Sulphated flavonoid glycosides from leaves of *Atriplex hortensis*

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**Abstract**

Two flavonoid sulphates, i.e. quercetin 3-O-sulphate-7-O-α-arabinopyranoside and kaempferol 3-O-sulphate-7-O-α-arabinopyranoside, were isolated from leaves of *Atriplex hortensis* L. The structures of these compounds were established by UV, \(^1\)H and \(^13\)C NMR, 2D NMR and MS spectra. The compounds were isolated for the first time from plant material.

**Introduction**

Flavonoids are important in plant biochemistry and physiology, acting as antioxidants, enzyme inhibitors, pigments and light screens. These compounds are involved in photosensitization and energy transfer, growth regulation, respiration control, photosynthesis and defence against infection (Harborne 1994).

A variety of pharmacological effects were confirmed for flavonoids including antioxidative, superoxide scavenging, variety of enzymes inhibitory activity and antiinflamatory, antiviral, anticarcino-

The investigations showed that all of these compounds possesses antioxidant properties stronger than α-tocopherol, a common natural antioxidant, and also act as lens aldose reductase inhibitors. (Yagi *et al.* 1994; Haraguchi *et al.* 1996).

Sulphate esters of flavonoids are relatively rare compounds. Up to now about 100 flavonoids substituted with the sulphate residue were isolated from natural sources, whereas more than 4000 common hydroxyflavones, hydroxyflavonols and their glycosylated derivatives are known (Harborne 1994). The flavonoid sulphates are found mainly in species occurring in coastal and swampy areas rich in mineral salts. The sulphates are also isolated from plants occurring in arid habitats. In plants binding of inorganic sulphate with polyphenolics, like flavonoids, is probably one of the mechanisms of its deactivation, and thereby is connected with...
biochemical adaptation of species to environment (Barron et al. 1988b).

The species from the genus Atriplex (Chenopodiaceae) often occur on saline and arid soils, and are common weeds, like Atriplex hortensis.

The aerial parts of A. hortensis were used in folk medicine against diseases of respiratory tract, digestive and urinary systems, and due to their analgesic properties, in rheumatism (Hoppe 1975; Siddiqui et al. 1994; Nicol 1994). The plant was used as a vegetable, but it may be allergenic on prolonged intake, causing skin eruptions (Hoppe 1975).

Previous chemical investigations on the species of the genus Atriplex showed the presence of saponin glycosides, alkaloids, betains, proteins, amino acids, ascorbic acid, mineral salts (Hegnauer 1989; Siddiqui et al. 1994; Nicol 1994) and phytoecdysteroids (Dinan 1995; Dinan et al. 1998). Previous studies on flavonoids included only the analysis of aglycones resulting from acid hydrolysis of extracts obtained from leaves of eight species from the genus Atriplex, excluding A. hortensis. The following aglycones were found using chromatography: quercetin, kaempferol, isorhamnetin and sometimes patuletin, spinacetin and tricin. Isorhamnetin 3-O-glucoside and 3-O-rhamnosylglucoside as well as naringenin and its 3-O-glucoside were isolated from A. farinosa L. (Al-Jaber et al. 1991). Barron indicated the presence of flavonoid sulphates in three species from the genus Atriplex. However, the species names were not given and the compounds were not identified (Barron et al. 1988b).

The present paper deals with the identification of two sulphated flavonoids isolated from leaves of Atriplex hortensis L and never reported earlier in plant material.

Material and methods

Plant material

Leaves of Atriplex hortensis L. (50 g) were collected from plants cultivated in 1998 in the garden at the Department of Medicinal Plants, K. Marcinkowski University of Medical Sciences, and air-dried. A voucher specimen is deposited at the Department of Pharmacognosy, K. Marcinkowski University of Medical Sciences, Poznań, Poland.

Extraction

The leaves were extracted subsequently with MeOH and 60 % MeOH. The combined extracts were concentrated under reduced pressure, treated with hot distilled water and the resulted precipitate was filtered off. The filtrate was extracted with CHCl₃.

Isolation procedure

Flavonoids present in the water layer were separated by preparative TLC using plates coated with microcrystalline cellulose Avicel (Merck) and n-BuOH-HOAc-H₂O (4:1:1) as a solvent system (Harborne 1989). The plates were viewed under a UV light (λ=366 nm), the bands were scraped off the plates and extracted subsequently with MeOH and 80 % MeOH at room temperature. The extract was filtrated, concentrated under reduced pressure and dissolved in 80 % MeOH. Compound (1) 15 mg crystallized from the corresponding fractions. The fractions containing compound (2) were purified on a Sephadex LH-20 column eluted with MeOH. The yield of compound (2) was ca 2 mg.

General

¹H NMR (300 MHz) and ¹³C NMR (75.5 MHz) spectra were recorded in DMSO-d₆ on a Varian 300 MHz spectrometer, using TMS as internal standard.

Mass spectra were performed on an AMD 604 two sector mass spectrometer (AMD Intectra, Germany) of B/E geometry, liquid secondary ion mass spectrometry (LSIMS) was used as an ionization method. Low and high resolution spectra and B/E linked scan mass spectra were registered. The ion gun supplied primary Cs⁺ ion beam at energy 10 keV. The secondary ion beam was accelerated to 8 kV. Triethanolamine was used as matrix in the negative mode and glycerol in the positive mode.

Gas chromatography-mass spectrometric analyses were performed on a Hewlett-Packard Gas Chromatograph model 5890/II equipped with Mass Se-