Isolation of Kaempferol-3-O-rhamnoglucoside, a Flavonoid Glycoside from Zephyranthes candida

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Zephyranthes candida, Rutin, Kaempferol-3-O-rhamnoglucoside

Kaempferol-3-O-rhamnoglucoside, a flavonoid glycoside, was isolated from fresh white petals of Zephyranthes candida.

Zephyranthes candida Herb. belonging to Amaryllidaceae (Japanese name: Tamasudare) bears white flowers in fall. From the petals of the plant the isolation of rutin has already been reported [1]. We now isolated an additional flavonoid in the fully examination of the same source, which was identified as kaempferol-3-O-rhamnoglucoside.

The flavonoid fraction isolated from the methanol extract was chromatographed over a silica-gel column with methyl ethyl ketone-water to give two flavonoids, less polar (m. p. 210 — 20 °C) [2] and more polar (m. p. 180 — 90 °C). The more polar component was identified as rutin based on the agreement with the mixed m. p., TLC and UV spectrum with those of the authentic sample.

The less polar component gave kaempferol (m. p. 273 — 5 °C) [2], glucose [TLC, phenyl osazone (m. p. 201 — 2 °C)], and rhamnose [TLC, phenyl osazone (m. p. 179 — 80 °C)] by acid hydrolysis, and exhaustive methylation of the less polar component with diazomethane followed by acid hydrolysis gave kaempferol 5,7,4'-trimethyl ether. Besides, the m. p. 191 — 4 °C for anhydrous materials of this flavonoid corresponded to that of the kaempferol-3-O-β-rutinoside synthesized by Vermes et al. [3], and the NMR spectrum of its nonaacetate was superimposable with that of rutin decaacetate in the sugar portion [4]. These results indicate that the flavonoid was kaempferol-3-O-rhamnoglucoside, which has been isolated from a number of plants [5].

Experimental

Fresh white petals (700 g) collected from the plant were digested with hot methanol for 30 min and the methanol solution was evaporated to 200 — 300 ml. The concentrated aqueous solution was washed with ether, further concentrated to ca. 50 ml and allowed to stand in a refrigerator to give precipitates (3 g), which were filtered and chromatographed over a silica gel column with methyl ethyl ketone saturated with water to separate it into less polar (1.33 g) and more polar (1.15 g) flavonoids. The less polar flavonoid was recrystallized from methanol-water as yellow needles, m. p. 210 — 20 °C (decomp.) [2]; UV λmax nm (log ε) 267.5 (4.38), 305 (4.16), 353 (4.25). Found: C, 51.33; H, 5.51. Calcd. for C27H30O14·2H2O: C, 51.43; H, 5.40%. Anhydrous materials (dried at 145 °C/1 mm Hg) ; m. p. 191 — 4 °C (sinter) and 225 — 8 °C (decomp.). Found: C, 53.93; H, 5.09. Calcd. for C27H30O14: C, 54.55; H, 5.09%.

The compound (200 mg) was hydrolyzed under refluxing with 5% sulfuric acid (20 ml) for 1 hr to give kaempferol as yellow needles (80 mg), which were filtered and recrystallized from methanol, m. p. 273 — 5 °C; UV λmax nm (log ε) 267 (4.33), 321 (4.13), 368 (4.38). Found: C, 62.93; H, 3.49. Calcd. for C18H16O6: C, 62.94; H, 3.52%. The filtrate, after neutralization with barium carbonate, was treated with phenylhydrazine to give gluco-osazone as yellow needles, m. p. 201 — 2 °C (recrystallization from methanol, mixed m. p. undepressed, TLC) and rhamno-osazone as yellow needles, m. p. 179 — 81 °C (recrystallization from 80% aqueous methanol, mixed m. p. undepressed, TLC). Methylation of the less polar component with diazomethane followed by hydrolysis with 10% hydrochloric acid gave kaempferol 5,7,4'-trimethyl ether as yellow needles, which were recrystallized from methanol, m. p. 150 — 1 °C [2]. Found: C, 62.25; H, 5.32.

Calcd. for C18H16O6·2H2O: C, 62.42; H, 5.24%. It was converted into nonaacetate (colorless precipitates) with cold acetic anhydride-pyridine. NMR (δ, ppm CDCl3) 1.04 (d, 3H, J = 7 Hz), 1.94 (s, 6H), 2.01 (s, 6H), 2.08 (s, 3H), 2.11 (s, 3H), 2.29 (s, 3H), 2.31 (s, 3H), 2.42 (s, 3H), 3.04—3.30 (m, 1H), 3.43—3.70 (m, 3H), 4.26 (bs, 1H), 4.75—5.30 (m, 6H), 5.41 (d, 1H, J = 7 Hz), 6.68 (d,
1H, $J = 2.5$ Hz), 7.12~7.28 (m, 3H), 8.02 (d, 2H, $J = 9$ Hz).

The more polar compound was recrystallized from methanol-water as yellow needles, m. p. 180~90 °C.

Found: C, 48.53; H, 5.40. Calcd. for C$_{27}$H$_{30}$O$_{16}$·3 H$_2$O: C, 48.80; H, 5.42%. UV $\lambda_{max}^{E_{10H}}$ nm (log ε) 259 (4.35), 305$_{sh}$ (4.00), 362 (4.25).