Flavonoids of *Echinops echinatus*

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Abstract: Six flavonoids, 7-hydroxyisoflavone, kaempferol-4'-methylether, kaempferol-7-methylether, kaempferol, kaempferol-3-O-\(\alpha\)-L-rhamnoside and myrecetin-3-O-\(\alpha\)-L-rhamnoside has been isolated from the whole plant of *Echinops echinatus*.

Keywords: Medicinal plants, flavonoids.

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*Echinops echinatus* Roxb. (Compositae) is distributed throughout India and used in Indian medicine for the treatment of chronic fever, inflammations and various other diseases\(^1\). A number of terpenoids, flavonoids and other constituents have earlier been reported\(^2\) from this plant. Here we report the isolation of further six flavonoids.

The whole plant (3.5 kg) was collected locally and dried material was extracted with MeOH in a soxhlet extractor. The methanolic extract (75 g) was chromatographed over SiO\(_2\) gel column. The eluants collected from benzene-ethylacetate (8 : 1), (4 : 1), (3 : 1), (1 : 2), (1 : 4), (4 : 1) on extractor. The methanolic extract (75 g) was dried material was extracted with MeOH furnished respectively 7-hydroxyisoflavone\(^3\) (15 mg), m.p. 215 °C, kaempferol-4'-methylether (21 mg), m.p. 223–225 °C; kaempferol-7-methylether (25 mg), m.p. 218–220 °C, kaempferol (32 mg), m.p. 273–275 °C, kaempferol-3-O-\(\alpha\)-L-rhamnoside\(^5\) (28 mg), m.p. 177–179 °C and myrecetin-3-O-\(\alpha\)-L-rhamnoside\(^5\) (24 mg), m.p. 211–213 °C.

7-Hydroxyisoflavone: It exhibited UV \(\lambda_{max}\) (MeOH) 260 (log \(\varepsilon\) 4.13), 290 sh (3.40), 315 sh (3.34) nm; IR \(\nu_{max}\) (KBr) 3200–3600 (OH), 1655 cm\(^{-1}\) (chelated carbonyl); 90 MHz \(^1\)H NMR (DMSO-\(d_6\)) \(\delta\) 8.11 (d, \(J\) 8 Hz, \(H-3'\), \(H-5'\)), 7.74 (d, \(J\) 8 Hz, \(H-2'\), \(H-6'\)), 7.39 (m, \(H-3'\), \(H-4'\), \(H-5'\)), 7.56 (m, \(H-2'\), \(H-6'\)), 7.92 (d, \(J\) 8 Hz, \(H-6\)), 8.36 (s, \(H-2\)), 10.80 (br s, OH); 100 MHz \(^13\)C NMR (DMSO-\(d_6\)) \(\delta\) 153.4 (C-2), 123.3 (C-3), 174.0 (C-4), 116.4 (C-4a), 127.0 (C-5), 115.0 (C-6), 162.4 (C-7), 101.9 (C-8), 157.1 (C-8a), 131.8 (C-1'), 127.8 (C-2'), 128.6 (C-3'), 127.4 (C-4'), 128.6 (C-5'), 127.8 (C-6'); HRMS; \(m/z\) 238.0629 (M\(^+\), \(C_{15}H_{10}O_3\)); 210, 137.0238 (C\(_7\)H\(_{3}\)O\(_3\)), 102.0469 (C\(_8\)H\(_6\)).

**Kaempferol-4'-methylether**: It exhibited UV \(\lambda_{max}\) (MeOH) 250 sh (log \(\varepsilon\) 4.17), 270 (4.20), 300 (3.70), 320 (3.92), 368 (4.30) nm; IR \(\nu_{max}\) (KBr) 3200–3600 (br, OH), 1660 cm\(^{-1}\) (chelated carbonyl); 90 MHz \(^1\)H NMR (DMSO-\(d_6\)) \(\delta\) 3.84 (s, Ar-\(OCH_3\)), 6.33 (d, \(J\) 2.2 Hz, H-6), 6.72 (d, \(J\) 2.2 Hz, H-8), 6.94 (d, \(J\) 9 Hz, H-3', H-5'), 8.09 (d, \(J\) 9 Hz, H-2', H-6'), 9.51 (s, OH), 10.15 (s, OH), 12.45 (s, OH); MS, \(m/z\) 300 (M\(^+\), \(C_{16}H_{12}O_6\)), 272, 257, 229, 154, 148, 124; with CH\(_2\)N\(_2\) it gave trimethylether derivative, m.p. 151–153 °C, \(C_{19}H_{18}O_6\) (M\(^+\), 342).

**Kaempferol-7-methylether**: It exhibited UV \(\lambda_{max}\) (MeOH) 254 (log \(\varepsilon\) 4.25), 266 (4.20), 323 (4.10), 365 (4.40) nm; IR \(\nu_{max}\) (KBr) 3150–3550 (OH), 1660 cm\(^{-1}\) (chelated carbonyl); 90 MHz \(^1\)H NMR (DMSO-\(d_6\)) \(\delta\) 3.70 (s, Ar-\(OCH_3\)), 6.11 (d, \(J\) 2 Hz, H-6), 6.46 (d, \(J\) 2 Hz, H-8), 6.67 (d, \(J\) 8 Hz, H-3', H-5'), 7.74 (d, \(J\) 8 Hz, H-2', H-6'), 9.11 (s, OH), 9.71 (s, OH), 11.98 (s, OH); MS, \(m/z\) 300 (M\(^+\), \(C_{16}H_{12}O_6\)), 272, 257, 229, 166, 138, 134; with acetic anhydride and pyridine, it gave triacetate, m.p. 201–203 °C, \(C_{22}H_{18}O_9\) (M\(^+\), 426).

**Kaempferol**: It exhibited UV \(\lambda_{max}\) (MeOH) 252 sh (log \(\varepsilon\) 4.20), 266 (4.25), 292 (3.95), 322 sh (4.10), 366 (4.38) nm; IR \(\nu_{max}\) (KBr) 3320 (OH), 1660 cm\(^{-1}\) (chelated carbonyl); 90 MHz \(^1\)H NMR (DMSO-\(d_6\)) \(\delta\) 6.22 (d, \(J\) 2.2 Hz, H-6), 6.46 (d, \(J\) 2.2 Hz, H-8), 6.68 (d, \(J\) 9 Hz, H-3', H-5'), 8.11 (d, \(J\) 9 Hz, H-2', H-6'), 9.44 (s, OH), 10.22 (s, OH), 12.56 (s, OH); MS, \(m/z\) 286 (M\(^+\), 342).

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C_{15}H_{10}O_{6}, 258, 152, 134, 124.

**Kaempferol-3-O-α-L-rhamnoside**: It exhibited UV \( \lambda_{\text{max}} \) (MeOH) 264 sh (log \( \varepsilon \) 4.12), 313 sh (3.82), 343 (4.00) nm; IR \( \nu_{\text{max}} \) (KBr) 3200–3600 (br, OH), 1660 cm\(^{-1}\) (chelated carbonyl); 90 MHz \(^{1}\)H NMR (DMSO-\( \text{d}_6 \)) \( \delta \) 6.10 (d, \( J_{2 \text{ Hz}, \text{ H-6}} \), 6.28 (d, \( J_{2 \text{ Hz}, \text{ H-8}} \)), 6.93 (d, \( J_{9 \text{ Hz}, \text{ H-3'}, \text{ H-5'}} \)), 7.75 (d, \( J_{9 \text{ Hz}, \text{ H-2'}, \text{ H-6'}} \)), 12.66 (br s, 3 \( \times \) OH) and eleven rhamnosyl protons [\( \delta \) 0.81 (d, \( J_{5 \text{ Hz}, \text{ CH}_3} \)), 3.13 (2H, m), 3.46 (1H, m), 4.00 (1H, br s), 4.88 (3H, br s, OH), 5.32 (d, \( J_{2 \text{ Hz}, \text{ anemic-H}} \))]; elemental analysis (Found : C, 57.90; H, 4.54. Calcd. for \( \text{C}_{21}\text{H}_{20}\text{O}_{12} \): C, 57.90; H, 4.32%); acid hydrolysis gave kaempferol (m.m.p., co-TLC, \(^{1}\)H NMR, MS and superimposable IR).

The structures of all the above compounds were supported by a study of UV with shift reagents and direct comparison with authentic samples (m.m.p., co-TLC and superimposable IR).

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