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NOTE

Flavonoids of *Aptenia cordifolia*

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Two flavanone glycosides, liquiritin and naringenin and one flavonol glycoside, 3′,4′-dihydroxy-7-methoxyflavonol 3-O-β-D-glucoside, were isolated and identified from the aerial parts of *Aptenia cordifolia*. In addition, the terpenoids sitosterol and stigmasterol and the anthocyanidin pelargonidin were also detected. The structures of all compounds were established by chromatographic and spectroscopic methods. This is the first report of flavonoids from *Aptenia cordifolia*.

Except for the report of terpenoids[1], no chemical studies have been conducted on A. *cordifolia* (L.F.) Schwantes, fam. Aizoaceae, a middle eastrn herb which thrives in air polluted areas. Because of the anti-oxidant properties[2–6] of flavonoids, an investigation of flavonoids in this air-pollution resistant species was undertaken. From *A. cordifolia* we report here two flavanone glycosides, liquiritin and naringenin, and one flavonol glycoside, 3′,4′-dihydroxy-7-methoxyflavonl 3-O-β-D-glucoside. In addition, we identified sitosterol, stimasterol and pelargonidin.

Concentrated aqueous ethanolic extracts of the dried aerial parts of *Aptenia cordifolia* were partitioned between organic solvents and water, followed by chromatographic separation of the organic-soluble constituents. Three compounds, in addition to pelargonidin, sitosterol and stigmasterol were obtained and identified as 3′,4′-dihydroxy-7-methoxyflovonol 3-O-β-D-glucoside (**1**), liquiritin[7–12] (4′-hydroxyflavanone 7-O-β-D glucoside) and naringenin. The blue color of **1** under UV light suggested that a 5-hydroxyl group was absent. Compound **1**, on acidic hydrolysis, gave glucose and an aglycone, and **1** exhibited a one-proton ^{1}H NMR signal at δ5.8 typical for the anomeric proton of a flavonoid 3-O-glucoside. The ^{1}H NMR of **1** also showed signals typical for H-5, 6 and 8 in the A-ring and H-2′, 5′ and 6′ in the B-ring. In addition, the shifts of band 1 in the $AlCl_3$ spectra in methanol and methanol with HCl confirmed the presence of a 3′,4′-dihydroxyl group and the absence of a 5-hydroxyl group. A methoxyl group (^{1}H NMR at δ3.83 and ^{13}C NMR at 54.9) was assigned to C-7. Therefore

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1 is 3′,4′-dihydroxy-7-methoxyflavonol 3-O-β-D-glucoside in accord with all spectroscopic and chromatographic data[13–18]. The two known flavanone glucosides, liquiritin and naringenin, were identified by hydrolytic chromatographic and spectral data.

Aptenia cordifolia, obtained from near Helwan, Egypt, in Spring, 1998, was identified by Dr. M. El-Gebally, Department of Taxonomy and Flora, N.R.C., Cairo, Egypt, where a voucher specimen is deposited.

Authentic reference compounds, liquiritigenin, naringenin, sitosterol and stigmasterol, were all obtained from the Department of Botany, The University of Texas at Austin.

^{1}H NMR spectra were recorded at 500 MHz, ^{13}C NMR spectra at 100 MHz and chemical shifts are given in the δ(ppm) with TMS as an internal standard. UV spectra were measured with a Shimadzu 1601 UV-visible spectrophotometer.

Isolation: Air dried powdered leaves of A. *cordifolia* were extracted with 70% aqueous ethanol. The extract was evaporated *in vacuo*, and the resulting aqueous syrup was successively extracted with $CHCl_3$ and *n*-BuOH. The *n*-BuOH layer was evaporated under reduced pressure giving 30 g material. This material was chromatographed on a silica gel column with chloroform followed by increasing amounts of methanol to give several fractions. Fractions, which by TLC appeared to contain flavonoids, were combined and the material was separated over a Sephadex LH-20 column eluted with water followed by increasing amounts of methanol to give **1** (44 mg) and liquiritin (59 mg). The $CHCl_3$ extract was subjected to column chromatography using silica gel eluted with chloroform with increasing amounts of methanol and one fraction (monitored by TLC) yielded sitosterol and stigmasterol, which were co-chromatographed with authentic samples using hexane-ethyl acetate (1 : 1), $CHCl_3$—MeOH (9 : 1), the silica gel plates were sprayed with 20% H_2SO_4 and a second plate was sprayed with antimony chloride in $CHCl_3$; the sprayed plates were heated for 10 minutes at 100°C. Pelargonidin was isolated from the fresh flowers using 2M HCl for 40 minutes at 100°C. The extract was washed with ethyl acetate and the red pigment was extracted with amyl alcohol; this latter extract was evaporated to dryness. The residue was dissolved in methanolic HCl and paper chromatographed using conc. HCl-HOAc-H_2O (3 : 30 : 10), conc. HCl-HCO_2H-H_2O (2 : 5 : 3) and BAW, R_f values were 0.67, 0.34 and 0.79, respectively, λ_{max} at 520 nm in MeOH-HCl, all in accord with pelargonidin.

Spectral data for 1: UV λ_{max} MeOH nm (log ε): 289, 330; +$AlCl_3$: 308, 375; +$AlCl_3$/HCl: 308, 328; ^{1}H NMR (DMSO-d_6): δ3.83 3H, s, OCH_3), 5.8 (1H, d, J = 7.5 Hz, H-1 of glc), 6.7 (1H, Q, J = 9, 2.5 Hz, H-6), 6.8 (1H, d, J = 2.5 Hz, H-8), 7.25 (1H, Q, J = 8.5, 2.5 Hz, H-5′), 7.36 (1H, d, J = 2.5 Hz, H-2′), 7.38 (1H, d, J = 8.5 Hz, H-6′), 8.1 (1H, d, J = 9 Hz, H-5) ^{13}C NMR (DMSO-d_6): δ54.9 (O—CH_3), 59.5 (C-4 of glc), 62.7 (C-6 of glc), 72.2 (C-2 of glc), 76.8 (C-3,5 of glc), 103.8 (C-1 of glc), 112 (C-2′), 116.4 (C-5′), 119.1 (C-10), 121.6 (C-6′), 125.4 (C-1′), 126.8 (C-5), 143 (C-3′), 144 (C-4′), 159.3 (C-9), 163 (C-7), 171.5 (C-4). Acidic hydrolysis of **1** in 10% H_2SO_4-EtOH gave glucose by TLC and PC.

Spectral data for liquiritin: UV λ_{max} MeOH nm (log ε): 328, 280;

+NaOMe: 345, 260; +$AlCl_3$ 330, 280; ^{1}H NMR (DMSO-d_6): δ2.57 (2H, dd, J = 12.5, 2.5 Hz, H-3), 3.34–3.42 (2H, m, H-2,5 of glc), 4.83 (1H, d, J = 7.5 Hz, H-1 of glc), 4.96 (1H, dd, J = 12.5 Hz, H-2), 6.72 (1H, d, J = 2.5 Hz, H-8), 6.76 (1H, dd, J = 8.5, 2.5 Hz, H-6), 7.18 (2H, d, J = 8.5 Hz, H–3′, 5′), 7.32 (2H, d, J = 8.5 Hz, H-2′,6′), 7.76 (1H, d, J = 8.5 Hz, H-5); ^{13}C NMR (DMSO–d_6); δ44.2 (C-3), 62 (C-6 of glc), 70 (C-4 of glc), 73.2 (C-2 glc), 76.6 (C-3 of glc), 77 (C-5 of glc), 79 (C-2) 100.5 (C-1 of glc), 101.7 (C-8), 110.5 (C-6), 114.8 (C-10, 5′), 127.6 (C-5), 128.1 (C-6′), 128.2 (C-2′), 130 (C-1′), 157.7 (C-4′), 173.8 (C-7), 194 (C-4). Acidic hydrolysis of liquiritin in 10% H_2SO_4- EtOH (1 : 1) gave glucose and liquiritigenin by TLC and PC.

Naringenin was separated from the $CHCl_3$ extract and purified by preparative TLC on silica gel; it was identified by co-chromatography with an authentic reference.

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