BIOLOGICALLY ACTIVE COMPOUNDS FROM Climacoptera

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We investigated the aerial part of wooly climacoptera (*Climacoptera lanata*) and aral climacoptera (*C. aralensis*) (Chenopodiaceae) [1] collected during flowering in the Aral region. They were analyzed qualitatively and quantitatively. Flavonoids, saponins, steroids, phenolic acids, and traces of coumarins were detected.

Ground air-dried raw material was extracted exhaustively with methanol. The combined methanol extract was evaporated in vacuum. The condensed solution was diluted with water and treated successively with hexane, CHCl₃, ethylacetate, and *n*-butanol.

Column chromatography over silica gel with elution by $CHCl_3$:hexane (9:1) isolated **1** from the $CHCl_3$ fraction; **2** and **3**, from the ethylacetate fraction ($CHCl_3:CH_3OH$ in various ratios). Gel chromatography over Sephadex LH-20 isolated **4** from the butanol fraction. The compounds were identified as below based on physicochemical data and comparison with the literature.

1, $C_{29}H_{28}O$, FAB/MS *m/z* 412. PMR spectrum (500 MHz, CDCl₃, δ , ppm, J/Hz): six methyl signals at 0.68 (s, H-18), 0.76 (d, J = 6.4, H-27), 0.78 (t, J = 7.0, H-29), 0.81 (d, J = 6.3, H-26), 0.88 (d, J = 6.2, H-21), 1.00 (s, H-19) and three olefinic signals at 4.96 (dd, J = 15.2, 8.2, H-23), 5.09 (dd, J = 15.2, 8.4, H-22), and 5.32 (br.s, H-6).

¹³C NMR (75 MHz, CDCl₃, δ, ppm): 39.2 (C-1), 29.3 (C-2), 79.6 (C-3), 40.4 (C-4), 141.1 (C-5), 122.4 (C-6), 32.4 (C-7), 32.5 (C-8), 51.9 (C-9), 37.3 (C-10), 21.6 (C-11), 40.3 (C-12), 42.8 (C-13), 57.5 (C-14), 25.8 (C-15), 26.8 (C-16), 56.7 (C-17), 12.2 (C-18), 19.3 (C-19), 36.7 (C-20), 19.1 (C-21), 138.8 (C-22), 129.9 (C-23), 46.6 (C-24), 29.8 (C-25), 20.0 (C-26), 19.6 (C-27), 23.6 (C-28), 12.4 (C-29). **1** was characterized as stigmasterol using PMR and ¹³C NMR spectral data [2].

2, $C_{28}H_{32}O_{16}$, mp 169-171°C, $[\alpha]_D^{20}$ -38.7° (*c* 0.3, MeOH), FAB/MS 641 (22%) [M - 1]⁺, 316 (15) [M - gluram]⁺; UV spectrum (EtOH, λ_{max} , nm): 356, 302(sh), 255; (+NaAc) 396, 299(sh), 270; (+AlCl₃) 402, 300(sh), 268; (+AlCl₃ + HCl) 396, 300(sh), 268; (+NaAc + H₃BO₃) 360, 265(sh), 255; (+NaOC₂H₅) 415, 318(sh), 275.

IR spectrum (mineral oil, v, cm⁻¹): 3520-3100 (OH), 2980 (OCH₃), 1660, 1650 (C=O), 1570, 1520, 1500 (C=C).

PMR spectrum (400 MHz, CD₃OD, δ, ppm, J/Hz): 6.18 (d, J = 1.8, H-6), 6.39 (d, J = 1.8, H-8), 6.8 (d, J = 8.2, H-5'), 7.60 (dd, J = 8.2, 1.8, H-6'), 7.93 (d, J = 1.8, H-2'), 4.5 (s, H-1'''), 5.23 (d, J = 7.3, H-1''), 1.1 (s, 3H, rhamnose CH₃). **2** was characterized as isorhamnetin 3-O-β-D-glucopyranosyl-($6 \rightarrow 1$)-O-α-L-rhamnopyranoside (narcissin) [3].

3, $C_{22}H_{22}O_{12}$, mp 232-235°C, $[\alpha]_D^{20}$ -71.5° (*c* 0.5, ethanol), UV spectrum (EtOH, λ_{max} , nm): 361, 298(sh), 259; (+NaAc) 370, 270; (+AlCl₃) 420, 280; (+AlCl₃ + HCl) 380, 280; (+NaAc + H₃BO₃) 380, 290; (+NaOC₂H₅) 410, 280.

IR spectrum (mineral oil, v, cm⁻¹): 3400-3200 (OH), 1670, 1620, 1615 (C=O), 1520, 1470 (C=C).

PMR spectrum (400 MHz, CD₃OD, δ, ppm, J/Hz): 5.4 (d, J = 7, H-1"), 6.12 (d, J = 2, H-6), 6.43 (d, J = 2, H-8), 6.85 (d, J = 8.5, H-5'), 7.2 (d, J = 2.5, H-3'), 7.53 (d, J = 2.5, H-2'), 7.85 (dd, J = 8.5, 2, H-6'). **3** was characterized as quercetin 3-O-β-D-galactopyranoside (hyperin) [4].

4, $C_{52}H_{82}O_{22}$, $[\alpha]_D^{20}$ -7.8°. Mass spectrum m/z 1057 [M - H], 925 [M - H - 132], 895 [M - H - 162 - 132], 881 [M - H - 176 - 162 - 132], 455 [M - H - 2×132 - 162 - 176].

PMR spectrum (500 MHz, CD₃OD, δ , ppm, J/Hz): 0.78-1.14 (s, 7CH₃), 2.86 (dd, J = 2.6, 13.1, H-18), 3.13 (dd, J = 4.6, 10.6, H-28), 5.24 (br.s, H-12), signals of four anomeric sugar protons 5.38, 4.83, 4.61, and 4.47 (d, J = 6.5-8).

 ${}^{13}C \text{ NMR spectrum (75 MHz, CD_3OD, \delta, ppm): 39.9 (C-1), 27.1 (C-2), 91.6 (C-3), 40.4 (C-4), 57.2 (C-5), 19.3 (C-6), 34.0 (C-7), 40.4 (C-8), 48.1 (C-9), 37.9 (C-10), 24.6 (C-11), 123.8 (C-12), 144.8 (C-13), 42.9 (C-14), 28.9 (C-15), 24.04 (C-16), 48.1 (C-17), 42.6 (C-18), 47.3 (C-19), 31.6 (C-20), 35.0 (C-21), 33.1 (C-22), 28.2 (C-23), 17.0 (C-24), 16.1 (C-25), 16.6 (C-26), 16.6 (C-26$

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26.3 (C-27), 178.1 (C-28), 33.4 (C-29), 23.9 (C-30), 105.5 (C-1'), 79.7 (C-2'), 87.2 (C-3'), 72.2 (C-4'), 78.0 (C-5'), 168.1 (C-6'), 104.4 (C-1''), 76.4 (C-2''), 78.0 (C-3''), 71.2 (C-4''), 67.4 (C-5''), 104.9 (C-1'''), 75.2 (C-2'''), 78.3 (C-3'''), 71.0 (C-4'''), 66.9 (C-5'''), 95.7 (C-1''''), 73.9 (C-2''''), 78.2 (C-3'''), 71.0 (C-4'''), 78.0 (C-5'''), 62.5 (C-6''').

Thus, **4** was characterized based on spectral data (mass spectrum, PMR, ¹³C NMR, HMBC spectra) as oleanolic acid 3-O-{[β -D-xylopyranosyl-(1 \rightarrow 2)-[β -D-xylopyranosyl-(1 \rightarrow 3)]- β -D-glucuronopyranosido}-28-O- β -D-glucopyranoside [5-8]. The compounds indicated above were isolated from *C. lanata* and *C. aralensis* for the first time.

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