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A flavonol triglycoside from *Chenopodium murale*

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Abstract

Four flavonol glycosides, three aglycones and one coumarin were isolated from the aerial parts of *Chenopodium murale*. One of the glycosides, kaempferol 3-rhamnoside-7-xylosyl(1 → 2)-rhamnoside, is new. The other known compounds include: kaempferol, its 7-rhamnoside, 3-rhamnoside 7-glucoside and 3,7-dirhamnoside, herbacetin, quercetin and scopoletin.

Keywords: *Chenopodium murale*; Chenopodiaceae; Kaempferol; 3-*O*-α-L-Rhamnopyranoside-7-*O*-β-D-xylopyranosyl(1 → 2)-*O*-α-L-rhamnopyranoside; Kaempferol diglycosides; Herbacetin; Scopoletin

1. Introduction

The genus *Chenopodium* consists of 200 species among which *C. murale* is a widespread weed in Egypt (Boulos, 1983). The leaves of *C. murale* are used in salads while seeds of other *Chenopodium* species are used in bread, drinks, fermented syrups and as animal feed (De Simone, Dini, Pizza, Saturnino, & Schettino, 1990). Various *Chenopodium* species have been reported to have anthelmintic properties (Lozoya, & Lozoya, 1982; Vasishta, 1989). Many species in the family contain essential oils (Nicholas, 1955) and a wide variety of flavonoids have been recorded (Crawford, & Mabry, 1978; Aritomi, & Kawasaki, 1984; De Simone et al., 1990; Neerujain et al., 1990). In a continuation of our phytochemical work on these taxa, we report here a new flavonol glycoside **1**, together with six known compounds, namely: kaempferol and its 7-rhamnoside; 3,7-dirhamnoside and 3-rhamnoside 7-glucoside, herbacetin, quercetin and scopoletin.

2. Results and discussion

The known compounds were identified through standard chemical and physical methods including UV, MS, ^{1}H, and ^{13}C-NMR (Mabry, Markham, & Thomas, 1970; Markham, & Mabry, 1975). Compound **1** appeared violet under UV light changing to fluorescent yellow with ammonia. Total acid hydrolysis of **1** with 2 N HCl yielded rhamnose and xylose in a 2:1 ratio and kaempferol, all identified by spectral and chromatographic comparison. Partial acid hydrolysis of **1** with 0.1 N HCl gave a diglycoside, which exhibited a yellow color under UV light indicating a release of a sugar moiety from the 3-position. The released sugar was identified as rhamnose by chromatographic comparison with an authentic sample. UV spectral data of **1** with diagnostic shift reagents (Mabry et al., 1970; Markham, & Mabry, 1975) suggested it is a 3,7-disubstituted kaempferol glycoside with free hydroxyl groups at the 5 and 4′-positions. Since rhamnose was the only released sugar moiety from the 3-position, then the other rhamnosyl and xylosyl moieties must be attached at the 7-position.

The ^{1}H-NMR spectrum of **1** showed the expected signals in the aromatic region, i.e. two *ortho* coupled doublets at δ 6.95 (J = 7.5 Hz) and δ 7.8 (J = 7.5 Hz)

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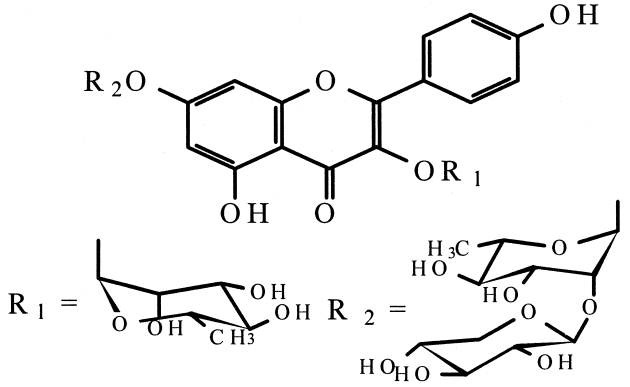
which correspond to the protons of the B-ring and the two *meta* coupled doublets at δ 6.42 and 6.75 ($J=2$ Hz) for the A-ring 6 and 8 protons. The anomeric protons at δ 5.55 and δ 5.39 ($J=1.2$ Hz) were attributed to two L-rhamnosyl moieties (α-configuration) directly linked to the aromatic rings at the 3 and 7 positions, respectively. A third anomeric proton was located upfield at δ 4.22 ($J=8$ Hz) and was assigned to a D-xylose (β-configuration) moiety linked to the 7-*O*-rhamnosyl moiety. The rhamnosyl methyls appeared as doublets at δ 1.15 and 0.95 ($J=6$ Hz). The remaining sugar protons were observed in the range δ 2.95–4.05. The +ve FAB-MS of **1** was in agreement with the assigned structure as it showed the molecular ion $[M+1]^+$ at *m/z* 711 and $[M+Na]^+$ at 733 accounting for kaempferol, one xylosyl and two rhamnosyl groups: ($286+2\times146+1\times132$) *m/z* 433 [kaempferol + rhamnose + 1]$^+$ and 287 [aglycone + 1]$^+$.

The ^{13}C-NMR spectrum exhibited three anomeric carbons at δ 101.0, 98.5 and 106.3, for C-1″ of rhamnosyl at the 3-position, C-1‴ for rhamnosyl at the 7-position and C-1 of the xylosyl linked to C-2‴ of rhamnosyl at the 7 position, and two methyl carbons at δ 17.8 and 18.1 for the rhamnosyl moieties. The upfield shift observed for C-3 and C-7, −2.7 and -2 ppm, respectively, confirmed glycosylation at both positions. The xylosyl group was assigned the (1→2) linkage to the rhamnosyl at the 7 position due to the observed downfield shift of C-2‴ by +10 ppm, and the upfield shift of the C-3‴ to δ 2.6 ppm (Yamoaka et al., 1971; Markham, Ternai, Stanley, Geiger, & Mabry, 1978; Nawwar, Ishak, Michael, & Buddrus, 1984). From these data, **1** is characterised as kaempferol 3-*O*-α-L-rhamnopyranoside-7-*O*-β-D-xylopyranosyl(1→2)-*O*-α-L-rhamnopyranoside.



3. Experimental

3.1. Plant materials

Aerial parts of *Chenopodium murale* L. were collected from Orman Garden, Giza, Egypt in November, 1993. A voucher specimen has been deposited in the Desert Research Institute, Cairo.

3.2. Extraction and isolation

Aerial parts of *C. murale* were extracted with $CHCl_3$ and then 70% EtOH by the author ASA. The conc. EtOH extract was fractionated by cellulose CC. The glycosidic fraction from *C. murale* was chromatographed using Whatman 3 MM paper with BAW as a developing solvent. Fractions obtained were resolved into pure components by repeated PPC using 15% HOAc. The pure compounds obtained were finally passed over Sephadex LH-20 using MeOH:H_2O, 1:1 for final purification. ^{1}H and ^{13}C-NMR were run in DMSO with TMS as an int. standard using a Nicolet NT 200 spectrometer with δ reported in ppm. EI, CI and FAB-MS were measured on a Finigan MAT TSQ 70 spectrometer.

Compound **1**, kaempferol 3-*O*-α-L-rhamnoside-7-*O*-β-D-xylosyl(1 → 2)-*O*-α-L-rhamnoside: yellow amorphous powder, UV λ_{max}^{MeOH}: 238 sh, 269, 310 sh, 358; +$AlCl_3$ 243 sh, 274, 305 sh, 359 sh,410; +$AlCl_3$ + HCl 265, 291 sh, 358, 405; +NaOMe 244, 275, 304 sh, 365, 420; +NaOAc 269, 319 sh, 363, 395; +NaOAc–H_3BO_3 265, 316 sh, 360 nm. ^{1}H-NMR of **1**, δ (ppm): 7.8 (2H, d, $J=7.5$ Hz, H-2′, H-6′), 6.95 (2H, d, $J=7.5$ Hz, H-3′, H-5′), 6.75 (1H, d, $J=2$ Hz, H-8), 6.42 (1H, d, $J=2$ Hz, H-6), 5.55 (1H, d, $J=1.2$ Hz, H-1″ anomeric rhamnosyl on 3-position), 5.39 (1H, d, $J=1.2$ Hz, H-1‴ anomeric rhamnosyl on 7-position), 4.22 (1H, d, $J=8$ Hz, H-1 anomeric xylosyl proton), 2.95–4.05 (m, other sugar protons), 1.15 and 0.95 (2 methyl protons, d, $J=6$ Hz).

^{13}C-NMR of **1**, δ (ppm): 177.6 (C-4), 161.7 (C-7), 160.9 (C-5), 159.4 (C-4′), 157.1 (C-2), 156.0 (C-9), 133.7 (C-3), 130.7 (C-2′, -6′), 120.8 (C-1′), 115.1 (C-3′, -5′), 105.8 (C-10), 99.4 (C-6), 94.6 (C-8), 101.0 (C-1″), 70.2 (C-2″), 69.9 (C-3″), 72.1 (C-4″), 70.1 (C-5″), 18.1 (C-6″), 98.5 (C-1‴), 80.8 (C-2‴), 67.3 (C-3‴), 71.8 (C-4‴), 70.1 (C-5‴), 17.8 (C-6‴), 106.3 (xyl C-1), 73.8 (x C-2), 76.8 (x C-3), 69.5 (x C-4), 66.0 (x C-5). FAB-MS *m/z* 711 $[M+1]^+$, 733 $[M+Na]^+$, 433 [M-hexose–pentose + 1]$^+$, 287 [aglycone + 1]$^+$.

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