SUPPLEMENTARY MATERIAL

On-line screening and identification of polyphenolic antioxidant compounds of Convolvulus trabutianus

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Convolvulus trabutianus Schweinf. & Muschl is an endemic plant from northern Sahara used in folk medicine. Herein we report the isolation, characterization and evaluation of the radical scavenging properties of twenty three compounds from the different extracts of this species by on-line HPLC-ABTS$^{\bullet+}$ screening. These compounds include nine phenolic acids: **2**, **6**, **10**, **11**, **12**, **13**, **14**, **15**, **16**, two phytosterols: **3-4**, four coumarins: **5**, **7**, **8** and **9**, two quinic acids: **21** and **22** and six flavonoids: **1**, **17-20** and **23** among which the most active were: **10**, **16**, **21** and **22**. All the extracts showed a significant antioxidant activity on-line. These results were validated off-line by ORAC and TEAC assays. Four compounds: **1**, **5**, **18** and **19** were described for the first time from the Convolvulaceae family, whereas compounds **2**, **6**, **8**, **10**, **13** and **21** were new for the genus *Convolvulus*.

Keywords: *Convolvulus trabutianus*, antioxidant activity, phenolic acid derivatives, flavonoids, coumarins, sterols, HPLC-ABTS$^{\bullet+}$

Experimental details

S1. Solvents and Chemicals:

Solvents: chloroform, ethanol and acetonitrile HPLC grade were purchased from fisher scientific; methanol, n-hexane and dichloromethane reagents grade were purchased from VWR (Fontenay-sous-Bois, France); dimethyl sulfoxide and acetic acid were purchased from sigma Aldrich; ethyl acetate, formic acid and hydrochloric acid were purchased from ACRŌS organics; Milli-Q water (18.2 MΩ) was generated by Millipore synergy system (Molsheim, France).

Chemicals: 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) diammonium salt ($ABTS^{\bullet+}$), ($C_{18}H_{24}N_6O_6S_4$) was purchased from Biochemica Applichem (Darmastadt, Germany); 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AAPH), ($C_8H_{18}N_6$, 2HCL) and (±)-6-hydroxy-2,5,7,8-tetramethyl-chromane-2-carboxylic acid (Trolox), ($C_{14}H_{18}O_4$), were purchased from Sigma-Aldrich (USA); Fluorescein ($C_{20}H_{12}O_5$) was purchased from Fluka (United Kingdom); sodium chloride was purchased from Fisher scientific; sodium hydroxide was purchased from ACRŌS organics; potassium chloride and potassium persulfate were purchased from Prolabo (Rhône-Poulenc); potassium dihydrogen phosphate and disodium hydrogen phosphate were purchased from Merck (Darmstadt, Germany).

Reagents: Phosphate Buffer Saline (PBS) (8 mmol/L): NaCl (4.1 g); Na_2HPO_4 (0.7 g); KH_2PO_4 (0.135 g) and KCl (0.075 g) were dissolved in 500 mL of Milli-Q water.

$ABTS^{\bullet+}$ work solution: ABTS (7.5 mmol/L) was dissolved in 10 mL of Milli-Q water, to which potassium persulfate (2.5 mmol/L) was added, generating the radical cation $ABTS^{\bullet+}$ overnight. This solution was used within one week. The solution of radical cation $ABTS^{\bullet+}$ (0.6 mL) was diluted in PBS (30 mL) in order to reach an absorbance of 1.2 at 412 nm and obtained $ABTS^{\bullet+}$ (2%) before use.

Fluorescein work solution: Fluorescein (2.8×10^{-2} g/L) was preparing by dissolved of fluorescein (4.2 mg) in PBS (150 mL); (20 µL) of fluorescein (2.8×10^{-2} g/L) was diluted in PBS (20 mL).

AAPH work solution: AAPH (207.5 mg) was dissolved in PBS (5 mL).

Trolox work solution: Trolox (1 mmol/L) was prepared by dissolving Trolox (12.51 mg) in solution of (H_2O-MeOH, 50:50).

S2. Materials

Ultraviolet 240 1PC: UV-Vis spectra were recorded using a SHIMADZU spectrophotometer. NMR spectra were recorded on a 500 MHz (125 MHz for ^{13}C) Bruker Avance II 500 Hz. equipped with crayosonde dude ^{1}H / ^{13}C (5 mm cryoprobe DCH ^{13}C / ^{1}H / Dz- grad). Mass spectra were performed on a Waters UHPLC Acquity system (Waters, Guyancourt, France) coupled with ESI mass spectrometer (micrOTOF-Q II) (Bruker Germany). Chromatographic separation was achieved on Acquity UPLC BEH Phenyl column (1.7 µm 2.1 × 100 mm, 1.7 µm, Waters) operating at 22 °C using water: acetonitrile: formic acid 0.1% as mobile phase at a flow rate of 0.3 mL/min. The gradient was as follow: 0 min, 10% B; 15 min, 90% B; maintained during 3 minutes, injection volume was 10 µL. UV-spectra of individual peaks were recorded within a wavelength range of 190 – 400 nm. Eluted components were ionized by electrospray ion source (ESI) operating in negative or positive mode, using N_2 as instrument gas, drying gas temperature 200 °C at 9 L/min; nebulizer pressure 40.6 psi. Set capillary voltage was 4000 V, end plate offset -500 V, collision cell RF 200 Vpp, energy transfer time of 110 µs, pre pulse storage of 1 µs. Data were acquired in MS (m/z range of 50–1000). Column chromatography (CC) was carried out with Si gel Fluka (cat. 60737, 40-63 µm), and Sephadex gel LH-20: GE Healthcare, fractions were monitored by TLC Silica gel 60 F_{254}. M (Merck), Germany analytical chromatography, Aluminum sheets. Separation of compounds was achieved by semi preparative HPLC from GILSON PLC 2020; purification was made by the Ultra High Performance Liquid Chromatography system (UHPLC, Ultimate 3000, Thermo Fisher Scientific, Villebon sur Yvette, France).

S3. Plant material

Convolvulus trabutianus Schweinf. & Muschl. This name is unresolved from IPNI data base. The original publication details are found in : Repert Spec Nov Regni Veg . 1911. 9: 566. This name is accepted in Tela botanica, African Data base, Plants of the world and World checklist of selected plant families (WCSP).

The plant material of *C.trabutianus* was collected during flowering in April 2012 in Oued Djedida (Bechar) in the south west of Algeria, latitude: 31°38'5.86" and longitude: -1°44'43.62". It was authenticated by M. Mohamed Benabdelhakem, director of the nature preservation agency of Bechar. A voucher specimen (CT-48-12-04) has been deposited at the Herbarium of the VARENBIOMOL research unit, Université des Frères Mentouri Constantine 1.

S4. Extraction and isolation procedures

A total of 1800 g air dried of *C.trabutianus* was macerated at room temperature with EtOH-H_2O (80:20 v/v) for 72 h, three times. After filtration, the filtrates were concentrated in vacuum (up to 35 °C); the concentrate (300 mL) was dissolved in 500 mL of distilled H_2O under magnetic stirring and then put at the refrigerator for one night. After filtration, the resulting solution (750 mL) was extracted successively with 250 mL of petroleum ether, $CHCl_3$, EtOAc and *n*-BuOH. The organic phases were filtered using common filter paper and concentrated in vacuum up to 35 °C to obtain the following dry extracts: petroleum ether (0.57 g), $CHCl_3$ (3.94 g), EtOAc (7.15 g), *n*-BuOH (45.08 g).

The $CHCl_3$ extract (3.74 g) was dissolved in 4 mL of $CHCl_3$ and subjected to column chromatography on silica gel (60-200 mesh, 140 g) eluted with CH_2Cl_2/Acetone step gradients to yield 11 fractions (F1 – F11) obtained by combining the eluates on the basis of TLC analysis silica gel 60 F_{254}. (CH_2Cl_2/MeOH, 9:1). Fraction F2 (60.2 mg) (100 % CH_2Cl_2) showed the formation of a yellow precipitate which was filtrated (19.8 mg) and washed with methanol to give chrysoeriol **1** (4.5 mg), supernatant of F_2 (40.4 mg) was submitted to preparative plates of silica gel (Hexane/AcOEt, 8:2) to give ((*E*) ferulic acid ethyl ester **2** (6.9mg), stigmasterol **3** and beta-sitosterol **4** as a mixture (73% and 27%, respectively) (5.8 mg). Fraction F_5 (75.9 mg) (CH_2Cl_2/Acetone, 99.5:0.5) was submitted to preparative plates of silica gel (Hexane/AcOEt, 7.5:2.5) to give 7-*O*-prenylscopoletin **5** (10.2 mg). Fraction F_7 (65.5 mg) (CH_2Cl_2/Acetone, 99-1) was submitted to preparative plates of silica gel (Hexane/AcOEt, 7:3) to give trans-*ρ*-coumaric acid ethyl ester **6** (1.2 mg). Fraction F_8 (80.5 mg) (CH_2Cl_2/Acetone, 98:2) was subjected to preparative plates of silica gel (Hexane/AcOEt, 7.5:2.5) to give isoscopoletin **7** (1.5 mg) and scoparone **8** (1 mg).

The EtOAc extract (6.95 g) was dissolved in 5 mL of MeOH and subjected to column chromatography on silica gel (60-200 mesh, 250 g) eluted with $CHCl_3$/MeOH step gradients to yield 10 fractions which were purified by semi preparative obtained by HPLC separation using Interchim column PHC 4 (5 µM, 250 mm × 10.0 mm), with a mobile phase delivered at 5 mL/min consisting of mixture of Mill-Q water containing 0.1% formic acid (solvent A) and acetonitrile containing 0.1% formic acid (solvent B). The gradient was as follow: 0 min, 5% B; 15 min, 25% B maintained during 10 min; 35 min, 40% B maintained during 5 min, to give scopoletin **9** (3.3 mg), ethyl trans-caffeate **10** (4.6 mg), vanillic acid **11** (4.7 mg), ferulic

acid **12** (17.6 mg), alfrutamide **13** (8.2 mg), trans-caffeic acid **16** (21.5 mg), benzoic acid, 4-hydroxy **14** (4.4 mg), trans-4-coumaric acid **15** (8.6 mg) and astragalin **17** (5.4 mg).

A part of *n*-BuOH extract (1 g) was dissolved in methanol and submitted to a semi preparative HPLC fractionation using Interchim column C18-AQ (5 µM, 250 mm × 10.0 mm), with a mobile phase delivered at 5 mL/min consisting of mixture of Mill-Q water containing 0.1% formic acid (solvent A) and acetonitrile containing 0.1% formic acid (solvent B). The gradient was as follow: 0 min, 5% B; 35 min, 25% B maintained during 10 min to give 9 fractions (F_{1BC}-F_{9BC}). Fraction F_{1BC} (56.6 mg, 15.3 mn) was dissolved in MeOH to give a yellow precipitate which was purified on TLC plates eluted AcOEt / methanol / H_2O system (9: 0.5: 0.5) to give vicenin-2 **18** (18.7 mg) and 4-*H*-1-Benzopyran-4-one, Isoscutellarein 6-C-β-D-glucopyranosyl **19** (20 mg). The other fractions were resubmitted to semi preparative HPLC under the same conditions to give 3, 5-di-caffeoylquinic acid **21** (10.6 mg), nicotiflorin **20**, (4.2 mg), vitexin **23** (2.1 mg) and 3, 4-di-caffeoylquinic acid **22** (12.1 mg).

S5. Structural of isolated compounds

The structures of compounds were established by chemical and spectral analysis, mainly LC/MS, UV, ^{1}H, ^{13}C and 2D-NMR (COSY, ROESY, HSQC and HMBC). The purity of all compounds was checked using HPLC and the minimum purity was 95%.

S6. Spectral data of isolated compounds

The detailed data of the compounds as mentioned above in the report are listed as follow.

Chrysoeriol **(1)**: Amorphous yellow powder; ESI-HRMS (-): m/z 299.0554 $[M-H]^-$, 599.1164 $[2M-H]^-$, formula: $C_{16}H_{12}O_6$; UV (DMSO) λ_{max} nm: 268.40, 344.60; ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 3.88 (3H, s, OMe-3′), 6.03 (1H, br s, H-6), 6.33 (1H, br s, H-8), 6.79 (1H, s, H3), 6.90 (1H, br d, *J*=7.93 Hz, H-5′), 7.49 - 7.55 (2H, m, H2′, H6′), 8.51 (1H, s, OH-7) 12.96 (1H, br s, OH-5); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 56.56 (C_{OMe}-3′), 94.42 (C-8), 99.21 (C-6), 103.63 (C-3), 104.32 (C-10), 110.85 (C-2′), 116.26 (C-5′), 120.87 (C-6′), 121.25 (C-1′), 148.44 (C-3′), 151.19 (C-4′), 157.66 (C-9), 161.81 (C-5), 164.21 (C-2), 164.78 (C-7), 182.27 (C-4) (Kim et al. 2004).

Ferulic acid ethyl ester **(2)**: Brown oily liquid; ESI-HRMS (+): m/z 177.0545 $[M-46]^+$ indicating the loss of the EtOH, 145.0286 $[M-78]^+$ indicating the loss of the ethyl ester, 223.0963 $[M+H]^+$, 245.0784 $[M+Na]^+$, formula: $C_{12}H_{14}O_4$; UV ($CHCl_3$) λ_{max} nm: 235.7, 323.8; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.36 (3H, t, *J*=7.17 Hz, H-11), 3.95 (3H, s, OMe-3), 4.28 (2H, q, *J*=7.02 Hz, H-10) 5.87 (1H, br s, OH-4), 6.32 (1H, d, *J*=15.90 Hz, H-8), 6.94 (1H, d, *J*=8.09, 1.98 Hz, H-5), 7.06 (1H, d, *J*=1.83 Hz, H-2), 7.10 (1H, dd, *J*=7.17 Hz, H-6), 7.64 (1H, d, *J*=15.90 Hz, H-7); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 14.37 (C-11), 55.93 (C_{OMe}-3), 60.38 (C-10), 109.24 (C-2), 114.68 (C-8), 115.65 (C-5), 123.04 (C-6), 127.04 (C-1), 144.66 (C-7), 146.72 (C-3), 147.87 (C-4), 167.29 (C-9) (Singh et al. 2010).

Stigmasterol **(3)**: This compound was obtained as a mixture with the compound **4** (73 and 27% respectively); white crystals; HRMS: *m/z* 453.3311 $[M-Ca^+]^-$, 907.6779 $[2M-Ca^+]^-$, formula: $C_{29}H_{48}O$; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.72 (3H, d, *J*=9.16 Hz, H-19), 0.81 - 0.84 (3H, m, H_3-26), 0.85 (3H, d, *J*=3.97 Hz, H_3-27), 0.86 - 0.88 (3H, m, H_3-29), 0.90 - 0.93 (3H, m, H_3-21), 1.03 - 1.04 (3H, m, H_3-18), 3.55 (1H, ddd, *J*=5.19 Hz, H-3), 5.04 (1H, br dd, *J*=14.95, 8.85 Hz, H-23), 5.18 (1H, td, *J*=8.54, 15.26 Hz, H-22), 5.38 (1H, br d, *J*=5.19 Hz, H-6) (Chemam et al. 2017).

β-Sitosterol **(4)**: White crystals; HRMS: *m/z* 455.3455 $[M-Ca^+]^-$, 909.6986 $[2M-Ca^+]^-$, formula: $C_{29}H_{50}O$; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.72 (3H, d, *J*=9.16 Hz, H-19), 0.81 - 0.84 (3H, m, H_3-26), 0.85 (3H, d, *J*=3.97 Hz, H_3-27), 0.86 - 0.88 (3H, m, H_3-29), 0.90 - 0.93 (3H, m, H_3-21), 1.03 - 1.04 (3H, m, H_3-18), 3.55 (1H, ddd, *J*=5.19 Hz, H-3), 5.04 (2H, br dd, *J*=14.95, 8.85 Hz, H-23), 5.18 (2H, td, *J*=8.54, 15.26 Hz, H-22)5.38 (1H, br d, *J*=5.19 Hz, H-6) (Chemam et al. 2017).

7-O-prenylscopoletin **(5)**: Amorphous yellow powder; ESI-HRMS (+): m/z 193.0505 $[M-68]^+$ indicating the loss of the Prenyl, 261.1124 $[M+H]^+$, 283.0935 $[M+Na]^+$, formula: $C_{15}H_{16}O_4$; UV ($CHCl_3$) λ_{max} nm: 229.5, 344.5; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.80 (6H, d, *J*=8.85 Hz, H-4′, H-5′), 3.92 (3H, s, OMe-6), 4.68 (2H, d, *J*=6.41 Hz, H-1′), 5.48 - 5.54 (1H, m, H-2′), 6.29 (1H, d, *J*=9.46 Hz, H-3), 6.85 (1H, s, H-5), 6.86 (1H, s, H8), 7.64 (1H, d, *J*=9.46 Hz, H-4); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 18.39 (C-4′), 25.88 (C-5′), 56.34 (C_{OMe}-6) 66.24 (C-1′), 101.08 (C-8), 107.94 (C-5), 111.28 (C-9), 113.29 (C-3), 118.62 (C-2′), 139.05 (C-3′), 143.40 (C-4), 146.62 (C-6), 149.90 (C-10), 152.09 (C-7), 161.58 (C-2) (Demyttenaere et al. 2004).

p-coumaric acid ethyl ester **(6)**: Amorphous white powder; ESI-HRMS (+): m/z 147.0410 $[M-46]^+$ indicating the loss of the EtOH, 193.0815 $[M+H]^+$, formula: $C_{11}H_{12}O_4$; UV ($CHCl_3$) λ_{max} nm: 215.2, 310.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.31 - 1.35 (3H, m, H-11), 3.50 (1H, s, OH-4), 4.25 (2H, q, *J*=7.03 Hz, H-10), 6.30 (1H, d, *J*=16.06 Hz, H-8), 6.84 (2H, br d, *J*=8.53 Hz, H-3, H-5), 7.43 (2H, br d, *J*=8.53 Hz, H-2, H-6), 7.63 (1H, br d, *J*=16.10 Hz, H7); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 13.33 (C-11), 59.38 (C-10), 114.77 (C-8), 114.84 (C-3, C-5), 126.34 (C-1), 128.90 (C-2, C-6), 156.57 (C-4), 143.23 (C-7), 166.40 (C-9) (Ohkatsu et al. 2008).

Isoscopoletin **(7)**: Amorphous yellow powder; ESI-HRMS (+): m/z 193.0456 $[M+H]^+$, formula: $C_{10}H_8O_4$; UV ($CHCl_3$) λ_{max} nm: 227.5, 343.8; ^{1}H NMR (500 MHz, Solvent) δ (ppm): 3.98 (3H, s, OMe-7), 6.30 (1H, d, *J*=9.46 Hz, H-3), 6.87 (1H, s, H-5), 6.95 (1H, s, H-8), 7.62 (1H, d, *J*=9.46 Hz, H-4); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 55.36 (C_{OMe}-7), 102.17 (C-8), 106.41 (C-5), 110.42 (C-4a), 112.35 (C-3), 142.27 (C-4), 142.98 (C-7), 148.72 (C-8a), 149.23 (C-6), 160.43 (C-2) (Ragasa et al. 2015).

Scoparone **(8)**: Amorphous yellow powder; ESI-HRMS (+): m/z 207.0653 $[M+H]^+$, formula: $C_{11}H_{10}O_4$; UV ($CHCl_3$) λ_{max} nm: 229, 343.4; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.95 (3H, s, OMe-6), 3.98 (3H, s, OMe-7), 6.32 (1H, d, *J*=9.46 Hz, H-3), 6.87 (1H, s, H-5), 6.88 (1H, s, H-8), 7.65 (1H, d, *J*=9.46 Hz, H-4); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 55.34 (C_{OMe}-6), 55.34 (C_{OMe}-7), 98.98 (C-8), 106.89 (C-5), 110.40 (C-4a), 112.54 (C-3), 142.28 (C-4), 145.30 (C-6), 149 (C-8a), 151.80 (C-7), 160.40 (C-2) (El-Demerdash et al. 2009).

Scopoletin **(9)**: Amorphous white powder; ESI-HRMS (-): m/z 191.0321 $[M-H]^-$, formula: $C_{10}H_8O_4$; UV (MeOH) λ_{max} nm: 227.4, 344; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm): 3.93 (3H, s, OMe-6), 6.22 (1H, d, *J*=9.46 Hz, H-3), 6.78 (1H, s, H-8), 7.13 (1H, s, H-5), 7.88 (1H, d, *J*=9.46 Hz, H-4); ^{13}C NMR (126 MHz, MeOH-d_4) δ (ppm): 56.36 (C_{OMe}-6), 102.56 (C-5), 108.42 (C-8), 110.87 (C-4a), 111.01 (C-3), 144.74 (C-4), 145.77 (C-6), 150.08 (C-8a), 151.85 (C-7), 162.69 (C-2) (Bhatt et et al. 2011).

Ethyl caffeate **(10)**: Amorphous yellow powder; ESI-HRMS (-): m/z 207.0685 $[M-H]^-$, formula: $C_{11}H_{12}O_4$; UV (MeOH) λ_{max} nm: 240.3, 324.9; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm): 1.33 (3H, t, *J*=7.17 Hz, H-11), 4.23 (2H, q, *J*=7.02 Hz, H-10), 6.27 (1H, d, *J*=15.87 Hz, H-8), 6.80 (1H, br d, *J*=8.24 Hz, H-5), 6.96 (1H, br dd, *J*=8.09, 1.68 Hz, H-6), 7.06 (1H, br d, *J*=1.83 Hz, H-2), 7.55 (1H, d, *J*=15.87 Hz, H-7) (Xiang et al. 2011).

Vanillic acid **(11)**: Amorphous yellow powder; ESI-HRMS (-): m/z 167.0351 $[M-H]^-$, formula: $C_8H_8O_4$; UV (MeOH) λ_{max} nm: 222.3, 260.3; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm): 3.92 (3H, s, OMe-3), 6.86 (1H, d, *J*=8.85 Hz, H-5), 7.55 - 7.60 (2H, m, H-2, H-6) (Shi et al. 2014).

Ferulic acid **(12)**: Amorphous yellow powder; ESI-HRMS (-): m/z 193.0516 $[M-H]^-$, formula: $C_{10}H_{10}O_4$; UV (MeOH) λ_{max} nm: 235.5, 323.1; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm): 3.91 (3H, s, OMe-3), 6.34 (1H, d, *J*=15.87 Hz, H-8), 6.83 (1H, d, *J*=8.24 Hz, H-5), 7.08 (1H, dd, *J*=8.24, 1.83 Hz, H-6), 7.19 (1H, d, *J*=1.83 Hz, H-2), 7.60 (1H, d, *J*=15.90 Hz, H-7) (Xiang et al. 2011).

Alfrutamide **(13)**: Brown oily liquid; ESI-HRMS (-): m/z 312.1248$[M-H]^-$, 625.2567 $[2M-H]^-$, formula: $C_{18}H_{19}NO_4$; UV (MeOH) λ_{max} nm: 219.4, 318; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm): 2.77 (2H, t, *J*=7.32 Hz, H-7′), 3.48 (2H, t, *J*=7.32 Hz, H-8′), 3.89 (3H, s, OMe-3), 6.43 (1H, d, *J*=15.56 Hz, H-8), 6.74 (2H, d, *J*=8.54 Hz, H-3′, H-5′), 6.81 (1H, d, *J*=8.24 Hz, H-5), 7.04 (1H, dd, *J*=8.09, 1.98 Hz, H-6), 7.07 (2H, d, *J*=8.54 Hz, H-2′, H-6′), 7.13 (1H, d, *J*=1.83 Hz, H-2), 7.46 (1H, d, *J*=15.56 Hz, H-7) (Forino et al. 2016).

Benzoic acid, 4-hydroxy **(14)**: Amorphous yellow powder; ESI-HRMS (-): m/z 137.0244 $[M-H]^-$, formula: $C_7H_6O_3$; UV (MeOH) λ_{max} nm: 255.3; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm): 6.83 (2H, dd, *J*=8.70, 1.00 Hz, H-2, H-6), 7.89 (2H, dd, *J*=8.85, 1.00 Hz, H-3, H-5) (Dhakal et al. 2008/2009).

Trans-4-coumaric acid **(15)**: Amorphous brown powder; ESI-HRMS (-): m/z 163.0377 $[M-H]^-$, formula: $C_9H_8O_3$; UV (MeOH) λ_{max} nm: 225.9, 310.1; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm): 6.31 (1H, d, *J*=15.87 Hz, H-8), 6.83 (2H, dd, *J*=9.16 Hz, H-3, H-5), 7.47 (2H, dd, *J*=8.54 Hz, H-2, H-6), 7.60 (1H, d, *J*=16.06 Hz, H-7); ^{13}C NMR (126 MHz, MeOH-d_4) δ (ppm): 114.37 (C-8), 115.37 (C-3, C-5), 125.92 (C-1), 129.60 (C-2, C-6), 144.83 (C-7), 159.66 (C-4), 170.02 (C-9) (Mohamadi et al. 2015).

Caffeic acid **(16)**: Amorphous yellow powder; ESI-HRMS (-): m/z 179.0343 $[M-H]^-$, formula: $C_9H_8O_4$; UV (MeOH) λ_{max} nm: 238.3, 323.8; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm): 6.24 (1H, d, *J*=15.87 Hz, H-8), 6.80 (1H, d, *J*=7.93 Hz, H-5), 6.95 (1H, dd, *J*=8.24, 2.14 Hz, H-6), 7.06 (1H, d, *J*=1.83 Hz, H-2), 7.55 (1H, d, *J*=15.87 Hz, H7); ^{13}C NMR (126 MHz, MeOH-d_4) δ (ppm): 113.68 (C-2), 114.33 (C-8), 115.09 (C-5), 121.41 (C-6), 126.45 (C-1), 145.40 (C-7), 145.49 (C-3), 148.02 (C-4), 169.75 (C-9) (Mohamadi et al. 2015).

Astragalin **(17)**: Brown oily liquid; ESI-HRMS (-): m/z 447.0912 $[M-H]^-$, 895.1929 $[2M-H]^-$, formula: $C_{21}H_{20}O_{11}$; UV (MeOH) λ_{max} nm: 264.7, 348.6; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm) aglycone: 6.22 (1H, d, *J*=1.00 Hz, H-6), 6.42 (1H, d, *J*=1.22 Hz, H-8), 6.91 (2H, dd, *J*=8.85, 1.00 Hz, H-3′, H-5′), 8.08 (2H, br dd, *J*=9.15, 1.00 Hz, H-2′, H-6′), 8.57 (1H, s, OH-4), sugar moiety: 3.23 (1H, dd, *J*=5.50, 2.40 Hz, H-5″), 3.36 (1H, m, H-4″), 3.43 (1H, m, H-3″), 3.46 (1H, br s, H-2″), 3.56 (1H, dd, *J*=5.49, 15.00 Hz, H-6_a″), 3.72 (1H, dd, *J*=2.44, 15.00 Hz, H-6_b″), 5.25 (1H, d, *J*=7.63 Hz, H_{anom}-1″); ^{13}C NMR (126 MHz, MeOH-d_4) δ ppm aglycone: 93.42 (C-8), 98.66 (C-6), 104.24 (C-10), 114.62 (C-3′, C-5′), 121.41 (C-1′), 130.81 (C-2′, C-6′), 134.11 (C-3), 157.00 (C-9), 157.69 (C-2), 160.27 (C-4′), 161.65 (C-5), 165.11 (C-7), 178.17 (C-4), 3-*O*-β-D-glucopyranosyl moiety: 61.14 (C-6″), 69.96 (C-4″), 74.41 (C-2″), 76.56 (C3″), 76.90 (C-5″), 102.55 (C_{anom}-1″) (Chemam et al. 2017).

Vicenin-2 **(18)**: yellow precipitate; ESI-HRMS (-): m/z 593.1487 $[M-H]^-$, formula: $C_{27}H_{30}O_{15}$; UV (DMSO) λ_{max} nm: 271.3, 328.73; ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) aglycone: 6.83 (1H, s, H-3), 6.92 (2H, d, *J*=8.24 Hz, H-3′, H-5′), 8.08 (2H, d, *J*=8.54 Hz, H-2′, H-6′), 13.72 (1H, s, OH-5), 6-C-glucopyranosyl moiety: 3.32 (1H, m, H-3″), 3.35 (1H, m, H-5″), 3.40 (1H, br d, *J*=4.88 Hz, H-4″), 3.51 (1H, m, H-2″), 3.65 (2H, br s, H-$6_{a,b}$″), 4.81 (1H, d, *J*=9.77 Hz, H_{anom}-1″), 8-C-glucopyranosyl moiety: 3.25 (1H, m, H-5‴), 3.28 (1H, br d, *J*=3.97 Hz, H-3‴), 3.40 (1H, br d, *J*=4.88 Hz, H-4‴), 3.51 (1H, m, H-6_a‴), 3.77 (1H, d, *J*=10.53, 4.73 Hz, H-$_b$‴), 3.89 (1H, br t, *J*=9.16 Hz, H-2‴), 4.77 (1H, br d, *J*=9.77 Hz, H_{anom}-1‴); ^{13}C NMR (126 MHz, DMSO-d_6) δ ppm aglycone: 103.08 (C-3), 104.35 (C-10), 105.76 (C-8), 107.97 (C-6), 116.0 (C-3′, C-5′), 121.99 (C-1′), 129.52 (C-2′, C-6′), 155.55 (C-9), 159.05 (C-5), 161.34 (C-7), 161.69 (C-4'), 164.56 (C-2), 182.81 (C-4), 6-C-glucopyranosyl moiety: 60.26 (C-6″), 69.52 (C-4″), 72.42 (C-2″), 74.54 (C_{anom}-1″), 78.28 (C-3″), 81.35 (C-5″), 8-C-glucopyranosyl moiety: 61.74 (C-6‴), 71.02 (C-4‴), 71.39 (C-2‴), 73.82 (C_{anom}-1‴), 79.31 (C3‴), 82.39 (C-5‴) (Chemam et al. 2017).

Isoscutellarein 6-C-β-D-glucopyranosyl **(19)**: yellow precipitate; ESI-HRMS (-): m/z 447.0912 $[M-H]^-$, formula: $C_{21}H_{20}O_{11}$; UV (MeOH) λ_{max} nm: 275.6, 335.2; ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) aglycone: 6.34 (1H, s, H-3), 6.84 (2H, br d, *J*=8.24 Hz, H-3′, H-5′), 7.85 (2H, br d, H-2′, H-6′), 13.80 (1H, br s, OH-5), *O*-glucopyranosyl moiety: 3.09 (1H, br d, *J*=2.67 Hz, H-5″), 3.18 (1H, t, *J*=8.54, H-3″), 3.35 (1H, t, *J*=9.16, H-4″), 3.53 (1H, br d, *J*=9.46 Hz, H-6_a″), 3.65 (1H, br d, *J*=11.37/2.67, H-6_b″), 4.15 (1H, br s, 2″), 4.55 (1H, d, *J*=9.61 Hz, H_{anom}-1″); ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) aglycone: 98.05 (C-10), 101.32 (C-3), 103.37 (C-8), 109.45 (C-6), 116.39 (C-3′, C-5′), 121.92 (C-1′), 128.32 (C-2′, C-

6′), 156.58 (C-9), 160.32 (C-5), 161.38 (C-2), 162.29 (C-4′), 177.25 (C-7), 179.84 (C-4), *O*-glucopyranosyl moiety: 60.25 (C-$6_{a,b}$″), 69.78 (C-4″), 70.43 (C-2″), 75.25 (C_{anom}-1″), 79.66 (C-3″), 81.08 (C-5″) (Rigano et al. 2007).

Nicotiflorin **(20)**: Amorphous yellow powder; ESI-HRMS (-): m/z 593.1472 $[M-H]^-$, formula: $C_{27}H_{30}O_{15}$; UV (MeOH) λ_{max} nm: 264.9, 350; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm) aglycone: 6.19 (1H, d, *J*=1.83 Hz, H-6), 6.37 (1H, d, *J*=1.83 Hz, H-8), 6.91 (2H, d, *J*=9.20 Hz, H-3′, H-5′), 8.09 (2H, d, *J*=9.50 Hz, H-2′, H-6′), 8.57 (1H, s, OH-7), *O*-glucopyranosyl moiety: 3.28 (1H, m, H-4″), 3.35 (1H, m, H-3″), 3.41 (1H, br d, *J*=6.41 Hz, H-6_a″), 3.44 (1H, d, *J*=8.24 Hz, H-5″), 3.47 (1H, br s, H-2″), 3.83 (1H, dd, *J*=11.30, 1.80 Hz, H-6_b″), 5.11 (1H, d, *J*=7.32 Hz, H_{anom}-1″), *O*-rhamnopyranosyl moiety: 1.15 (3H, d, *J*=6.10 Hz, H-$6_{a,b}$‴) 3.30 (1H, m, H-4‴) 3.48 (1H, br d, *J*=3.36 Hz, H-5‴) 3.55 (1H, dd, *J*=9.50, 3.40 Hz, H-3‴) 3.66 (1H, dd, *J*=3.36, 1.53 Hz, H-2‴) 4.54 (1H, d, *J*=1.53 Hz, H_{anom}-1‴); ^{13}C NMR (126 MHz, MeOH-d_4) δ (ppm) aglycone: 94.09 (C-8), 99.40 (C-6), 103.50 (C-10), 114.75 (C-3′, C-5′), 121.35 (C-1′), 130.92 (C-2′, C-6′), 134.02 (C-3), 157.33 (C-9), 157.66 (C-2), 160.16 (C-4′), 161.45 (C-5), 167.22 (C-7), 177.67 (C-4), *O*-glucopyranosyl moiety: 67.17 (C-6″), 70.01 (C-4″), 74.34 (C-2″), 75.79 (C-3″), 76.77 (C-5″), 103.45 (C-1″), *O*-rhamnopyranosyl moiety: 16.53 (C-6‴), 68.33 (C-5‴), 70.68 (C-2‴), 70.86 (C-3‴), 72.48 (C-4‴), 101.03 (C-1‴) (Chemam et al. 2017).

3,5-di-caffeoylquinic acid **(21)**: Amorphous yellow powder; ESI-HRMS (-): m/z 515.1194 $[M-H]^-$, 353.874 $[M-161]^-$ indicating the presence of a quinic acid moiety, formula: $C_{25}H_{24}O_{12}$; UV (MeOH) λ_{max} nm: 241.2, 327.6; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm) coumaroyles moiety: 6.34 (2H, dd, *J*=15.90 Hz, H-8′, H-8″), 6.80 (2H, dd, *J*=8.24, 1.53 Hz, H-5′, H-5″), 6.99 (2H, ddd, *J*=8.24, 4.73, 1.98 Hz, H-6′, H-6″), 7.09 (2H, t, *J*=1.98 Hz, H-2′, H-2″), 7.62 (2H, dd, *J*=19.23, 15.87 Hz, H-7′, H-7″), quinic acid moiety: 2.19 (1H, br dd, *J*=14.04, 6.71 Hz, H-2_a), 2.24 (2H, br s, H-$6_{a,b}$), 2.34 (1H, br dd, *J*=14.00, 3.70 Hz, H-2_b), 4.00 (1H, dd, *J*=7.63, 3.36 Hz, H-4), 5.40 - 5.48 (2H, m, H-5, H-3); ^{13}C NMR (126 MHz, MeOH-d_4) δ (ppm) coumaroyles moiety: 113.84 (C-8′), 114.21 C-8″), 113.84 (C-2′, C-2″), 115.08 (C-5′, C-5″), 121.63 (C-6′), 121.69 (C-6″), 126.52 (C-1′), 126.39 (C-1″), 145.36 (C-3′), 145.37 (C-3″), 145.64 (C-7′), 145.86 (C-7″), 148.08 (C-4′), 148.18 (C-4″), 167.03 (C-9′), 167.52 (C-9″), quinic acid moiety: 34.75 (C-2), 36.54 (C-6), 69.48 (C-4), 70.71 (C-5), 71.32 (C-3), 73.48 (C-1), 176.35 (C_{COOH}-1) (Zhu et al. 2009).

3,4-di-caffeoylquinic acid **(22)**: Amorphous brown powder; ESI-HRMS (-): m/z 515.1194 $[M-H]^-$, formula: $C_{25}H_{24}O_{12}$; UV (MeOH) λ_{max} nm: 241.2, 322.16; ^{1}H NMR (500 MHz, MeOH-d_4) δ (ppm) coumaroyles moiety: 6.21 - 6.31 (2H, dd, *J*=15.87 Hz, H-8′, H-8″), 6.76 (2H, dd, *J*=7.93, 2.75 Hz, H-5′, H-5″), 6.92 (2H, br t, *J*=7.93 Hz, H-6′, H-6″), 7.03 (2H, dd, *J*=9.46, 1.83 Hz, H-2′, H-2″), 7.53 - 7.62 (2H, br dd, *J*=15.87 Hz, H-7′, H-7″), quinic acid moiety: 2.13 (1H, dd, *J*=14.30, 4.00 Hz, H-$6_{a\ ax}$), 2.26 (1H, br d, *J*=3.36 Hz, H-$6_{b\ eq}$), 2.32 (2H, br d, *J*=14.34 Hz, H-$2_{a,b}$), 4.40 (1H, br d, *J*=2.75 Hz, H-5), 5.15 (1H, dd, *J*=9.00, 2.90 Hz, H-4), 5.62 - 5.69 (1H, m, H-3); ^{13}C NMR (126 MHz, MeOH-d_4) δ (ppm) coumaroyles moiety: 113.29 (C-8′), 113.33 (C-8″),113.76 (C-2′), 113.79 (C-2″), 115.08 (C-5′, C-5″), 121.77 (C-6′), 121.78 (C-6″), 126.22 (C-1′), 126.28 (C-1″), 145.32 (C-3′), 145.33 (C-3″), 146.19 (C-7′), 146.32 (C-7″), 148.25 (C-4′, C-4″), 166.87 (C-9′), 167.17 (C-9″), quinic acid moiety: 37 (C-6), 38.06 (C-2), 67.63 (C-3), 68.07 (C-5), 74.42 (C-4), 74.82 (C-1), 175.76 (C_{COOH}-1) (Wan et al. 2017).

Vitexin **(23)**: yellow precipitate; ESI-HRMS (-): m/z 431.1037 $[M-H]^-$, 863.2074 $[2M-H]^-$, formula: $C_{21}H_{20}O_{10}$; UV (DMSO) λ_{max} nm: 269.20, 338.80; ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) aglycone: 4.63 (1H, br s, OH-7), 6.27 (1H, s, H-6), 6.79 (1H, s, H-3), 6.90 (2H, br d, *J*=8.54 Hz, H-3′, H-5′), 8.03 (2H, br d, *J*=7.93 Hz, H-2′, H-6′), 13.18 (1H, s, OH-5), *C*-β-D-glucopyranosyl moiety: 3.22 - 3.25 (1H, m, H-5″), 3.27 (1H, m, H-3″), 3.38 - 3.39 (1H, m, H-4″), 3.52 (1H, br d, *J*=8.54 Hz, H-6_a″), 3.75 - 3.78 (1H, m, H-6_b″), 3.85 (1H, br t, *J*=9.16 Hz, H-2″), 4.70 (1H, dd, *J*=9.46, 1.00 Hz, H_{anom}-1″); ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) aglycone: 98.66 (C-6), 102.88 (C-3), 105.07 (C-8), 104.40 (C-10), 116.26 (C3′, C-5′), 122.07 (C-1′), 129.41 (C-2′, C-6′), 155.32 (C-9), 161.48 (C-5), 161.50 (C-7), 161.60 (C-4′), 164.31 (C-2), 182.49 (C-4), *C*-glucopyranosyl moiety: 61.72 (C-6″), 70.96 (C-4″), 71.31 (C-2″), 73.87 (C-1″), 79.10 (C-3″), 82.30 (C-5″) (Cuong et al. 2015).

S7. On-line HPLC $ABTS^{\bullet+}$ assay

$ABTS^{\bullet+}$ assay was based on the procedure described by (Re et al. 1999) and (Siddhuraju 2006). ABTS (7.5 mmol/L) was dissolved in 10 mL of Milli-Q water, to which potassium persulfate (2.5 mmol/L) was added, generating the radical cation $ABTS^{\bullet+}$. The solution was left overnight at 4 °C protected from light exposure. The radical cation $ABTS^{\bullet+}$ was diluted in PBS Buffer Saline (8 mmol/L) before use. Chromatographic online antioxidant detection system was carried out by Ultra High Performance Liquid Chromatography system (UHPLC, Ultimate 3000, Thermo Fisher Scientific, Villebon sur Yvette, France); it was consisting in a

Dionex Ultimate Autosampler WPS3000FC, a Dual Gradient Pump 3600 SD, a Diode Array Detector 3000 (RS), a Variable Wavelength Detector 3100. The column used in the separation of $CHCl_3$, AcOEt, *n*-butanol extracts and pure compounds was an ACE C18-PFP (250 x 4.6 mm; 5 μM), the flow rate was of 1 mL/min and the injection volume was 20 μL. The mobile phase was a gradient of a solvent (A) consisting in Milli-Q a mixture of water and formic acid (99.9/0.1, v/v) and a solvent (B) consisting in mixture of acetonitrile and formic acid (99.9/0.1, v/v). The following gradient was used: 0 min, 5% B; 35 min, 55% B, 36 min, 100 % B; maintaining during 2 minutes; 39 min, 5 % B; maintaining during 10 minutes. The pure components concentration was 0.5 mg/mL and 1 mg/mL for extracts. After their separation, the eluted compounds were diverted to a DAD detector (200 nm < λ< 800 nm); at the output of the DAD there is a mixer tee, which receives at the same time the $ABTS^{\bullet+}$ radical cation pumped with second pump at a flow rate of 0.5 mL/min. The mixture was guided through a 20 meter long reaction coil with 0.25 mm internal diameter loaded in a temperature controlled oven to a second UV detector, where discoloration is monitored at 412 nm and detection of the reduced form of $ABTS^{\bullet+}$ radical and thus a reduced absorbance. The result is presented as a double chromatogram, the upper part representing the free radical scavenging activity of the active compounds, while the lower part representing the compounds, detected by their absorbance at 280 nm. A negative peak indicated that a compound having radical scavenging activity elutes out of the chromatographic column and react with the $ABTS^{\bullet+}$ radical cation. The area of the chromatographic negative peak gives an indication on the radical scavenging activity of the considered compounds. The antioxidant potential was calculated as the concentration of Trolox required producing an equivalent negative peak area by absorption at 412 nm and expressed as μg_{TE}/mL.

S8. Trolox equivalent antioxidant capacity (TEAC)

Traditional Trolox antioxidant capacity:

The TEAC method is a spectrophotometric technique based on the use of a stable colored (blue-green) cationic radical $ABTS^{\bullet+}$, which is discolored when reduced by an antioxidant, following an electron transfer and until exhaustion of the $ABTS^{\bullet+}$ cation radical; slow reduction of this radical is directly proportional to the latency. The area under the curve of the kinetics of absorbance is directly proportional to the amount and effectiveness of the free

radical scavengers present in a sample. The solution of the $ABTS^{\bullet+}$ cation radical (2%) was added at 200 µL per well in triplicate in 96 wells micro-plate. Trolox a water-soluble structural analog of vitamin E was used as reference. The different extracts and pure products were dissolved in MeOH (100%) at 1 mg/mL, and then have to be diluted with MeOH (between 5 – 80 µg/mL) before being placed in triplicate in 96 wells micro-plate up to 10 µL/well. A trolox standard range for extracts was between 10 – 900 µmol/L and 10 – 700 µmol/L for pure products. The plate was incubate at 37 °C for 5 min before the solution of the $ABTS^{\bullet+}$ cation radical was filed in triplicate to 200 µL/well by an automatic dispenser.

This constitutes a measurement in full stop. In our approach we introduced a modification allowing to several measurements during thirty minutes in order to take into account the kinetics of the reactions:

The absorbance micro-plate reader (Thermo Scientific Skanit Software for Varioskan Flash) made Reading for pure compounds every minute during 30 mn as kinetic measure, the wavelength was at 734 nm. The results were therefore expressed in $\mu Mol_{TE}/L$ for extracts and in percentage inhibition (%) for pure compounds.

Percentage inhibition (%) = $[(A_{control} - A_{sample}) / A_{control}] \times 100$

Where $A_{control}$ is the absorbance of reaction without samples and A_{sample} is the absorbance of reaction with samples.

S9. Oxygen radical absorbance capacity (ORAC)

The ORAC assay, developed and validated by (Ou et al. 2001), was performed as described by (Dávalos et al. 2004) with minor modifications (Volden et al. 2008). The assay measures the oxidative degradation of fluorescein by peroxyl radicals initiated by 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AAPH) at 37 °C. Free radical scavenging molecules protect fluorescein from the oxidative degradation and until exhaustion; slow reduction of the fluorescence is directly proportional to the latency. The area under the curve of the kinetics of fluorescence is directly proportional to the amount and effectiveness of the free radical scavengers present in a sample. Trolox is used as standard antioxidant reference. The $CHCl_3$, EtOAc, *n*-BuOH extracts and pure products, were dissolved in MeOH (100%) at 1 mg/mL, and then have to be diluted with MeOH (between 5 – 80 µg/mL) before being placed in triplicate in 96 wells micro-plate up to 10 µL/well. A trolox standard range between 10 – 900 µmol/L was also filed in triplicate to 10 µL/well. An aqueous solution of fluorescein (2.8 ×

10^{-2} g/L); (150 µL) was added per well. An automatic dispenser of fluorescence micro-plate reader then permits the initiation of the reaction by the addition of AAPH (30 µL) to each well from the initiation to generate radicals. The plate was incubated at 37 °C for 10 min before the fluorescence reading by the fluorescence micro-plate reader (Thermo Scientific Skanit Software for Varioskan Flash); the intensity of fluorescence emitted at 530 nm is measured every 5 min for 3 h, with a wavelength of excitation of 485 nm. The results are therefore expressed as trolox equivalent ($\mu mol_{TE}/L$).

S10. Statistical analysis

All measurements were made in triplicate and the values were reported as means of the measurements with standard deviations (SD) in tables.

Table S1. Free radical scavenging activities of phenolic compounds in $CHCl_3$, EtOAc and *n*-BuOH extract of *C.*trabutianus based on HPLC-ABTS$^{\bullet+}$ and their participation (%) in total antioxidant capacities with ABTS assay.

Peaks	**Pure compounds**	**ABTS (μg_{TE}/mL)**	**Radical-Scavenging Activity (mAU)**	**Scavenging Activity (%)**
$CHCl_3$				
7	isoscopoletin	2.19	23	2.07
8	scoparone	-	-	-
10	ethyl caffeate	86.90	755	79.91
6	*ρ*-coumaric acid ethyl ester	-	-	-
2	ferulic acid ethyl ester	-	-	-
5	7-O-prenylscopoletin	-	-	-
EtOAc				
14	benzoic acid, 4-hydroxy	-	-	-
11	vanillic acid	-	-	-
16	caffeic acid	69.35	632	33.68
15	trans-4-coumaric acid	-	-	-
12	ferulic acid	4.87	44	2.51
17	astragaline	-	-	-
21	3,5-di-caffeoylquinic acid	60.14	499	28.77
22	3,4-di-caffeoylquinic acid	17.00	154	8.00
13	alfrutamide	11.42	112	5.60
9	scopoletin	-	-	-
10	ethyl caffeate	23.42	192	11.06
***n*-BuOH**				
18	vicenin-2	-	-	-
19	isoscutellarein 6-C-β-D-glucopyranosyl	-	-	-
20	Nicotiflorin	-	-	-
21	3,5-di-caffeoylquinic acid	35.20	396	41.06
22	3,4-di-caffeoylquinic	29.04	379	34.52

	acid			
23	vitexin	-	-	-

Table S2. Free radical scavenging activities of extracts of *C.trabutianus* based on Oxygen Radical Capacity (ORAC) and Trolox Equivalent Antioxidant Capacity (TEAC) assays.

Extracts	**ORAC (μMol_{TE}/L)**	**TEAC (μMol_{TE}/L)**
$CHCl_3$ extract	307.59 ± 38.38	117.47 ± 4.88
EtOAc extract	414.33 ± 10.31	125.29 ± 9.80
n-BuOH extract	389.90 ± 0.95	87.34 ± 0.45

Table S3. Free radical scavenging activities of the pure compounds of *C.trabutianus* based on ABTS, Oxygen Radical Capacity (ORAC) and Trolox Equivalent Antioxidant Capacity (TEAC) assays.

Peaks	**Name of compounds**	**ABTS (μg_{TE}/mL)**	**Radical-Scavenging Activity (mAU)**	**ORAC (μMol_{TE}/L)**	**TEAC (%)**
1	chrysoeriol	-	-	-	-
2	ferulic acid ether ester	-	-	-	-
3	stigmasterol	-	-	-	-
4	beta-sitosterol	-	-	-	-
5	7-*O*-prenylscopoletin	-	-	229.98 ± 14.98	8.65
6	trans-*ρ*-coumaric acid ethyl ester	-	-	302.97 ± 0.72	15.64
7	isoscopoletin	-	-	520.23 ± 6.31	32.95
8	scoparone	-	-	-	-
9	scopoletin	5.60	0.48	-	-
10	ethyl trans-caffeate	244.65	664.02	673.17 ± 33.43	48.25
11	vanillic acid	9.86	17	741.66 ± 55.08	31
12	ferulic acid	24.54	70	268.5 ± 4.18	21.62
13	alfrutamide	12.14	29	729.66 ± 49.16	46.93
14	benzoic acid, 4-hydroxy	-	-	-	-
15	trans-4-coumaric acid	-	-	341.67 ± 29.05	32.61
16	trans-caffeic acid	84.80	302	455.16 ± 38.47	21.28
17	astragaline	-	-	-	-

18	vicenin-2	-	-	338.48 ± 3.85	25.22
19	isoscutellarein 6-C-β-D-glucopyranosyl	-	-	237.04 ± 4.03	-
20	nicotiflorin	-	-	469.13 ± 20.56	39.40
21	3,5-di-caffeoylquinic acid	50.63	115	840.87 ± 3.95	43.33
22	3,4-di-caffeoylquinic acid	55.07	193	526.28 ± 19.60	42.17
23	vitexin	6.15	3	669.45 ± 36.25	71.89

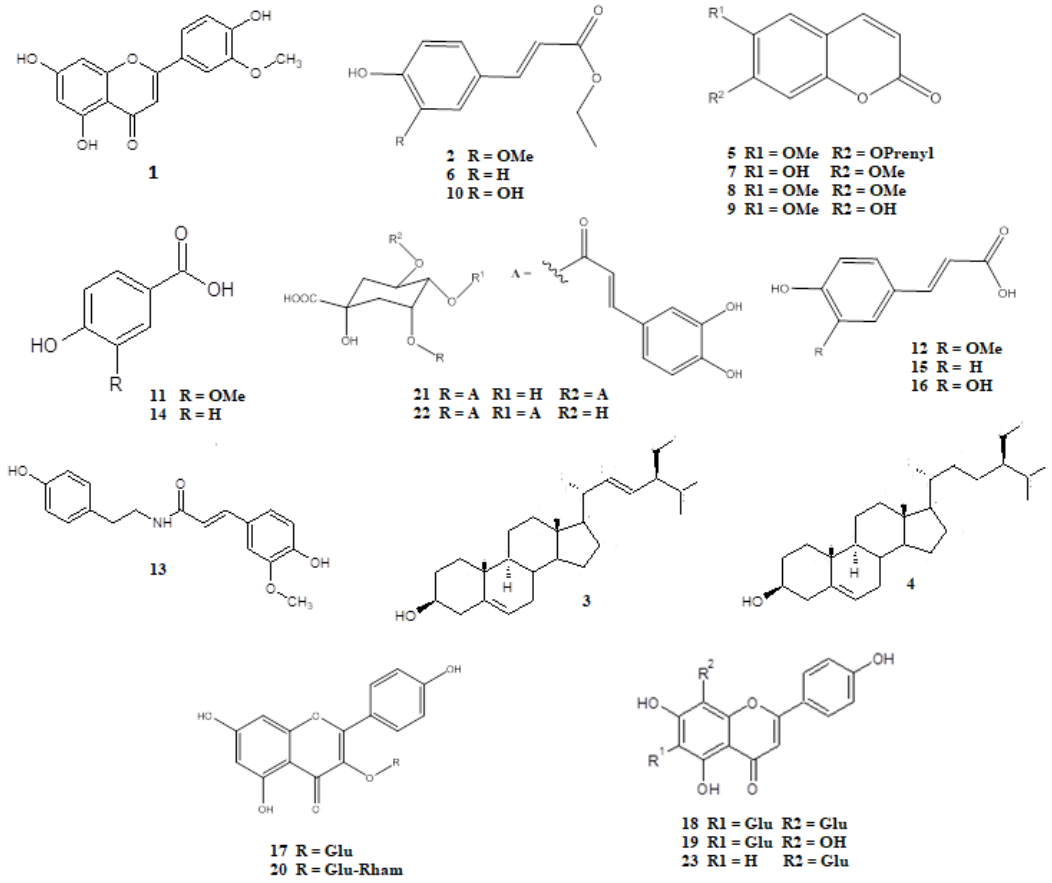

Figure S1. Structures of the isolated compounds from the *C.trabutianus*.

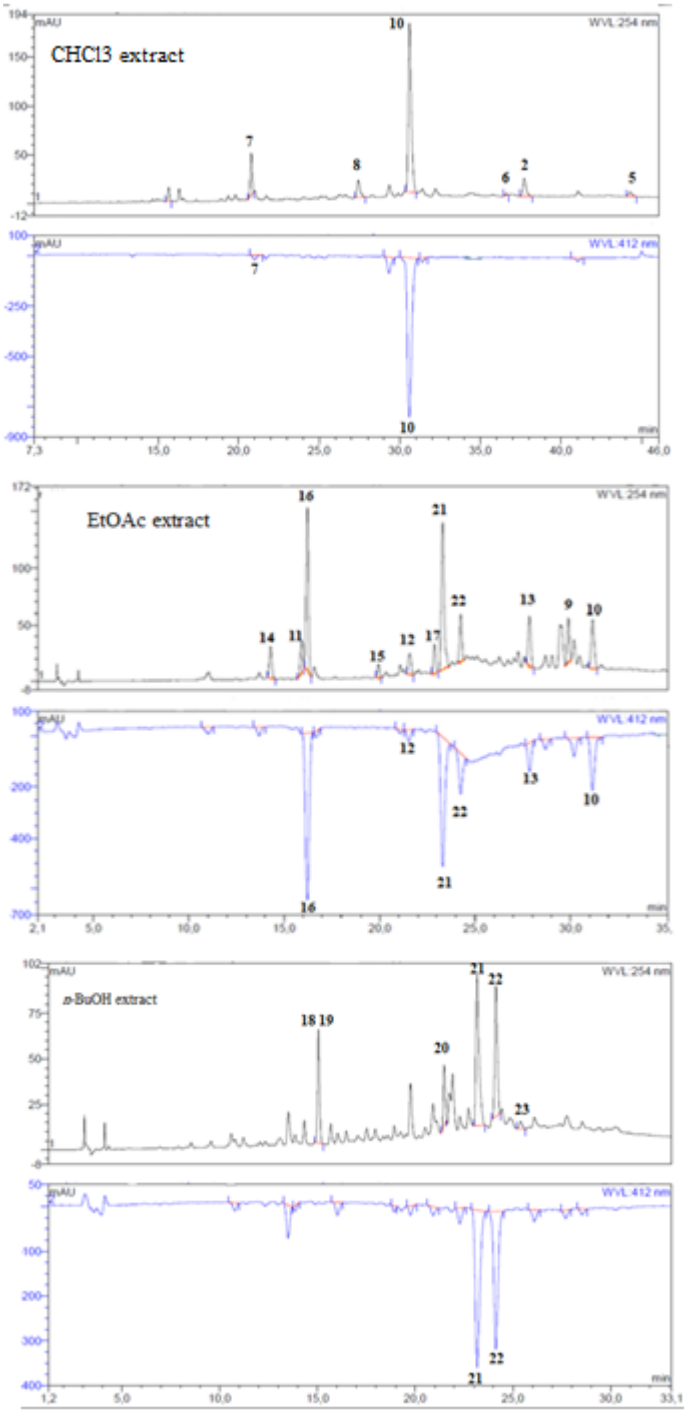

Figure S2. Chromatographic determination of antioxidant compounds (upper chromatogram) and their corresponding antioxidant activity (lower chromatogram) in chloroform, ethyl acetate and *n*-butanol extract of *C.trabutianus*, peaks: ferulic acid ethyl ester **2**, 7-*O*-prenylscopoletin **5**, *ρ*-coumaric acid ethyl ester **6**, isoscopoletin **7**, scoparone **8**, scopoletin **9**, ethyl *trans*-caffeate **10**, vanillic acid **11**, ferulic acid **12**, alfrutamide **13**, 4-hydroxy-benzoic acid **14**, 4-coumaric acid **15**, caffeic acid **16**, astragalin **17**, vicenin-2 **18**, 4-*H*-1-benzopyran-4-one, isoscutellarein 6-C-β-D-glucopyranosyl **19**, nicotiflorin **20**, 3.5-di-*O*-caffeoylquinic acid **21**, 3.4-di-*O*-caffeoylquinic acid **22** and vitexin **23**.

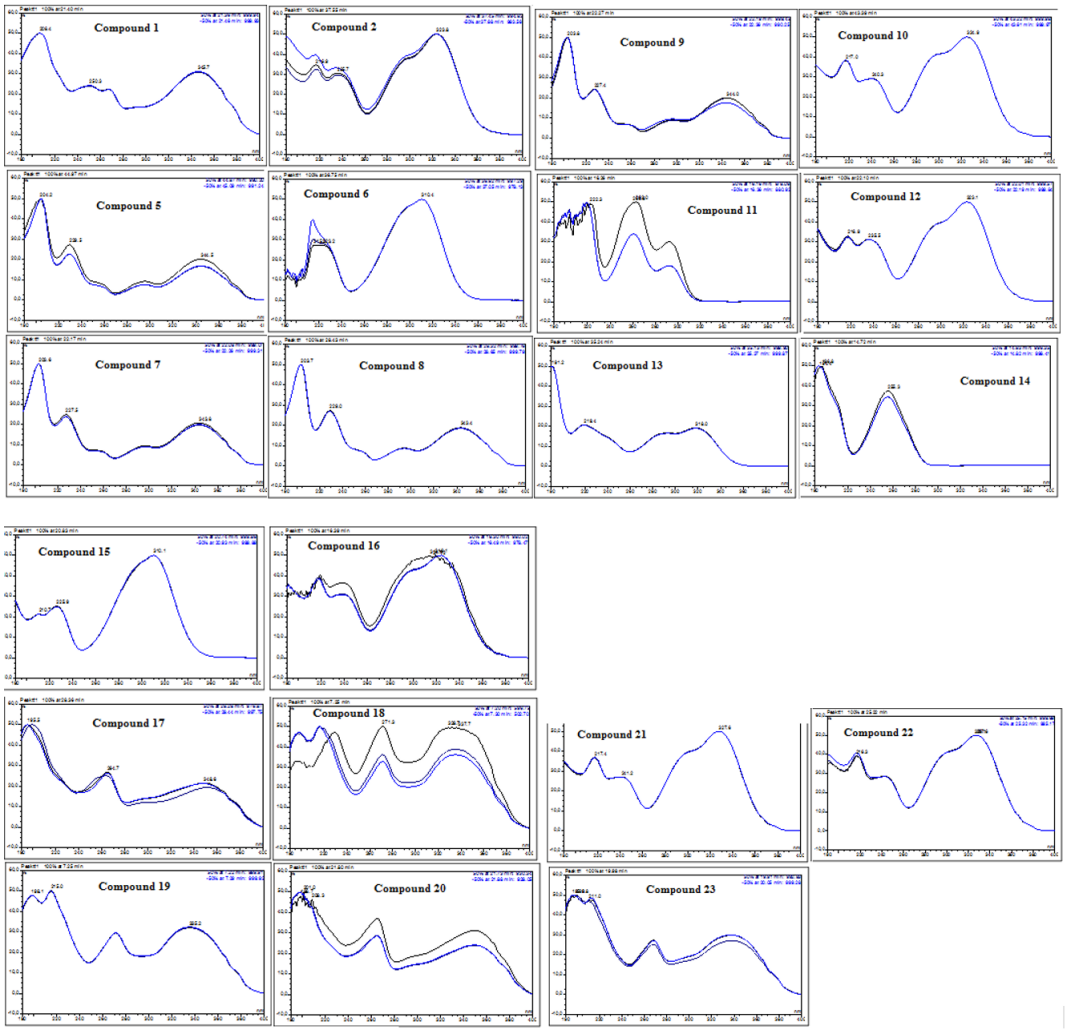

Figure S3: UV spectra of isolated compounds

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