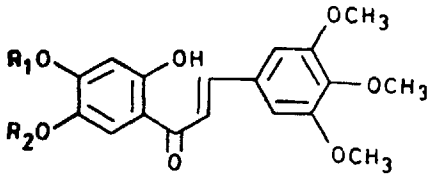
IV, $R_1 = C_7H_7$; $R_2 = CH_3$

V , $R_1 = H$; $R_2 = CH_3$

VI, $R_1 = COCH_3$; $R_2 = CH_3$

VIII, $R_1 = CH_3$; $R_2 = C_7H_7$

IX, $R_1 = CH_3$; $R_2 = COCH_3$



III, $R_1 = CH_3$; $R_2 = C_7H_7$

VII, $R_1 = C_7H_7$; $R_2 = CH_3$

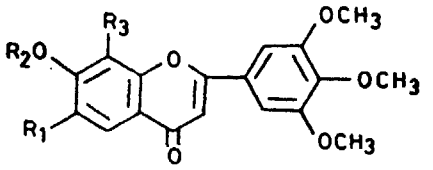
Prosogerin-E

Prosogerin-E, another new flavonoid also isolated (Bhardwaj *et al.*, 1981) [from the seeds of *Prosopis spicigera*, on the basis of studies of colour reactions, spectral data and degradation was proposed its constitution as 6,7-dihydroxy-3',4',5'-trimethoxyflavone (II). Prosogerin-E has a free hydroxyl at C_7 position as shown by its solubility in aqueous sodium carbonate (10 per cent). UV spectral shifts with sodium acetate/boric acid and positive Quastel test (Quastel, 1931) showed the presence of an ortho-dihydroxy system. Consequently, two possible isomeric structures were considered for prosogerin-E. viz., 7,8-dihydroxy-3',4',5',-trimethoxyflavone (XII) and 6,7-dihydroxy-3,'4',5'-trimethoxyflavone (II). In order to confirm the proposed

constitution, the syntheses of the isomeric flavones (II & XII) needed to characterise prosogerin-E, have been now accomplished as described in this paper. For this purpose, 2-hydroxy-4,5-dibenzyloxyacetophenone (Bhardwaj *et al.*, 1980*b*) and 2-hydroxy-3,4-dibenzyloxyacetophenone (Kamkhalia *et al.*, 1965) have been used as the starting materials. 2-Hydroxy-3,4-dibenzyloxyacetophenone on condensation with tri-0-methylgallaldehyde gave 2′-hydroxy-3′,4′-dibenzyloxy-3,4,5-trimethoxychalkone (X) which when treated with selenium dioxide, underwent cyclodehydrogenation to give 7,8-dibenzyloxy-3′,4′,5′-trimethoxyflavone (XI). Debenzylation of this flavone (XI) yielded 7,8-dihydroxy-3′,4′,5′-trimethoxyflavone (XII) which yielded its corresponding 7,8-di-0-acetyl derivative (XIII). Similarly, 2-hydroxy-4,5-dibenzyloxyacetophenone was treated with tri-0-methylgallaldehyde to obtain 6,7-dihydroxy-3′,4′,5′-trimethoxyflavone (II) and its corresponding 6,7-di-0-acetyl derivative (XVI) through its 2′-hydroxy-4′,5′-dibenzyloxy-3,4,5-trimethoxychalkone (XIV) and corresponding 6,7-dibenzyloxy-3′,4′,5′-trimethoxyflavone (XV) (*see* Chart II).

Identity of prosogerin-E and its acetate with the synthetic flavone (II) and its acetate (XVI) respectively, but not with the other isomeric flavone (XII) and its acetate (XIII) respectively, confirmed the proposed constitution of prosogerin-E as 6,7-dihydroxy-3′,4′,5′-trimethoxyflavone (II).

Chart II



II , $R_1 = OH$; $R_2 = R_3 = H$

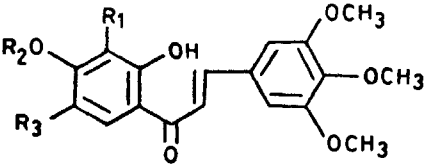
XI , $R_1 = H$; $R_2 = C_7H_7$; $R_3 = OC_7H_7$

XII, $R_1 = R_2 = H$; $R_3 = OH$

XIII, $R_1 = H$; $R_2 = COCH_3$; $R_3 = OCOCH_3$

XV, $R_1 = OC_7H_7$; $R_2 = C_7H_7$; $R_3 = H$

XVI $R_1 = OCOCH_3$; $R_2 = COCH_3$; $R_3 = H$



X , $R_1 = OC_7H_7$; $R_2 = C_7H_7$; $R_3 = H$

XIV $R_1 = H$; $R_2 = C_7H_7$; $R_3 = OC_7H_7$

EXPERIMENTAL

Synthesis of Isoprosogerin-D

2'-Hydroxy-3,4,5,4'-tetramethoxy-5'-benzyloxychalkone (III) : A solution of 2-hydroxy-4-methoxy-5-benzyloxyacetophenone (Bhardwaj *et al.*, 1979*b*) (4.0g) and tri-O-methylgallaldehyde (Dornow & Petsch, 1951) (3.2g) in ethanol (75ml) was treated with aqueous potassium hydroxide (6g, 15ml) and kept at room temperature for 48 hours. The reaction product was worked up as usual. The chalkone (III) thus obtained crystallised from ethanol as yellowish-orange needles (3.3g), m.p. 136–37 °C (*Found* : C, 69.8; H, 6.2. $C_{26}H_{26}O_7$ requires C, 69.32; H, 5.82 per cent). It gave brown colouration with alcoholic ferric chloride.

N.M.R. Spectrum (δ, *$CDCl_3$, TMS as Internal Standard*) : 3.90 (12 H, s, 4X —OCH_3), 5.06 (2H, s, —$OCH_2C_6H_5$), 6.47 (1H, s, C_3'-H), 6.78 (2H, s, C_2-H and C_6-H), 7.22–7.36 (7H, m, C_α-H, C_6'-H and —$OCH_2C_6H_5$), 7.7 (1H, *d*, $J = 16$Hz, C_β-H), 13.3 (1H, s, —OH).

6-Benzyloxy-7,3',4',5'-tetramethoxyflavone (IV) : A solution of the above chalkone (III) (2.5g) in iso-amyl alcohol (25ml) was treated with selenium dioxide (1.1g) and then heated under reflux for 48 hours. The hot solution was filtered and the solvent was removed from the combined filtrate under reduced pressure. The reaction product thus obtained crystallised from ethyl acetate-petroleum ether to give the flavone (IV) as colourless needles (2.1g), m.p. 206–7 °C (*Found* : C, 69.66; H, 5.6. $C_{26}H_{24}O_7$ requires, C, 69.63; H, 5.39 per cent). It did not give any colouration with alcoholic ferric chloride.

N.M.R. Spectrum (δ, *$CDCl_3$, TMS as Internal Standard*) : 3.89–3.97 (12H, 4X —OCH_3), 5.15 (2H, s, -$OCH_2C_6H_5$), 6.62 (1H, s, C_3-H), 6.90 (1H, s, C_8-H), 7.0 (2H, s, C_2'-H and C_6'-H), 7.17–7.49 (5H, m, —$OCH_2C_6H_5$), 7.55 (1H, s, C_5-H).

6-Hydroxy-7,3',4',5'-tetramethoxyflavone (isoprosogerin-D) (V) : A solution of the above flavone (IV) (2.0g) in acetic acid (20ml) and palladized charcoal (1.1. g; 10 per cent) was stirred in an atmosphere of hydrogen for 5 hours. The catalyst was filtered and washed with acetic acid. Removal of the solvent gave the flavone (V) that crystallised from acetic acid as colourless needles (1.4g), m.p. 244–45 °C (*Found*: C, 63.26; H, 4.8. $C_{19}H_{18}O_7$ requires C, 63.68; H, 5.06 per cent).

6-Acetoxy-7,3',4',5'-tetramethoxyflavone (VI) : The above flavone (V) (50mg) was treated with acetic anhydride (1ml) and dry pyridine (1ml) and then left overnight at room temperature. The acetate (VI) that was worked up as usual, crystallised from chloroform-petroleum ether as colourless needles (45mg), m.p. 216 °C (*Found* : C, 62.5; H, 5.0. $C_{21}H_{20}O_8$ requires C, 62.99; H, 5.04 per cent).

N.M.R. Spectrum (δ, *$CDCl_3$, TMS as Internal Standard*): 2.30 (3H, *s*, —$OCOCH_3$), 3.90 (12H, s, 4X—OCH_3), 6.57 (1H, s, C_3-H), 6.9 (1H, s, C_8-H), 6.97 (2H, s, C_2'-H and C_6'-H), 7.71 (1H, s, C_5-H).

On direct comparisons, the synthetic flavone (V) and its acetate (VI) were found to be different from the natural sample of prosogerin-D and its acetate.

Synthesis of Prosogerin-D

2'-Hydroxy-4'-benzyloxy-3,4,5,5'-tetramethoxychalkone (*VII*) : A solution of 2-hydroxy-4-benzyloxy-5-methoxyacetophenone (Laumas *et al.*, 1957) (3.0g) and tri-0-methylgallaldehyde (2.5g) in ethanol (60ml) was treated with aqueous potassium hydroxide (5g, 15ml) and kept at room temperature for 48 hours. The reaction product (VII) which was worked up as usual, crystallised from ethanol as yellowish-orange needles (2.8g), m.p. 174–75 °C (*Found* : C, 69.0; H, 6.2. $C_{26}H_{26}O_7$ requires C, 69.32; H, 5.82 per cent). It gave brown colouration with alcoholic ferric chloride.

N.M.R. Spectrum (δ, *CDCl*$_3$, *TMS as Internal Standard*) : 3.92 (12H, s, 4X —OCH_3), 5.16 (2H, s, —$OCH_2C_6H_5$), 6.52 (1H, s, C_3'-H), 6.82 (2H, s, C_2—H and C_6-H), 7.23–7.38 (7H, m, C_α-H, C_6'-H and —$OCH_2C_6H_5$), 7.8 (1H, *d*, J = 15Hz, C_β-H), 13.4 (1H, s, —OH).

6,3',4',5'-Tetramethoxy-7-benzyloxyflavone (*VIII*) : A solution of the above chalkone (VII) (2.5g) in iso-amyl alcohol (25ml) was treated with selenium dioxide (1.1g) and then heated under reflux for 48 hours and the reaction product was worked up as described earlier. It crystallised from ethyl acetate-petroleum ether to give the flavone (VIII) as colourless needles (2.2g), m.p. 222–23 °C (*Found* : C, 69.9; H, 5.3. $C_{26}H_{24}O_7$ requires C, 69.63; H, 5.39 per cent).

N.M.R. Spectrum (δ, *CDCl*$_3$, *TMS as Internal Standard*) : 3.95 (12H, s, 4X —OCH_3), 5.28 (2H, s, —$OCH_2C_6H_5$), 6.72 (1H, s, C_3-H), 7.05 (1H, s, C_8-H), 7.10 (2H, s, C_2'-H and C_6'-H), 7.35–7.53 (5H, m, —$OCH_2C_6H_5$), 7.60 (1H, s, C_5-H).

6,3',4',5'-Tetramethoxy-7-hydroxyflavone (*Prosogerin-D*) (*I*) : A solution of the above flavone (VIII) (2.0g) in ethyl acetate (50ml) and palladized charcoal (1.1g; 10 per cent) was stirred in an atmosphere of hydrogen till the absorption completed. The reaction product was worked up as usual. It crystallised from ethyl acetate-petroleum ether to give the flavone (I) as colourless needles (1.4g), m.p. 234–35 °C (*Found* : C, 63.7; H, 5.3. $C_{19}H_{18}O_7$ requires C, 63.68; H, 5.06 per cent).

6,3',4',5'-Tetramethoxy-7-acetoxyflavone (*IX*) : The above flavone (I) (50mg) was treated with acetic anhydride (1ml) and dry pyridine (1ml) and then left overnight at room temperature. The acetate (IX) thus obtained was worked up as usual. It crystallised from chloroform-petroleum ether as colourless needles (40mg), m.p. 221–22 °C (*Found* : C, 62.5; H, 5.2. $C_{21}H_{20}O_8$ requires C, 62.99; H, 5.04 per cent).

N.M.R. Spectrum (δ, *CDCl*$_3$, *TMS as Internal Standard*) : 2.35 (3H, s, —$OCOCH_3$), 3.92 (12H, s, 4X—OCH_3), 6.70 (1H, s, C_3 -H), 7.05 (2H, s, C_2'-H and C_6'-H), 7.3 (1H, s, C_8-H), 7.62 (1H, s, C_5-H).

On direct comparisons the, synthetic flavone (I) and its acetate (IX) were found to be identical with the natural sample of prosogerin-D and its acetate.

Synthesis of Isoprosogerin-E

2'-Hydroxy-3',4'-dibenzyloxy-3,4,5,-trimethoxychalkone (*X*) : A solution of 2-hydroxy-3,4-dibenzyloxyacetophenone (Kamkhalia *et al.*, 1965) (5.0g) and tri-0-

methylgallaldehyde (3.2g) in ethanol (150ml) was treated with aqueous potassium hydroxide (8g, 20ml) and kept at room temperature for 48 hours. The reaction product (X) was worked up as usual. It crystallised from ethanol as bright yellow needles (4.5g), m.p. 159–60 °C (*Found*: C, 72.64; H, 6.1. $C_{32}H_{30}O_7$ requires C, 72.99; H, 5.74 per cent). It gave brown colouration with alcoholic ferric chloride.

N.M.R. Spectrum (δ, *$CDCl_3$, TMS as Internal Standard*): 3.87 (9H, s, 3X —OCH_3), 5.1 (4H, s, 2X—$OCH_2C_6H_5$), 6.46 (1H, *d*, J = 10Hz, C_5'-H), 6.78 (2H, s, C_2-H and C_6-H), 7.28–7.65 (12H, m, C_α-H, C_β-H, 2X—$OCH_2C_6H_5$), 7.88 (1H, *d*, J = 10Hz, C_6' —H), 13.3 (1H, s, —OH).

7,8-Dibenzyloxy-3',4',5'-trimethoxyflavone (*XI*): A solution of the above chalkone (X) (4g) in iso-amyl alcohol (50ml) was treated with selenium dioxide (1.8g) and then heated under reflux for 48 hours. The reaction product which was worked up as usual, crystallised from ethyl acetate-petroleum ether to give the flavone (XI) as colourless needles (3.5g), m.p. 174–75 °C (*Found*: C, 73.2; H, 5.3. $C_{32}H_{28}O_7$ requires C, 73.23; H, 5.38 per cent). It did not give any colouration with alcoholic ferric chloride.

N.M.R. Spectrum (δ, *$CDCl_3$, TMS as Internal Standard*): 3.75 (6H, s, 2X—OCH_3), 3.88 (3H, s, —OCH_3), 5.17 (2H, s, —$OCH_2C_6H_5$), 5.22 (2H, s, —$OCH_2C_6H_5$), 6.65 (1H, s, C_3-H), 7.05 (1H, *d*, J =9Hz, C_8-H), 7.07 (2H, s, C_2'-H and C_6'-H), 7.20–7.35 (10H, m, 2X—$OCH_2C_6H_5$), 7.85 (1H, *d*, J = 9Hz, C_5-H).

7,8-Dihydroxy-3',4',5'-trimethoxyflavone (*Isoprosogerin-E*) (*XII*): A solution of the above flavone (XI) (2.0g) in ethyl acetate (100ml) and palladized charocoal (1.0g; 10 per cent) was stirred in an atmosphere of hydrogen till the absorption completed. The reaction product (XII) was worked up as usual. It crystallised from ethyl acetate-petroleum ether as colourless needles (1.1g), m.p. 274–75 °C (*Found*: C, 62.4; H, 4.5. $C_{18}H_{16}O_7$ requires C, 62.79; H, 4.68 per cent). It gave green colouration with alcoholic ferric chloride.

7,8-Diacetoxy-3',4',5'-trimethoxyflavone (*XIII*): The above flavone (XII) (50mg) was treated with acetic anhydride (1ml) and dry pyridine (1ml) and then left overnight at room temperature. The acetate (XIII) was worked up as usual. It crystallised from chloroform-petroleum ether as colourless needles (45mg), m.p. 210–11 °C (*Found*: C, 61.4; H, 4.8. $C_{22}H_{20}O_9$ requires C, 61.68; H, 4.71 per cent). It did not give any colouration with alcoholic ferric chloride.

N.M.R. Spectrum (δ, *$CDCl_3$, TMS as Internal Standard*): 2.32 (3H, s, —$OCOCH_3$), 2.39 (3H, s, —$OCOCH_3$), 3.89 (9H, s, 3X—OCH_3), 6.70 (1H, s, C_3-H), 7.02 (2H, s, C_2'-H and C_6'-H), 7.25 (1H, *d*, J = 9Hz, C_8-H), 8.08 (1H, *d*, J = 9Hz, C_5-H).

On direct comparisons, the synthetic flavone (XII) and its acetate (XIII) were found to be different from prosogerin-E and its acetate.

Synthesis of Prosogerin-E

2'-Hydroxy-4',5'-dibenzyloxy-3,4,5-trimethoxychalkone (*XIV*): A solution of 2-hydroxy-4,5-dibenzyloxyacetophenone (Bhardwaj *et al.*, 1980*b*) (4g) and tri-0-methyl-

gallaldehyde (2.5g) in ethanol (120ml) was treated with aqueous potassium hydroxide (6g, 15ml) and kept at room temperature for 48 hours. The reaction product (XIV) which was worked up as usual, crystallised from ethanol as yellowish-orange needles (3.6g), m.p. 128 °C (*Found*: C, 73.2; H, 6.0. $C_{32}H_{30}O_7$ requires C, 72.99; H, 5.74 per cent). It gave brown colouration with alcoholic ferric chloride.

N.M.R. Spectrum (δ, *CDCl₃*, *TMS as Internal Standard*): 3.92 (9H, s, 3X—OCH_3), 5.08 (2H, s, —$OCH_2C_6H_5$), 5.18 (2H, s, —$OCH_2C_6H_5$), 6.58 (1H, s, C_3'-H), 6.84 (2H, s, C_1-H and C_2-H), 7.26–7.48 (12H, m, C_8-H, C_6'-H and 2X —$OCH_2C_6H_5$), 7.76 (1H, *d*, *J* = 16Hz, C_β-H), 13.4 (1H, s, —OH).

6,7-Dibenzyloxy-3',4',5'-trimethoxyflavone (*XV*) : A solution of the above chalkone (XIV) (2.5g) in iso-amyl alcohol (30ml) was heated under reflux with selenium dioxide (1.2g) for 48 hours. The reaction product was worked up as described earlier to obtain the flavone (XV) which crystallised from ethyl acetate-petroleum ether as colourless needles (2.2g), m.p. 192–93 °C (*Found*: C, 73.6; H, 5.1. $C_{32}H_{28}O_7$ requires C, 73.23; H, 5.38 per cent). It did not give any colouration with alcoholic ferric chloride.

N.M.R. Spectrum (δ, *CDCl₃*, *TMS as Internal Standard*): 3.92 (9H, s, 3X—OCH_3), 5.20 (2H, s, —$OCH_2C_6H_5$), 5.25 (2H, s, —$OCH_2C_6H_5$), 6.67 (1H, s, C_3-H), 7.05 (3H, s, C_8:H, C_2'-H and C_6'-H), 7.23–7.54 (10H, m, 2X—$OCH_2C_6H_5$), 7.65 (1H, s, C_5-H).

6,7-Dihydroxy-3',4',5'-trimethoxyflavone (*Prosogerin-E*) (*II*): A solution of the above flavone (XV) (2g) in ethyl acetate (100ml) and palladized charcoal (1.0g; 10 per cent) was stirred in an atmosphere of hydrogen till the obsorption completed. The reaction product was worked up to obtain the flavone (II) which crystallised from ethyl acetate-petroleum ether as yellow needles (1.1g), m.p. 263–64 °C (*Found*: C, 62.5; H, 4.5. $C_{18}H_{16}O_7$ requires C, 62.79; H, 4.68 per cent). It gave green colouration with alcoholic ferric chloride.

6,7-Diacetoxy-3,'4',5',-trimethoxyflavone (*XVI*) : The above flavone (II) (50mg) was treated with acetic anhydride (1ml) and dry pyridine (1ml) and then left overnight at room temperature. The acetate (XVI) was worked up as usual. It crystallised from chloroform—petroleum ether as colourless needles (45mg), m.p. 218–19 °C (*Found*: C, 61.8; H, 5.1. $C_{22}H_{20}O_9$ requires C, 61.68; H, 4.71 per cent). It did not give any colouration with alcoholic ferric chloride.

N.M.R. Spectrum (δ, *CDCl₃*, *TMS as Internal Standard*) : 2.35 (6H, s, 2X—$OCOCH_3$), 3.93 (9H, s, 3X—OCH_3), 6.69 (1H, s, C_3-H), 7.03 (2H, s, C_2'-H and C_6'-H), 7.5 (1H, s, C_8-H), 7.92 (1H, s, C_5-H).

On direct comparisons, the synthetic flavone (II) and its acetate (XVI) were found to be identical with the natural sample of prosogerin-E and its acetate.

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