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FLAVONOIDS AND OTHER CONSTITUENTS FROM *PEDALIUM MUREX**

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Key Word Index—*Pedalium murex*; Pedaliaceae; fruits; 2′,4′,5′-trihydroxy-5,7-dimethoxyflavone; luteolin; rubusic acid; triacontanyl dotriacontanoate; lipids.

Abstract—Two new compounds isolated from the fruits of *Pedalium murex* were characterized as 2′,4′,5′-trihydroxy-5,7-dimethoxyflavone and triacontanyl dotriacontanoate by physico-chemical methods. Luteolin, rubusic acid, nonacosane, tritriacontane, triacontanoic acid, tritriacontanoic acid and sitosterol-β-D-glucoside have also been isolated and identified.

INTRODUCTION

Pedalium murex is a small herb distributed in tropical Africa, Ceylon, India and Mexico [1]. The fruits are reported to possess diuretic, antispasmodic and aphrodisiac properties [2]. In the past the fruits were reported to yield a number of phenolic acids [3]. Recently we have characterized several lipid constituents and vanillin from the fruits [4]. Our continued interest on the fruits has led to the isolation of a new flavone and eight other compounds.

RESULTS AND DISCUSSION

Silica gel column chromatography of the *n*-hexane extract yielded compounds **1–5**, whereas the *n*-butanol fraction furnished compounds **6–9**.

Compound **6** was obtained as yellow needles, mp 274–276°. The IR spectrum of this compound indicated the presence of aromatic, α,β-unsaturated keto, phenolic hydroxy and ether functions. The UV spectrum showed absorption maxima at 242, 270 and 348 nm, typical of a flavonoid. The mass spectrum of **6** displayed a $[M]^+$ at *m/z* 330 ($C_{17}H_{14}O_7$) which is in accord with a flavone containing three hydroxy and two methoxy groups. The prominent ions at *m/z* 150, 153 [5] and 178 indicated the presence of three hydroxy groups in ring B while the ion at *m/z* 180 showed two methoxy groups in ring A. The substitution pattern is established by UV shifts and ^{1}H NMR spectra.

The proton corresponding to C-3 appeared as a sharp singlet at δ6.45. A sharp six-proton singlet at δ3.80 is assigned to two methoxy groups linked to C-5 and C-7. The protons at C-6 and C-8 appeared as a *meta*-coupled doublet $J=2.5$ Hz at δ6.18 and 6.32, respectively [6]. This substitution pattern of ring A is also consistent with the UV spectrum which did not show shifts in band II. (see Experimental). In view of the shifts in UV maxima as well as the chemical shifts in the ^{1}H NMR spectrum, the two *ortho* dihydroxy groups are placed at C-4′ and C-5′ positions. The third hydroxy group is placed at C-2′ position as C-3′ and C-6′ protons appeared as singlets at δ7.25 and 7.58, respectively [7]. These data led to the identity of **6** as 2′,4′,5′-trihydroxy-5,7-dimethoxyflavone.

Compound **3** had IR absorption bands at 1730 (ester CO) and 720 cm^{-1} (long chain), suggesting it to be a saturated long chain ester. Its ^{1}H NMR spectrum showed signals at δ4.19 and 2.29 for $-CH_2-O-CO-$ and $OC-CH_2$ functions, respectively. Alkaline hydrolysis of **3** afforded triacontanol (IR, mass spectrometry, mp) and dotriacontanoic acid (IR, mass spectrometry, CO-TLC). This compound, therefore, is characterized as triacontanyl dotriacontanoate.

Compounds **1**, **2**, **4**, **5**, **7–9** were identified as nonacosane, tritriacontane, triacontanoic acid, tritriacontanoic acid, rubusic acid [8], sitosterol-β-D-glucoside and luteolin, respectively, by comparison with authentic samples (IR, mass spectrometry, ^{1}H NMR, co-TLC). Flavonoids which are 2′-oxygenated are of interest from a chemotaxonomic point of view. A 2′,4′,5′-trioxygenated pattern in the B ring is uncommon among flavones [9].

EXPERIMENTAL

Mps: uncorr. UV spectra were determined in MeOH; IR spectra in KBr and 80 MHz NMR spectra in $CDCl_3$ with TMS as int. standard. TLC: silica gel G; spots visualized by exposure to I_2 vapours. The plant material was purchased from a local market and identified in our Botany Department where a voucher specimen is maintained.

Extraction and isolation of compounds. Dried and powdered fruits (3.3 kg) of *P. murex* L. were extracted with EtOH (9 l × 8) and the extracts were concd *in vacuo* to 200 ml. H_2O (200 ml) was added and the extract was then fractionated with *n*-hexane (300 ml × 7, 122.70 g) and *n*-BuOH (300 ml × 6, 30.20 g). A portion (30 g) of *n*-hexane extract was chromatographed over silica gel (1050 g, 60–120 mesh, BDH) and the column was eluted with varying proportions of hexane, C_6H_6 and $CHCl_3$. Fractions of 250 ml were collected and monitored by TLC. Similarly, *n*-BuOH fraction (20 g) was chromatographed over silica gel (800 g) eluting with increasingly polar mixtures of $CHCl_3$ and MeOH. Fractions (250 ml each) were collected and monitored by TLC.

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Compound **3** (*triacontanyl dotriacontanoate*). Residue from hexane–C_6H_6 (3:1) fractions 63–68 furnished a solid, (45 mg), mp 52–53°. IR ν_{max} cm^{-1}: 2910, 2840, 1730, 1460, 1380, 1175, 720. ^1H NMR: δ0.90 (6H, *t*, $J=6$ Hz, Me × 2), 2.29 (2H, *t*, $J=6$ Hz, $-CH_2-CO-$), 4.19 (2H, *t*, $J=6$ Hz, $-CH_2-O-CO-$), 1.23 [114H, *br s*, $(CH_2)_{57}$]. Compound **3** (30 mg) was hydrolysed with ethanolic KOH (5%, 20 ml, 5 hr). When the reaction was complete, the mixture was diluted with H_2O (100 ml) and after work-up it gave triacontanol, mp 86° (IR, MS, co-TLC) and dotriacontanoic acid, mp 95–96° (IR, MS).

Compound **6** (*2′,4′,5′-trihydroxy-5,7-dimethoxyflavone*). Removal of solvent from $CHCl_3$–MeOH (49:1) fractions 99–102 yielded yellow needles, mp 274–276° (MeOH), 22 mg, $R_f=0.60$ ($CHCl_3$–MeOH, 9:1) and 0.51 ($CHCl_3$–EtOAc, 4:1). UV λ_{max} nm: 242, 270, 348: (NaOMe) 236, 277, 417: (NaOAc) 242, 272, 404: ($AlCl_3$) 254, 274, 390: ($AlCl_3$ + HCl) 250, 270, 355; ^1H NMR (CD_3OD): δ3.80 (6H, *s*, –OMe × 2) 6.12 (1H, *d*, $J=2.5$ Hz, H-6), 6.32 (1H, *d*, $J=2.5$ Hz, H-8), 6.45 (1H, *s*, H-3), 7.25 (1H, *s*, H-3′), 7.58 (1H, *s*, H-6′). MS *m/z* (rel. int.): 330 $[M]^+$ ($C_{17}H_{14}O_7$) (100), 315 $[M-Me]^+$ (4), 300 $[M-2Me]^+$ (16), 287 (7), 259 (4), 244 (3), 213 (5), 180 (5), 178 (13), 163 (4), 153 (30), 152 (4), 151 (11), 150 (4), 148 (3), 135 (5), 69 (5).

REFERENCES

1. (1966) *The Wealth of India, Raw Material*, Vol. 7, p. 284. Publications and Information Directorate, CSIR, New Delhi.
2. Kirtikar, K. R. and Basu, B. D. (1933) *Indian Med. Plants* **3**, 1856.
3. Das, V. S. R., Rao, K N. and Rao, J. V. S. (1966) *Curr. Sci.* **35**, 160.
4. Shukla, Y. N. and Thakur, R. S. (1983) *Phytochemistry* **22**, 973.
5. Mabry, T. J. and Markham, K. R. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds), p. 78. Chapman & Hall, London.
6. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*, p. 261. Springer, Berlin.
7. Shilin, Y., Roberts, M. F. and Phillipson, J. D. (1989) *Phytochemistry* **28**, 1509.
8. Bhattacharya, A. K. and Dutta, H. K. (1969) *J. Indian Chem. Soc.* **46**, 381.
9. Iinuma, M. and Mizuno, M (1989) *Phytochemistry* **28**, 681.