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Flavonoids from *Atriplex farinosa*

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Abstract. Two flavonol glycosides, isorhamnetin 3-0-rhamnosyl (1-6) glucopyranoside and isorhamnetin 7-0-glucopyranoside have been isolated from *Atriplex farinosa* in addition to two known flavanone glycosides, naringin and naringenin 7-0-glucoside. The latter two glycosides have been observed for the first time among the members of the plant family Chenopodiaceae while isorhamnetin 7-0-glucopyranoside has been isolated for the first time in nature. Structures of the isolated flavonoids were elucidated by spectroscopic methods.

Introducation

The genus *Atriplex* comprises about 200 species and belongs to subfamily chenopodioideae (Chenopodiaceae) [1]. Flavonols form the major chemical components of *Atriplex* species [2]. However, triterpene saponins occur in some species [3]. In the course of our search for natural products from Saudi plants and in view of the absence of any information about the chemistry of *Atriplex farinosa*, we have undertaken an investigation of this species. The present paper deals with isolation and structural elucidation of four flavonoid glycosides (1-4) occurring in the aerial parts of *A. farinosa*.

Experimental

Melting points were taken on a Kofler hot stage and are uncorrected. UV spectra were recorded on uv/vis PU-8800 Pye Unicam spectrometer. NMR spectra were obtained in CD_3OD or DMSO-d_6 on a Jeol-100 MHz spectrometer using TMS as an internal reference. EIMS were obtained on a Hewlett-Packard Model 5987 spectrometer at 70 eV. Known compounds were identified by comparison of the Spectral data with those of authentic. Analytical TLC was performed on precoated

silica gel plates G. Flavonoid sponts on TLC plates were visualized by UV light and by spraying with freshly mixed aq. solutions of $K_3Fe(CN)_6$ and $FeCl_3$(1:1) or diluted aq. ammonical $AgNO_3$.

Plant material

Fresh plant material (*Atriplex farinosa*) was collected from western area of Hijaz (seaside) in Saudi Arabia during September, 1987. The plant was identified by Dr. Shawkat A. Chaudhury, Regional Agriculture and Water Research Center, Ministry of Agriculture, Saudi Arabia.

Extraction and Isolation

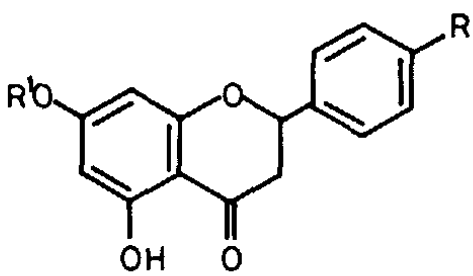
The air dried plant (1.8 Kg) was extracted successively with 80% and 50% MeOH. The two extracts were concentrated in vacuo and the resulting solution was then fractionated into CH_2Cl_2, EtOAc and n-BuOH soluble fractions. Flavonoids were detected only in the EtOAc and n-BuOH extracts. The EtOAc extract was diluted with absolute methanol and chromatographed on silica gel (300 gm) using $CHCl_3$-MeOH (8:2) as eluants. The flavonoid containing fractions were combined and concentrated. The residue was separated by prep. TLC employing $CHCl_3$-MeOH (9:1) as eluant to give compound 1 (30 mg), mp 173-174° and 2 (18 mg). The n-BuOH extract was concentrated and chromatographed on Sephadex LH-20 (100 gm) using MeOH as eluant to separate non-flavonoid material from a mixture of flavonol glycosides. The latter mixture was then separated by prep. TLC (silica gel, EtOAc-BuOH-HCOOH-H_2O; 5:3:1:1). The TLC plates showed three spots (deep purple under UV), all of them gave a positive colour tests for flavonoids and for glycosides. The bands were eluted with MeOH-H_2O (1:1). The middle major band yielded compound 3 (59 mg) while the slightly more polar band gave 4 (20 mg) which was identified as isorhamnetin 7-0-β-D-glucopyranoside (4), Mp, 144-148°; R_f 0.18 (silica gel, EtOAc-BuOH-HCOOH-H_2O; 5:3:1:1), UV λ_{max}^{MeOH} nm: 254, 266 sh, 282 sh, 347, NaOMe: 270, 331 sh, 402, $AlCl_3$: 270, 331, sh, 370, 480, + $AlCl_3$-HCl: 269, 297 sh, 355, 402; + NaOAc and + NaOAc-H_3BO_3 no change; EIMS: m/e 478 (M^+). Acid hydrolysis (6N HCl in EtOH) gave the aglycone isorhamnetin (5), MS m/e 316 (M^+), identified by comparison with authentic specimen (TLC, mp, IR and ^1H NMR). The hydrolysate from 4 revealed the presence of D-glucose.

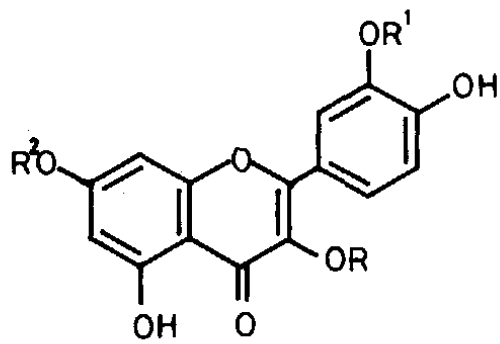
Results and Discussion

EtOAc and n-BuOH extracts of *Atriplex farinosa* were found to contain a mixture of flavonoid glycosides. Extensive chromatographic fractionation yielded four components (1-4) which were then characterized spectroscopically. Naringin (1) and naringenin 7-O-glucoside (2) were obtained from EtOAc extract and identified on the basis of their UV and NMR spectral data. Further, the ^{13}C NMR spectrum of 1

was in good agreement with that of naringin [4]. This is the first report of compounds 1 and 2 from species of Chenopodiaceae although both compounds are very common in other species.

The identify of 3 as isorhamnetin (1 → 6) β-D-glucopyranoside was readily established from its spectral data (UV and NMR) and its acid hydrolysis which gave isorhamnetin (5), D-glucose and L-rhamnose. Another isorhamnetin glycoside 4 was detected in the n-BuOH extract of *Atriplex farinosa* but its amount was too small to allow its full characterization. However, the structure of 4 was suggested on the basis of UV studies, its mass spectrum (M^+, 478) and chromatographic behaviour of the aglycone and sugars obtained by hydrolysis. Systematic studies of the UV spectrum of 4 established the presence of a substituent at position 7 [5] since no shift was observed on addition of sodium acetate reagent to the methanolic solution. The UV spectrum also exhibited a bathochromic shifts of band I upon addition of $AlCl_3$ and NaOMe indicating the presence of free hydroxyl groups at C-5 and C-4' respectively. Acid hydrolysis of 4 afforded the same aglycone obtained from the hydrolysis of 3 as well as D-glucose. Thus, compound 4 has been assigned as isorhamnetin 7-O-glucopyranoside which does not appear to have been reported before.





	R	R^1
1.	OH	Rham $\overset{2}{-}$ Glu
2.	OH	Glu

	R	R^1	R^2
3.	Rham $\overset{6}{-}$ Glu	Me	H
4.	H	Me	Glu
5.	H	Me	H

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مركبات فينولية من أتريبلكس فارينوزا

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(استلم في ١٣ جمادى الأولى ١٤١٠هـ، قُبل للنشر في ١٨ ربيع الأول ١٤١١هـ)

ملخص البحث. لقد استخلص مركبان فلافونويدية جلايكوزيدية من نبات أتريبلكس فارينوزا وهما ٣ ـ رامنوزايل (١ـ٦) جلوكوبيرانوزايد ايزورامنتين و٧ ـ جلوكوبايرانوزيد ايزورامنتين بالإضافة إلى مركبين يوجدان في الطبيعة هما نارينجين ونارينجنين ٧ ـ جلوكوزيد. والمركبان الأخيران لقد تمَّ عزلهما لأول وهلة من نباتات الفصيلة الرمرامية بينما المركب ٧ ـ جلوكوبايرانوزيد أيزورامنتين، فقد تم عزله في الطبيعة لأول وهلة. هذا وقد تم التعرف على التركيب البنائي للمركبات الجلايكوزيدية الأربعة والمستخلصة من النبات المذكور أعلاه بالطرق الطيفيّة.