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Luteolin-7-glucoside as a Characteristic Component of the Plant Genera *Juncus* and *Luzula* (Family Juncaceae)

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Luteolin-7-glucoside has been isolated in a crystalline state from *Juncus gerardi* Lois. and *Luzula silvatica* (Huds.) Gaud., and has been identified in another 13 species of *Juncus* L. and 4 species of *Luzula* DC.

The flavonoids of the Monocotyledoneae are little known, and only a few monocotyledonous families have been investigated in any detail. Most work has been carried out on the anthocyanins, and, to a lesser extent, the flavones and flavonols of a restricted number of genera within the families Liliaceae, Amaryllidaceae, Iridaceae, and Gramineae.[1]

Very little work has been done on the Juncaceae,[2,3] and practically nothing is known of the chemistry of this family. The Juncaceae comprises about 320 species in 8 genera, of which *Juncus* and *Luzula* are by far the most important, with *ca.* 230 and *ca.* 80 species, respectively.

RESULTS AND DISCUSSION

From the ethanolic extracts of *Juncus gerardi* a pale yellow crystalline substance was isolated. By means of chromatography on a polyamide column and recrystallisation from ethanol, two pure substances were obtained; these proved to be luteolin (5,7,3′,4′-tetrahydroxyflavone) and luteolin-7-glucoside, the latter being the major component.

By means of preparative paper chromatography, luteolin-7-glucoside was furthermore isolated from *Juncus articulatus*, *J. conglomeratus*, *J. filiformis*, and *J. tenuis*, and from *Luzula silvatica*. Free luteolin was isolated from *J. articulatus* and *L. silvatica*. The substances were chromatographically indistinguishable from authentic specimens isolated from *Daucus* leaves,[1] when examined in at least three different systems. The ultraviolet spectra were

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also identical, both in ethanol and after addition of $AlCl_3$, NaOEt, NaOAc, or $NaOAc/H_3BO_3$.

By comparative paper chromatography luteolin-7-glucoside was shown to be present in *Juncus alpinus*, *J. arcticus*, *J. biglumis* (dubious, very small sample), *J. bufonius*, *J. bulbosus*, *J. effusus* (Plouvier [3] mentions the isolation of luteolin-7-glucoside from this species), *J. kochii*, *J. trifidus*, *J. triglumis*, *Luzula multiflora*, *L. pilosa*, *L. spicata*, and *L. sudetica*. In most cases weak spots corresponding to free luteolin were observed.

Chlorogenic acid was also shown to be present in the plants.

The flavone luteolin and its *O*-glycosides seem to be rather widespread among the Dicotyledoneae, and their taxonomic value is uncertain, although they seem to be particularly common in the Tubiflorae and in the Compositae.

The flavonoids of the Monocotyledoneae are still little known, however, there do appear to be regularities which may be of taxonomic value. The Liliaceae are characterised by their contents of flavonols, while flavones with few exceptions,[4] seem to be absent, as distinct from the Iridaceae, and particularly the Gramineae, where flavones are widespread, mostly as *C*-glycosyl derivatives.[1] Thus *C*-glycosyl luteolins have been isolated from the leaves of several graminaceous species (*e.g. Hordeum vulgare* L.[5]). Monoglycosides of luteolin have also been found in the Gramineae in a few cases (*e.g. Paspalum conjugatum* Berg.[6]), but in the majority of cases the only flavone found is tricin (5,7,4′-trihydroxy-3′,5′-dimethoxyflavone) and glycosides thereof.[7]

In this connection it is of interest that the occurrence of luteolin-7-glucoside seems to be a characteristic feature of the genera *Juncus* and *Luzula*, as distinct from the Liliaceae and Gramineae. Unfortunately, no representatives of the remaining six genera of the family Juncaceae were available for investigation.

EXPERIMENTAL

The plants used for this investigation were collected at the following localities:

Tingvoll, Norway: *Juncus alpinus* Vill., *J. articulatus* L., *J. biglumis* L., *J. bulbosus* L., *J. conglomeratus* L., *J. effusus* L., *J. filiformis* L., *J. gerardi* Lois., *J. kochii* Schultz, *J. trifidus* L., *J. triglumis* L., *Luzula multiflora* (Retz.) Lej., *L. silvatica* (Huds.) Gaud., *L. spicata* (L.) DC., *L. sudetica* (Willd.) DC.

Ås, Norway: *Juncus bufonius* L., *J. tenuis* Willd., *Luzula pilosa* (L.) Willd.

Abisko, Sweden: *Juncus arcticus* Willd.

Melting points are corrected and were determined on a Berl block.

Ultraviolet spectra were determined in a Beckman DB spectrophotometer.

Chromatography was performed on Whatman No. 1 paper, and, for preparative work, on Whatman No. 3MM paper. The solvent used was in most cases BAW 6:1:2 (butanol:acetic acid:water); for identification 15 % acetic acid, 22 % propanol, and Forestal (acetic acid:conc. HCl:water, 30:3:10) were also used. The substances were detected by their colours in ultraviolet light, before and after fuming with ammonia. Polyamide powder (Woelm) was used for column chromatography, using methanol as eluent. The columns were prewashed with methanol to remove soluble material.

Extraction and purification

Juncus gerardi: Powdered plant material (leaves, stems, inflorescences) was extracted with ethanol until the extracts were almost colourless. The combined extracts were concentrated *in vacuo* at 40°, water was added, and the solution was repeatedly extracted

with light petroleum (60—80°). During the extractions a yellowish precipitate appeared, which proved to be a flavonoid substance. Additional quantities could be obtained when the aqueous phase was further concentrated and left for some time. When the flavonoids were chromatographed on polyamide powder, two crystalline fractions were obtained; the major fraction proved to be luteolin-7-glucoside, the minor fraction being free luteolin.

Remaining *Juncus* and *Luzula* species: Powdered and dried plant material was exhaustively extracted with ethanol. The extracts were evaporated to dryness, and lipids were removed by extraction with hot petroleum ether (60—80°). The flavonoids were dissolved in methanol and isolated by preparative paper chromatography. Crystalline luteolin-7-glucoside was isolated from *L. silvatica*; from *J. articulatus*, *J. conglomeratus*, *J. filiformis*, and *J. tenuis* enough substance was obtained for spectroscopical identification in the five different media mentioned.

Luteolin-7-glucoside. The substance isolated from *J. gerardi* and *L. silvatica* was crystallised from ethanol and melted at 258—60°. There was no depression on mixture with an authentic specimen. Absorption spectra: λ_{max} (EtOH) 352, 268, 257 mμ; ($AlCl_3$) 395, 360, 275 mμ; (NaOEt) 402, 267 mμ; (NaOAc) 413, 257 mμ; ($NaOAc/H_3BO_3$) 380, 264 mμ. All spectra were identical with those of an authentic specimen prepared from *Daucus carota* leaves.

Acid hydrolysis, to which the glucoside was remarkably resistent, yielded glucose and an aglycone, which proved to be identical with the previously isolated free luteolin; m.p. 325°. Absorption spectra: λ_{max} (EtOH) 352, 269, 254 mμ; ($AlCl_3$) 393, 362, 276 mμ; (NaOEt) 406, 279 mμ; (NaOAc) 392, 269 mμ; ($NaOAc/H_3BO_3$) 378, 260 mμ.

After acetylation the substance had absorption bands at 300 and 258 mμ, which are identical with the values given for luteolin tetraacetate.[8]

All ultraviolet spectra were in good agreement with previously published values.[1,8,9]

The sugar moiety was identified as glucose by means of paper chromatography.

R_F values were 0.78 for luteolin and 0.40 for luteolin-7-glucoside (BAW).

In ultraviolet light luteolin appeared as dull ochre spots, turning bright greenish yellow when fumed with ammonia. The dull ochre spots of luteolin-7-glucoside turned bright yellow when exposed to ammonia.

From *Juncus gerardi* a colourless substance was isolated, which was chromatographically and spectroscopically identical with an authentic sample of chlorogenic acid. Corresponding spots were observed in chromatograms of all *Juncus* and *Luzula* species investigated. The absorption spectra were as follows: λ_{max} (EtOH) 328, 299, 243, 217 mμ; ($AlCl_3$) 348 mμ; (NaOEt) 370, 308, 260 mμ; (NaOAc) 328, 300 mμ; ($NaOAc/H_3BO_3$) 348, 304, 252 mμ.

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