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Chemical Examination of Fruits and Leaves of *Peucedanum grande*

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PEUCEDANUM grande an aromatic umbellifer is reported[1] to be used in the indigenous system of medicine as carminative, stimulant and diuretic. Osthol, byakangelicin and imperatorin have been isolated from its roots[2,3], while columbianadin, phellopterin and byakangelicol have been additionally reported in fruits[4,5]. The present work concerns with the isolation of a few more coumarins from the leaves and fruits as well a report on the composition of the essential oil from the fruits.

Isolation of coumarins from leaves :

Air-dried powder (850 g) of the leaves of *P. grande* was extracted with petroleum ether (b.p. 60–80°) in a Soxhlet apparatus to obtain a dark green oil (44.5 g), a part (20 g) of which was chromatographed over silica gel (600 g). Elution with benzene gave a white solid which was crystallised as prismatic needles (1.7 g, m.p. 83–84°) from benzene–petroleum ether mixture, and characterised as osthol by comparison of its uv[6], pmr[7] and mass[8] spectra, ν_{max} (KBr) 1 720 (C=O) and 1 600 cm^{-1} (C=C). Further elution with benzene yielded another solid which was purified by washing repeatedly with petroleum ether followed by crystallisation from benzene. The white needles (20 mg), m.p. 184–86°, could be identified as bergapten from uv[6] and pmr[7] spectra ; ν_{max} (KBr) 1 720, 1 600 and 1 578 cm^{-1} ; *m/e* 216 (M^+), 201 (M^+-CH_3), 188 (M^+-CO) and 173 $M^+-(CO+CH_3)$.

Elution with benzene–ethyl acetate (19 : 1) gave yellow needles (120 mg), m p. 149–51°, upon crystallisation from ethyl acetate–benzene ; ν_{max} (KBr) 1 710, 1 600 and 1 590 cm^{-1}. The compound was characterised as isopimpinelline from its uv[9], pmr[7] and mass[10] spectra.

Elution with benzene–ethyl acetate (9 : 1) afforded small quantity of a compound (10 mg), m.p. 107–09° ; λ_{max} (MeOH) 221, 248 and 300 nm ; ν_{max} (KBr) 1 700, 1 620 and 1 580 cm^{-1}. The pmr spectra of the compound was in full agreement with that of heraclenin[7]. The gummy mass obtained from benzene–ethyl acetate (4 : 1) fractions was treated with hot benzene to give a solid and crystallised as needles (110 mg), m.p. 163–67° by slow evaporation of its chloroform solution at room temperature ; λ_{max} (MeOH) 212, 218, 250, 263 and 325 nm ; ν_{max} (KBr) 3 480 (OH), 1 700 and 1 600 cm^{-1}. It was identified as columbianetin by comparison of its pmr[7] and mass[11] spectra.

Isolation of coumarins from fruits :

The fruits (1.0 kg) purchased from local market were powdered and extracted successively with petroleum ether, chloroform and methanol in a Soxhlet apparatus. The petroleum ether extract, a dark yellowish green oil (67 g), deposited a yellow solid (8.0 g) which was chromatographed over silica gel (250 g). Elution with benzene gave bergapten (0.75 g). Elution with benzene–ethyl acetate (9 : 1) afforded a yellow solid (40 mg), m.p. 226–30° which was characterised as alloimperatorin on the basis of its msss spectrum[12] ; λ_{max} (MeOH) 226, 242, 252, 268 and 315 nm ; ν_{max} (KBr) 3 320 (OH), 1 720 and 1 590 cm^{-1} ; δ ($CDCl_3$) 6.3 (1H, d, *J* 9.5 Hz, H–3), 8.1 (1H, d, *J* 9.5 Hz, H–4), 6.85 (1H, d, *J* 2.5 Hz, H–3′), 7.7 (1H, d, *J* 2.5 Hz, H–2′), 5.2 (1H, t, CH olefinic), 3.7 (2H, d, CH_2–benzylic), 1.83 (3H, s) and 1.67 (3H, s, allylic methyls) and 2.74 (br, D_2O exchangeable OH). Further elution with benzene–ethyl acetate (9 : 1) gave another yellow compound which crystallised as needles from methanol (180 mg), m p. 209–12°, and was characterised as 5-methoxy-8-hydroxypsoralen ; λ_{max} (MeOH) 226, 276 and 316 nm[13] ; ν_{max} (KBr) 3 340–20, 1 700, 1 600 and 1 585 cm^{-1} ; δ($CDCl_3$) 6.3 (1H, d, *J* 9.5 Hz, H–3), 8.1 (1H, d, *J* 9.5 Hz, H–4), 6 98 (1H, d, *J* 2.5 Hz, H–3), 7 65 (1H, d, *J* 2.5 Hz, H–2), 4 12 (3H, s, OCH_3) and 2.78 (br s, D_2O exchangeable OH) ; *m/e* 232 (M^+), 217 (M^+-CH_3), 201 (M^+-OCH_3) and 189 $M^+-(CO+CH_3)$. No change in the chemical shifts of H–4 proton after acetylation confirmed the position of OH group at C–8. Elution with benzene–ethyl acetate (4 : 1 to 1 : 1) gave byakangelicin (1.95 g), m.p. 124–26°, which was identified on the basis of the reported data[4,12].

The oil remaining after removal of the solid deposit was steam-distilled and the residue (20 g) was chromatographed over silica gel (600 g). It led to the isolation of bergapten (100 mg, benzene fractions) and byakangelicin (400 mg, benzene–ethyl acetate 4 : 1 to 1 : 1 fractions).

Elution with petroleum ether–benzene (1 : 1) gave an oil containing uv fluorescent substances. Since attempts to separate any solid failed, the oil was saponified. The unsaponifiable matter (2.9 g) was chromatographed over silica gel (100 g) to yield osthol (55 mg from benzene fractions) and columbianetin (130 g from benzene–ethyl acetate 9 : 1 fraction). Tlc studies indicated the formation of columbianetin during saponification by hydrolysis of columbianadin which has already been reported[4] in fruits.

Resolution of chloroform extract (11 g) on silica gel again afforded bergapten (210 mg from benzene eluates) and byankangelicin (315 mg from benzene–ethyl acetate 9 : 1 eluates). Similarly, methanol extract provided a further quantity of byakangelicin (125 mg) from benzene–ethyl acetate (1 : 1) eluates.

The composition of the volatile oil of the fruits :

Volatile oil of the fruits obtained by hydrodistillation (2.2%, v/w) was examined by tlc and glc. Glc carried out over SE-30 (3.5%) exhibited thirty seven peaks and revealed the following percentage composition : α-pinene, 10.99 ; sabinene, 15.27 ; limonene, 10.14 ; *p*-cymene, 4.22 ; 1,8-cineol, 1.00 ; α-terpineol, 5.61 ; bornyl acetate, 29.6. The components were identified by comparison of their retention time with that of the reference standards.

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Sterols from *Anacardium occidentale*

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THE genus *Anacardium* of family *Anacardiaceae* comprises[1,2] of 15 species mostly found in tropical America from Mexico to Peru, Brazil, South Africa, Madaguscar, Mozambique, West Indies and South East Asia, and from Ceylon to Philippines. The species, *Anacardium occidentale* Linn. (local name : *Kaju Badam*) has been introduced in the hotter parts of India like West Bengal, Tripura, Orissa, Madras, Bombay, Goa, Cochin and Travancore. The bark tar of this plant is used[3] in the treatment of leprosy and ulcers. The plant yields a pale yellow to reddish gum which exudes in stalactiform masses. This gum has insecticidal properties[1]. Previous investigations[4-12] on various parts of this plant have revealed the presence of anacardic acid, fatty acids, phenolics, amino acids, proteins, sugars and tannins. As a part of our programme to exploit the medicinal plants of India, we reinvestigated the stem-bark of this plant and could be able to isolate four sterols from the petrol extract. In this note, we report the isolation, characterisation and relative occurrence of these sterols. To the best of our knowledge, this is the first report of sterols from the genus *Anacardium*.

The stem-barks of *A. occidentale* collected from the campus area of this centre in September 1985 were air-dried and milled. The milled stem-bark (1 kg) was extracted with petrol (b.p. 60–80°) in a soxhlet for 48 h. The petrol extract was distilled to a small volume and the concentrated extract was evaporated to a gummy residue (2.1 g). This residue was column chromatographed over silica gel (60–120 mesh). The benzene eluate on evaporation of solvent gave a solid residue which was homogeneous on tlc. This solid residue on repeated crystallisation from benzene–chloroform mixture afforded shining crystals (0.04 g), m.p. 130°.

The crystalline solid gave positive Salkowski reaction and Liebermann–Burchard test for steroids. The ir spectrum (KBr) of the solid showed ν_{max} at 3 420 (OH), 2 940(CH), 2 880 (CH), 1 640 (C=C), 1 465, 1 385, 1 080 and 980 cm^{-1}. The EI-mass spectrum of the solid was diagonstic to ascertain the skeletal structure. The spectrum showed significant peaks at *m/z* (relative abundance in percent) 414 $[M]^+$(84.9), 399 $[M-Me]^+$(30.2), 396 $[M-H_2O]^+$(51.2), 381 $[M-Me-H_2O]^+$(38.4), 329 $[M-85]^+$(34.9), 303 $[M-C_7H_{11}O]^+$(51.2), 273 [*M*–SC(side chain)]$^+$[37.2), 272 $[M-SC-H]^+$(9.4), 271 $[M-SC-2H]^+$(9.8), 255 $[M-SC-H_2O]^+$(53.5), 253 $[M-SC-H_2O-2H]^+$(2.8), 231 $[M-SC-C_3H_6]^+$ (32.6), 229 $[M-SC-C_3H_8]^+$(16.4), 213 $[M-SC-C_3H_6-H_2O]^+$(67.4), 211 $[M-SC-C_3H_8-H_2O]^+$ (2.3), 144(74.4), 10/(57.0), 105(39.5), 55(73.3) 43(100.0), 412$[M_1]^+$(14.0), 394 $[M_1-H_2O]^+$(2.3), 379