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TRITERPENOIDS AND STEROLS OF *KALANCHOE SPATHULATA*

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Key Word Index—*Kalanchoe spathulata*; Crassulaceae; triterpenoids; freidelin; taraxerol; glutinol.

INTRODUCTION

Kalanchoe spathulata DC (Crassulaceae) is a herb distributed in the tropical Himalayas, Burma, China and Java [1]. The leaves of the plant are reported to be useful for the treatment of abscesses and of cholera [1], and the expressed juice is employed as an antiperiodic [2] and a drastic purgative [2, 3] in Indian indigenous medicine. Previous reports on the genus *Kalanchoe* indicated the presence of wax hydrocarbons, wax alcohols, sterols, triterpenoids [4, 5] phenolic compounds [6] and flavonoids [7] in *K. pinnata*. We now report the isolation and characterisation of long chain hydrocarbons and alkanols, sterols, and friedelin, glutinol and taraxerol (all triterpenoids) from the flowers of *K. spathulata*. This is the first report of the occurrence of such rearranged pentacyclic triterpenoids in the genus *Kalanchoe*.

RESULTS

Column chromatography on alumina of a petroleum ether extract of the air dried flowers of *K. spathulata* yielded a white wax, mp 63–64° (mixture of long chain hydrocarbon homologues by GLC) followed by a similar mixture of *n*-alkanols, mp 72–73°. On further elution three triterpenoids were obtained. Friedelin (D:A-friedooleanan-3-one), mp and mmp with an authentic sample 262–266°, NMR: δ 0.71, 0.86, 0.94, 1.04 and 1.18 (each 3H, *s*), 0.86 (3H, *d*, J = 7 Hz), and 1.00 (6H, *s*). Taraxerol (D-friedoolean-14-en-3β-ol) [8], mp 280–282°; acetate, mp 302–304°, NMR: δ 0.83, 0.87, 0.88, and 1.10 (each 3H, *s*), 0.91 and 0.96 (each 6H, *s*), 2.02 (3H, *s*, acetate), 4.45 (1H, *t*, J = 7 Hz), and 5.52 (1H, *dd*, J = 3 and 9 Hz). Glutinol (D:B-friedoolean-5-en-3β-ol), mp 208–210°, $[\alpha]_D$ + 61.5°, NMR: δ 0.85, 0.94, 0.99, 1.00, 1.05, 1.09, 1.14 and 1.17 (each 3H, *s*), 3.46 (1H, broad *s*, $W_{1/2}$ = 7 Hz) and 5.62 (1H, broad *s*, $W_{1/2}$ = 9 Hz), MS (*m/e*): 426 (M^+) 408, 393, 274 and 259; acetate, mp 189–191°, $[\alpha]_D$ + 77°, NMR: δ 0.85, 0.95, 0.99, 1.00, 1.05, 1.08, 1.10, 1.18 and 2.00 (each 3H, *s*), 4.70 (1H, broad *s*, $W_{1/2}$ = 6 Hz), and 5.58 (1H, broad *s*, $W_{1/2}$ = 9 Hz). The major peaks in the MS of glutinol and its acetate were those deriving from a *retro*-Diels–Alder type process in ring B analogous to that previously observed [9] in, for example, taraxerol. The final fractions from the column yielded a mixture of the plant sterols sitosterol (71%), stigmasterol (23%), and campesterol (6%).

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TRITERPENOIDS OF *PHELLINUS GILVUS*

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Key Word Index—*Phellinus gilvus*; Fungi; pinicolic acid; trametanolic acid.

Fungi. Phellinus gilvus (Schw. exFr.) Pat. Syn. *Polyporus gilvus* Schw. exFr. *Previous work.* Recently Japanese [1] workers have described the distribution of tetracyclic triterpenoids of the lanostane group. They have reported the absence of triterpene carboxylic acids in *Phellinus gilvus.*

Present work. We now describe the isolation and identification of two triterpene carboxylic acids along with other compounds.

The fruiting bodies of the fungus *Phellinus gilvus* (1.5 kg) collected from the Changa Manga Forest near Lahore in August (Specimen No. 6376 deposited at herbarium PCSIR Peshawar (PES)) were extracted with EtOH at room temp. for 24 days. The brown extract when conc under red. press. gave 7.3 g of dark brown gum. It was chromatographed on Si gel (200 g). Elution with C_6H_6 and crystallization with MeOH gave colourless flakes (61 mg) of ergosterol mp 163–65°. Identified by mp and mmp and by direct comparison with an authentic specimen [2]. Further elution with C_6H_6 gave a crystalline mixture (0.182 g) mp range 153–72° (Fraction A). Elution with $CHCl_3$ and crystallization with MeOH gave colourless needles (14 mg) of pinicolic acid, mp 198–202°, $[\alpha]_D$ + 65° ($CHCl_3$), $C_{30}H_{46}O_3$ (M^+ 454), ν_{max} 1700 and a shoulder at 1730 cm^{-1} indicated a keto acid. The acid was methylated and compared directly with a sample of methyl pinicolate [3]. Both were found to be identical. Elution with Me_2CO–$CHCl_3$ (5:95) and crystallization from MeOH gave colourless needles of trametanolic acid, mp 252–58° (lit. [4] 253–58°), $[\alpha]_D$ + 45° ($CHCl_3$), $C_{30}H_{48}O_3$ (M^+ 456), ν_{max} 1705 and 3405 cm^{-1}. (Found C, 78.40; H, 10.34 calculated for $C_{30}H_{48}O_3$; C, 78.94; H, 10.52%). Elemental analysis, spectral data, optical rotation and mp of the natural product showed that it is trametanolic acid [5].

Fraction A (0.162 g) was chromatographed on an alumina column (20 g). Elution with C_6H_6 and crystallization from MeOH gave colourless needles mp 170–73°, λ_{max} 262, 270, 281 and 292 nm. UV of the mixture was reminiscent of 'ergosterol-like' compounds [6]. When repeated crystallization failed to give a pure sample, it was rechromatographed on neutral alumina. Elution with C_6H_6 followed by four crystallizations from MeOH gave pure ergosta-7,22-dien-3β-ol, mp 175° (lit. [7] mp 176°), $[\alpha]_D$ – 19°; acetate mp. 176–78° (lit. [7] mp 178–80°). benzoate mp 198–200° (lit. [7] mp 200°). The $[\alpha]_D$ and mp of the natural product and of its derivatives are in accord with the published values [7].

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