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CIRSIMARITIN-4′-*O*-RUTINOSIDE, A NEW FLAVONE GLYCOSIDE FROM *CIRSIUM BREVISTYLUM*

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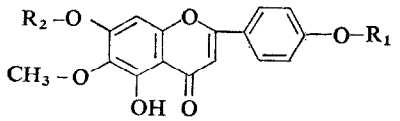
Abstract—An examination of five species of *Cirsium* disclosed the presence of a new flavone glycoside in *C. brevistylum*. The structure of the compound was established as cirsimaritin-4′-*O*-rutinoside (4′-rutinosyloxy-5-hydroxy-6,7-dimethoxyflavone). The compound was not present in *C. edule*, *C. undulatum*, *C. vulgare*, or *C. arvense*.

INTRODUCTION

ONLY a few reports concerning the phenolic chemistry of the relatively large genus *Cirsium* Mill. have appeared;[1–8] of 1100 recorded species[9] only 25 have been examined for polyphenols. As part of a program of comparative phytochemical research within the Compositae a brief survey of thistles of southwestern British Columbia was undertaken. This report describes the identification of a new glycoside cirsimaritin-4′-*O*-rutinoside (II) from leaf extracts of *C. brevistylum*. Cirsimaritin-4′-*O*-glucoside (I) has already been identified in *C. maritimum*,[4] *C. aomorense* and *C. tanakae*[5] as well as in *Helichrysum viscosum* Compositae.[10]



(I) R_1 = glucosyl, R_2 = CH_3
(II) R_1 = rutinosyl, R_2 = CH_3
(III) R_1 = CH_3, R_2 = rutinosyl

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RESULTS AND DISCUSSION

The new glycoside was isolated as cream-white microneedles from leaf extracts of *Cirsium brevistylum*. Its melting point of 278–281° contrasted with that of pectolinarin, (III), 254–256°,[3] a known constituent of *Cirsium*. The structure was assigned on the basis of NMR and u.v. spectral data.[11,12]

The NMR spectrum of the trimethylsilyl ether displayed signals typical of a 4′-substituted B-ring: H-2′ and -6′ doublet centered at 7·8 ppm; and H-3′ and -5′ doublet centered at 6·9 ppm. A single C-ring proton centered at 6·3 ppm indicated that we were dealing with a flavone. A singlet at 6·7 ppm and lack of a signal in the 6·0–6·4 region indicated the presence of only a C-8 proton in the A-ring. Two methoxyl groups were indicated by the signals at 3·8 and 3·9 ppm. The NMR spectrum was also instructive with regard to the nature of the glycosidic moiety. The spectrum indicated that 12 protons, including a methyl group, were

TABLE 1. CHROMATOGRAPHIC AND U.V. SPECTRAL DATA FOR CIRSIMARITIN AND ITS 4′-RUTINOSIDE

4′-Rutinoside	Cirsimaritin
MeOH 328, 274	325, 270
NaOMe 366, 294	357, 292 sh, 278 (broad)
$AlCl_3$ 350, 290 sh, 280	sh 348, 292
$AlCl_3$/HCl 338, 292, 276	340, 290
NaOAc 328, 277	354, 290 sh, 272

Chromatographic data (on Whatman 3 mm paper)

4′-Rutinoside	Cirsimaritin
R_f (T BA) 0·59	0·84
R_f (15% HOAc) 0·80	0·19

associated with the sugars. The presence of a disaccharide agreed with the finding of both glucose and rhamnose after acid hydrolysis of the glycoside. The signal for the rhamnose methyl protons was centered at 0·9 ppm. This, together with the signal at 4·3 ppm (rhamnose C-1‴ proton), indicated that the sugar was rutinose rather than neohesperidose.

The u.v. spectral characteristics of the glycoside and its aglycone (cirsimaritin) are presented in Table 1. Neither the glycoside nor the aglycone showed a bathochromic shift with sodium acetate, indicating 7-*O*-substitution in both. In addition the band I shift of 29 nm with NaOAc reagent indicates that the 4′ position was blocked before hydrolysis. The $AlCl_3$ shift in band I of 22 nm indicates the presence of a free 5-hydroxyl function and implies a 5-OH-6-OR grouping.[13] These observations and the absence of a 6-proton are entirely in accord with a 5-OH-6, 7-di-OCH_3 substitution. If such is the case and since 2′, 6′, 3′ and 5′ protons are present in ring-B then the rutinosyl function must be in position 4′. The structure of the glycoside is then 4′-rutinosyloxy-5-hydroxy-6,7-dimethoxyflavone(II).

Four other *Cirsium* species were examined chromatographically for this glycoside, but we were unable to detect it in *C. edule*, *C. undulatum*. *C. vulgare* and *C. arvense*.

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EXPERIMENTAL

Plant material was collected in southwestern British Columbia during the summer of 1969, *C. brevistylum* Cronq. and *C. arvense* (L.) Scop. were collected on the campus of the University of British Columbia, *C. vulgare* (Savi) Airy-Shaw was collected in Seymour Provincial Park, Vancouver, B.C., *C. edule* Nutt. was collected in Manning Provincial Park, B.C., and *C. undulatum* (Nutt.) Spreng. was collected on the Lillooet-Lytton Road, B.C.

Plant material was extracted thoroughly with 80% ethanol. Extracts were pooled, evaporated to dryness, and the residue extracted with boiling water with the aid of Celite. Filtration yielded the water soluble fraction which was extracted first with Et_2O and then exhaustively with EtOAc. Chromatography of the EtOAc fraction in *t*-BuOH–HOAc–H_2O (3:1:1) followed by 15% HOAc disclosed at least 10 compounds most of which appeared not to be flavonoids. The new glycoside, the major constituent, (R_fs in Table 1) was obtained by banding in these solvents and purification by re-running in *iso* PrOH–H_2O (4:1). It was eluted with 80% ethanol, the solvent removed and the residue crystallized from EtOAc. Two recrystallizations yielded cream-white microneedles with m.p. 278–281° (Kofler hotstage).

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A THIOPHEN FROM *LIATRIS PYCNOSTACHYA**

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Abstract—2-Acetyl-3-hydroxy-5(prop-1-ynyl)thiophen (II) was isolated from the roots of *Liatris pycnostachya*.

LARGE numbers of polyacetylenes and thiophens have now been isolated from the Compositae[1] but most of the isolation studies have been confined to a very few tribes in the family. There is, apparently, only one example of the isolation of a polyacetylene from a member of the tribe Eupatorieae, viz. the tridecapentaynene (I) which has been reported to be present as a trace component of *Piqueria trinervia* (Jacq.) Cav.;[2] we now report the first isolation of a thiophen from the Eupatorieae.

Liatris Schreb (sub tribe, Adenostylinae) "Blazing Star" or "Button Snake-Root" is represented by about thirty species native to temperate North America[3] and several are common in Europe. The species is reported as having been used for treatment of snakebite, the roots for various medicinal purposes and the leaves as a substitute for vanilla. There has been little chemical examination but the flavonoids[4] and the seed oils[5] have been investigated.

* Paper VI in the series "Naturally occurring Thiophens"; for Part V see *J. Chem. Soc.* (C) 1813 (1969).

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