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TWO COUMARINS AND A THIENYLBUTYLAMIDE FROM *Anacyclus cyrtolepioides* FROM THE ALGERIAN SEPTENTRIONAL SAHARA

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The *Anacyclus* genus is not well documented. A germacranolide has been reported from *Anacyclus radiatus* [1] and two eudesmanolides have been isolated from *Anacyclus alexandrinus* Willd. [2]. Cytotoxic [3], anti-insect [4], and immunostimulating [5] effects and inhibitory activity on hepatitis C virus (HCV) protease [6] have been established for different extracts of various *Anacyclus* species. We report here two coumarins, herniarin (**1**) and 3,4-dehydroherniarin (**2**), and a thienylbutylamide, (2*E*,4*E*)-6-(2-thienyl)-2,4-hexadiene-isobutylamide (**3**), for the first time from the genus and the endemic species *Anacyclus cyrtolepioides* [7]. This Saharian plant is widely used by the Saharian population as a condiment in couscous or in milk drink and greatly enjoyed by camels.

The air-dried aerial parts (700 g) of *Anacyclus cyrtolepioides*, collected during flowering (April 2004) at Ghardaia (Algerian Septentrional Sahara), were macerated at room temperature in a methanol solution (70%). The extract was concentrated under low pressure, diluted, and filtered to remove chlorophyll, then successively extracted with petroleum ether, dichloromethane, ethyl acetate, and *n*-butanol.

The dichloromethane extract (5 g) was column chromatographed on silica gel (35–70 μm) and eluted with petroleum ether-ethyl acetate with increasing polarity, then with methanol.

The major fraction (0.158 g) was subjected to column chromatography on silica gel (20–45 μm) and eluted with cyclohexane-ethyl acetate with increasing polarity; TLC on silica gel plates eluted with cyclohexane–ethyl acetate (87:13) led to compounds **1** and **2**.

The other important fraction (0.46 g) was subjected to column chromatography on silica gel (35–70 μm) and eluted with cyclohexane–ethyl acetate with increasing polarity. TLC on silica gel plates eluted with cyclohexane–ethyl acetate (80:20) led to compound **3**.

All compounds were identified by using ^{1}H NMR, ^{13}C NMR, EI/MS, IR and UV analytical methods.

Compound 1, $C_{10}H_8O_3$, mp 115–117°C (diethyl ether), UV spectrum (MeOH, λ_{max}, nm): 203.4 (1.332); 204 (1.903); 214 (1.191); 322 (1.162). IR (KBr, ν, cm^{-1}): 1707 (CO), 2840 (OCH_3), 1613 (aromatic ring). ^{1}H NMR data (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.65 (1H, d, J =10, H-4), 7.35 (1H, d, J = 8, H-5), 6.85 (1H.d, J =2, H-6), 6.75 (1H, dd, J = 8 and 2, H-8), 6.25 (1H, d, J = 10, H-3), 3.85 (3H, s, OCH_3). ^{13}C NMR data (125 MHz, $CDCl_3$, δ, ppm): 162.8 (C-7), 161.1 (C-2), 155.9 (C-9), 143.4 (C-5), 128.7 (C-5), 113.1 (C-3), 112.6 (C-6), 112.5 (C-10), 100.9 (C-8), 55.7 (OCH_3). Mass spectrum (DiC, NH_3), *m/z*: 177 $[MH]^+$. Characterized as herniarin [8].

Compound 2, $C_{10}H_{10}O_3$, UV spectrum (MeOH, λ_{max}, nm): 204.4 (1.189) and 279.7 (0.107). IR (KBr, ν, cm^{-1}): 1752 (CO), 2850 (OCH_3), 1652 (aromatic ring). ^{1}H NMR data (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.06 (1H, d, J = 8, H-5), 6.66 (2H, dd, J = 8 and 2, H-6), 6.02 (1H, d, J = 2, H-8), 4.28 (2H, dd, J = 14 and 6, H-4), 4.18 (2H, dd, J = 14 and 6, H-3), 3.75 (3H, s, OCH_3). ^{13}C NMR data (125 MHz, $CDCl_3$, δ, ppm): 160.5 (C-7), 151.4 (C-5), 146.1 (C-2), 129.4 (C-9), 120.2 (C-8), 111.6 (C-6), 108.8 (C-10), 55.4 (OCH_3), 40.3 (C-3), 36.9 (C-3). Mass spectrum (DiC, NH_3), *m/z*: 179 $[MH]^+$. Characterized as 3,4-dehydroherniarin.

Compound 3, $C_{14}H_{19}NOS$, ^{1}H NMR data (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.25 (1H, dd, J = 15 and 8, H-3), 7.17 (1H, d, J = 5, H-5′ thienyl), 6.95 (1H, dd, J = 5 and 3.5, H-4′ thienyl), 6.81 (1H, d, J= 3.5, H-3′ thienyl), 6.22 (2H, m, H-4 and

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H-5), 5.82 (1H, d, J = 15, H-2), 5.61 (3H, t, J =6.5, NH), 3.69 (2H, d, J = 5, CH_2), 3.18 (2H, dd, J =7 and 6.5, $NHCH_2CH$), 1.81 (1H, nonat, J = 7, $CHMe_2$), 0.93 (6H, d, J = 6.5, 2 CH_3). ^{13}C NMR data (125 MHz, $CDCl_3$, δ, ppm): 166.2 (C-1), 141.6 (C-2′ thienyl), 140.2 (C-3), 139.1 (C-5), 129.6 (C-4), 127.0 (C-4′ thienyl), 125.0 (C-3′ thienyl), 124.0 (C-5′ thienyl), 123.5 (C-2), 147.0 (N-CH_2), 33.1 (C-6), 29.6 (C-isobutyl), 20.1 (2 Me). Mass spectrum (DiC/NH_3), *m/z*: 250 $[MH]^+$ and *m/z*: 177, 149 corresponding to the loss of $NHCH_2Me_2$ then CO, respectively. Characterized as (2*E*,4*E*)-6-(2-thienyl)-2,4-hexadiene-isobutylamide [9].

All the compounds from the *Anacyclus* genus are reported for the first time .

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