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ZINGIBERACEAE

CARDAMONIN AND ALPINETIN FROM THE SEEDS OF *ALPINIA SPECIOSA*

B. M. KRISHNA and R. B. CHAGANTY

Department of Chemistry, Andhra University, Waltair, A.P., India

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Cardamonin (2′,4′-dihydroxy-6′-methoxy chalcone) and alpinetin (7-hydroxy-5-methoxy flavanone) have been isolated from the seeds of *Alpinia speciosa* Schum. of Indian origin. An earlier chemical investigation on the seeds[1] did not indicate the presence of these two compounds.

The constitution of the chalcone was established by hydrolytic cleavage, isomerization to the corresponding flavanone and UV, IR, NMR and MS data and by comparison with a synthetic sample. The compounds also occur in *Alpinia katsumadai* Hayata[2] and an endemic *Piper* species of New Guinea.[3]

EXPERIMENTAL

All m.ps are uncorrected.

Isolation. Powdered dry ripe seeds of *Alpinia speciosa* Schum. were extracted with *n*-hexane, Et_2O and MeOH successively. The Et_2O extract gave a yellow powder which was separated into chalcone and flavanone by chromatography over silica gel, using benzene–acetone (7:3) mixture for elution.

Cardamonin. Yellow prisms from EtOAc, m.p. 207°, red-brown with $FeCl_3$. (Found: C, 71·32; H, 5·34; –OMe, 11·22. $C_{15}H_{11}O_3$ (OMe) required: C, 71·10; H, 5·22; –OMe, 11·49%.) UV λ_{max} 214 nm (log ϵ 4·43), 345 nm (log ϵ 4·44). IR (KBr) ν_{max} 3170 cm^{-1} (–OH), 1625 cm^{-1} (C=O) and 970 cm^{-1} (H–C=C–H). NMR in $(CD_3)_2C=O$ with TMS as external standard –OC$\underline{H}_3$ (*s*, 3·81 δ), 2 Ar$\underline{H}$ (*d*, 5·86 δ and *d*, 6·12 δ-meta coupled—*J* 2·5 Hz), 5 Ar$\underline{H}$ (*m*, 7·18–7·60 δ) and trans olefinic 2 H (*s*, 7·67 and *s*, 7·76 δ). MS (T, 240°; E, 70 eV; I.C., 20 a) *m/e* 270 (M^+), 269 (M-1), 253 (M-17), 242 (M-28), 193 (M-77), 167 (M-103), 166 (M-104, 100%), 151 (*m/e* 166-15).

Methylation of the chalcone (Me_2SO_4) gave its 4′-*O*-monomethyl ether crystallized from benzene–hexane mixture m.p. 93° (lit.[4] 90–91°). UV λ_{max} 214 nm (log ϵ 4·43) and 343 nm (log ϵ 4·47). IR (Nujol) ν_{max} 1635 cm^{-1} (C=O) and 970 cm^{-1} (H–C=C–H). NMR in $CDCl_3$ 6′–OC$\underline{H}_3$ (*s*, 3·80 δ), 4′–OC$\underline{H}_3$ (*s*, 3·88 δ), 2 Ar$\underline{H}$ (*d*, 5·93 δ; *d*, 6·07 δ-meta coupled—*J* 2 Hz), 5 Ar$\underline{H}$ (*m*, 7·32–7·64 δ), trans olefinic 2 H (*s*, 7·80; *s* 7·83 δ) and 2′–O$\underline{H}$ (*s*, 14·24 δ, disappeared by D_2O exchange).

Hydrolytic cleavage of the chalcone following usual procedure gave benzaldehyde and 2,4-dihydroxy-6-methoxy acetophenone, and isomerization using aq.–alcoholic (1:1) 3% H_2SO_4 yielded alpenitin. The chalcone and its monomethyl ether were synthesized in the usual way[5] and found to be identical in all respects with the natural specimens.

Alpinetin. Colourless needles from MeOH, negative $FeCl_3$ and positive Shinoda test. (Found: C, 71·15; H, 5·20; –OMe, 11·32. $C_{15}H_{11}O_3$ (OMe) required: C, 71·10; H, 5·22; –OMe, 11·49%.) UV λ_{max} 286 nm (log ϵ 4·26). It was identical with the flavanone obtained by isomerization of the chalcone. Methylation (Me_2SO_4) gave 5,7-dimethoxy flavanone, m.p. 144–145° (lit.[4] m.p. 143°).

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