Supporting Information

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Chemical Constituents of Two Endemic *Sideritis* Species from Turkey with Antioxidant Activity

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Table S1. LC-MS/MS paramaters of phenolic compounds

C2/6 C1/5

Compound Name	Parent Ion	Daughter Ion	Collision Energy (V)
p-Hydoxybenzoic acid	136,8	92,9	10
Vanillin	151	135,5	10
p-Coumaric acid	163	118,7	10
Caffeic acid	179	134	11
Ferulic acid	193	177,5	10
Ellagic acid	301	150,5	10
Syringic acid	197	181,6	10
Quercetin	301	178,6	10
Apigenin	268,6	116,6	25
Keampferol	285	143	33
Keampferol-3- glucoside	447	284	20
Luteolin-7-glucoside	447	284	20
^{13}C p-hydroxybenzoic acid	137,9	92,9	10

Table S2. Validation parameters for antioxidant phenolics from the species

Compound Name	**Linear regression equation**	**R^2**	**Linear Range (ppm)**
p-Hydroxybenzoic acid	y=0.008218948x+0.020704	0,993	0-25
Vanillin	y=0.002947902x-0.00051	0,998	0-25
p-Coumaric acid	y=0.025426162x+0.015864	0,995	0-25
Caffeic acid	y=0.022653254x+0.0051188	0,998	0-25
Ferulic acid	y=1.20e-03x+3.28e-04	0,997	0-10
Ellagic acid	y=0.001521436x+0.000227	0,996	0-25
Syringic acid	y=0.000210138x-4.34e-05	0,998	0-25
Quercetin	y=0.001503664x+9.95e-05	0,996	0-25
Apigenin	y=0.00700313x+0.002687	0,996	0-10
Kaempferol	y=3.05e-04x-3.86e-06	0,995	0-25
Kaempferol-3-*O*-glucoside	y=0.009830761x+0.004833	0,994	0-25
Luteolin-7-*O*-glucoside	y=0.10395824x+0.004304	0,995	0-25

Spectral data of the isolated compounds

Siderol (1) ^{1}H-NMR (600 MHz, $CDCl_3$): δ 5.26 (1H, s, H-15), 4.69 (1H, t, *J*=2.5 Hz, H-7), 2.99 (1H, d, *J*=11.5 Hz, H-18a), 3.32 (1H, d, *J*=11.5 Hz,H-18b), 2.30 (1H, m, H-13), 2.07 (3H, s, OAc), 1.69 (3H, s, Me-17), 1.07 (3H, s, Me-20), 0.71 (3H, s, Me-19)

^{13}C-NMR (150.82 MHz, $CDCl_3$): δ 44.54 (C-1), 18.28 (C-2), 35.22 (C-3), 36.96 (C-4), 44.54 (C-5), 23.46 (C-6), 78.29 (C-7), 51.84 (C-8), 44.82 (C-9), 39.08 (C-10), 17.92 (C-11), 24.77 (C-12), 39.80 (C-13), 39.83 (C-14), 129.81 (C-15), 143.75 (C-16), 15.36 (C-17), 71.33 (C-18), 17.35 (C-19), 17.76 (C-20), 21.45 (O-CO<u>C</u>H_3), 170.83 (O-<u>C</u>OCH_3)

EIMS (rel.int.) *m/z*: 346.0 $[M]^+$ (33) ($C_{22}H_{34}O_3$), 315.0 $[M-31]^+$ (4), 303.9 $[M-44]^+$ (71), 287.0 $[M-OAc]^+$ (76), 268.1 $[M-60-H_2O]^+$ (76), 256.0 (92), 241.0 (32), 227.0 (33), 203.0 (34), 185.1 (61), 161.0 (64), 147.0 (54), 133.0 (54), 118.0 (79), 109.0 (100), 93.0 (75), 81.0 (74), 67.0 (57)

Sideridiol (2) ^{1}H-NMR (600 MHz, $CDCl_3$): δ 5.45 (1H, br s, H-15), 3.58 (1H, t, *J*=2.5 Hz, H-7), 3.45 (1H, d, *J*=11.5 Hz, H-18a), 2.95 (1H, d, *J*=11.5 Hz, H-18b), 2.35 (1H, m, H-13), 1.73 (3H, br s, Me-17), 1.05 (3H, s, Me-20), 0.68 (3H, s, Me-19)

^{13}C-NMR (150.82 MHz, $CDCl_3$): δ 42.02 (C-1), 18.35 (C-2), 35.24 (C-3), 37.10 (C-4), 44.60 (C-5), 25.00 (C-6), 75.42 (C-7), 51.80 (C-8), 44.80 (C-9), 39.29 (C-10), 18.05 (C-11), 26.32 (C-12), 44.24 (C-13), 44.24 (C-14), 129.65 (C-15), 146.08 (C-16), 15.53 (C-17), 71.08 (C-18), 17.72 (C-19), 17.72 (C-20)

EIMS (rel.int.) *m/z*: 304.2 $[M]^+$ (94) ($C_{20}H_{32}O_2$), 286.2 $[M- H_2O]^+$ (58), 273.2 $[M-CH_2OH]^+$ (54), 268.2 $[M-2H_2O]^+$ (6), 255.2 (92), 241.2 (23), 227.2 (28), 211.1 (15), 199.1 (19), 185.1 (16), 173.1 (22), 164.1 (87), 149.1 (50), 131.1 (42), 123.1 (99), 109.0 (87), 94.0 (100), 81.0 (71), 67.0 (37), 57.0 (21)

7- epicandicandiol (3) ^{1}H-NMR (600 MHz, $CDCl_3$): δ 4.80 (2H, br s, H_2-17), 3.66 (1H, t, *J*=2.2 Hz, H-7), 3.47 (1H, d, *J*=12 Hz, H-18a), 2.92 (1H, d, *J*=12 Hz, H-18b), 2.69 (1H, m, H-13), 1.05 (3H, s, Me-20), 0.69 (3H, s, Me-19)

^{13}C-NMR (150.82 MHz, $CDCl_3$): δ 39.65 (C-1), 17.93 (C-2), 38.29 (C-3), 37.77 (C-4), 37.12 (C-5), 26.57 (C-6), 77.05 (C-7), 48.18 (C-8), 50.37 (C-9), 39.65 (C-10), 17.93 (C-11), 33.54 (C-12), 43.78 (C-13), 34.39 (C-14), 45.16 (C-15), 155.13 (C-16), 103.38 (C-17), 70.50 (C-18), 17.93 (C-19), 17.75 (C-20)

EIMS (rel.int.) *m/z*: 304.0 $[M]^+$ (4) ($C_{20}H_{32}O2$), 286.2 $[M- H_2O]^+$ (44), 271.0 $[286-CH_3]^+$ (21), 268.0 $[M-2H_2O]^+$ (15), 256.0 $[286-CH_3]^+$ (100), 241.0 (42), 213.0 (39), 199.0 (36), 185.0 (32), 173.0 (36), 159.0 (29), 145.0 (33), 131.0 (35), 121.0 (42), 109.0 (43), 93.0 (46), 81.0 (44), 67.0 (27)

Sidol (4) ^{1}H-NMR (600 MHz, $CDCl_3$): δ 4.90 (1H, dd, *J*=5 ve 11 Hz, H-3), 4.80-4.82 (2H, br s, H_2-17), 3.62 (1H, t, *J*=3 Hz, H-7), 3.32 (1H, d, *J*=12 Hz, H-18a), 2.97 (1H, d, *J*=12 Hz, H-18b), 2.68 (1H, m, H-13), 2.06 (3H, s, OAc), 0.72 (3H, s, Me-20), 0.68 (3H, s, Me-19)

^{13}C-NMR (150.82 MHz, $CDCl_3$): δ 38.40 (C-1), 23.41 (C-2), 74.50 (C-3), 43.62 (C-4), 37.38 (C-5), 26.47 (C-6), 76.90 (C-7), 50.21 (C-8), 50.23 (C-9), 38.10 (C-10), 17.36 (C-11), 33.57 (C-12), 44.07 (C-13), 39.09 (C-14), 44.8 (C-15), 153.90 (C-16), 103.64 (C-17), 64.14 (C-18), 12.82 (C-19), 15.37 (C-20), 21.23 (O-CO<u>C</u>H_3), 170.83 (O-<u>C</u>OCH_3)

EIMS (rel.int.) *m/z*: 362.3 $[M]^+$ (1) ($C_{22}H_{34}O_4$), 344.3 $[M\text{-}H_2O]^+$ (4), 326.3 $[M\text{-}2H_2O]^+$ (9), 302.3 $[M\text{-}OAc]^+$ (3), 284.3 $[M\text{-}60\text{-}H_2O]^+$ (12), 272.3 (20), 254.3 (100), 239.2 (71), 233.2 (6), 225.2 (13), 211.2 (25), 199.2 (13), 183.1 (16), 171.1 (14), 157.1 (13), 149.0 (17), 131.1 (15), 121.1 (30), 107.0 (28), 93.0 (30), 79.1 (25), 66.9 (14)

Eubotriol (5) ^{1}H-NMR (600 MHz, $CDCl_3$): δ 5.10-5.23 (2H, br s, H_2-17), 4.12 (1H, br s, H-15), 3.92 (1H, t, *J*=2.5 Hz, H-7), 3.52 (1H, d, *J*=12 Hz, H-18a), 2.97 (1H, d, *J*=12 Hz, H-18b), 1.04 (3H, s, Me-20), 0.71 (3H, s, Me-19)

^{13}C-NMR (150.82 MHz, $CDCl_3$): δ 42.79 (C-1), 18.18 (C-2), 35.05 (C-3), 36.95 (C-4), 44.54 (C-5), 26.16 (C-6), 71.30 (C-7), 51.74 (C-8), 44.82 (C-9), 38.50 (C-10), 17.60 (C-11), 27.01 (C-12), 39.90 (C-13), 39.14 (C-14), 71.31 (C-15), 157.80 (C-16), 107.60 (C-17), 63.70 (C-18), 17.00 (C-19), 17.60 (C-20)

Eubol (6) ^{1}H-NMR (600 MHz, $CDCl_3$): δ 5.12-5.28 (2H, s, H_2-17), 5.01 (1H, t, *J*=2 Hz, H-7), 4.22 (1H, br s, H-15), 3.25 (1H, d, *J*=12 Hz, H-18a), 2.97 (1H, d, *J*=12 Hz,H-18b), 2.78 (1H, m, H-13), 2.07 (3H, s, OAc), 1.02 (3H, s, Me-20), 0.72 (3H, s, Me-19)

^{13}C-NMR (150.82 MHz, $CDCl_3$): δ 41.02 (C-1), 18.20 (C-2), 35.90 (C-3), 31.80 (C-4), 45.90 (C-5), 23.80 (C-6), 71.02 (C-7), 52.20 (C-8), 46.10 (C-9), 40.75 (C-10), 18.22 (C-11), 24.85 (C-12), 39.15 (C-13), 39.03 (C-14), 70.36 (C-15), 156.13 (C-16), 110.0 (C-17), 71.21 (C-18), 18.72 (C-19), 18.14 (C-20), 21.80 (O-CO<u>C</u>H_3), 172.10 (O-<u>C</u>OCH_3)

Athonolone (7) ^{1}H-NMR (600 MHz, $CDCl_3$): δ 5.85 (1H, s, H-11), 4.82 (2H, s, H_2-17), 3.06 (1H, t, *J*=2.5 Hz, H-7), 3.49 (1H, d, *J*=11.5 Hz, H-18a), 2.96 (1H, d, *J*=11.5 Hz,H-18b), 2.57 (1H, d, H-13), 1.06 (3H, s, Me-20), 0.69 (3H, s, Me-19)

Linearol (8) ^{1}H-NMR (600 MHz, $CDCl_3$): δ 4.82-4.78 (2H, br s, H_2-17), 4.04 (1H, d, *J*=11.5 Hz, H-18a), 4.00. (1H, d, *J*=11.5 Hz,H-18b), 3.61 (1H, t, *J*=2.5 Hz, H-7α), 3.53 (1H, dd, *J*=7.5 Hz ve 9 Hz, H-3β) 2.68 (1H, m, H-13), 2.09 (3H, s, O-CO<u>C</u>H_3), 1.06 (3H, s, Me-20), 0.76 (3H, s, Me-19)

^{13}C-NMR (150.82 MHz, $CDCl_3$): δ 38.01 (C-1), 27.68 (C-2), 72.21 (C-3), 38.81 (C-4), 38.01 (C-5), 27.68 (C-6), 76.84 (C-7), 48.21 (C-8), 50.11 (C-9), 37.90 (C-10), 13.92 (C-11), 32.90 (C-12), 44.11 (C-13), 42.01 (C-14), 44.05 (C-15), 154.95 (C-16), 103.55 (C-17), 66.0 (C-18), 11.91 (C-19), 17.93 (C-20), 21.15 (O-CO<u>C</u>H_3), 171.82 (O-<u>C</u>OCH_3)

EIMS (rel.int.) *m/z*: 362.2 $[M]^+$ (12) ($C_{22}H_{34}O_4$), 344.2 $[M\text{-}H_2O]^+$ (43), 326.2 $[M\text{-}2H_2O]^+$ (98), 302.2 $[M\text{-}OAc]^+$ (36), 284.2 $[M\text{-}60\text{-}H_2O]^+$ (55), 272.2 (100), 253.2 (67), 241.1 (30), 233.1 (56), 227.1 (47), 213.1 (33), 199.1 (52), 185.1 (51), 157.1 (44), 145.1 (50), 131.0 (46), 119.1 (52), 105.0 (57), 91.0 (58), 79.0 (56), 67.1 (36)

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