Supporting Information

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Phenolic compounds from section *Majorana* (Mill.) Benth of *Origanum* L. species extracts via validated LC-MS/MS method

Sema Çarıkçı[1], Turgut Kılıç[2], Tuncay Dirmenci[3] and Ahmet C. Gören[4*]

[1] *Vocational School, Izmir Democracy University, Izmir, Türkiye*

[2] *Department of Science Education, Necatibey Faculty of Education, Balikesir University, Balikesir,Türkiye*

[3] *Department of Biology Education, Necatibey Faculty of Education, Balikesir University, Balikesir,Türkiye*

[4] *Department of Chemistry, Faculty of Basic Sciences, Gebze Technical University, Gebze, Kocaeli, Türkiye*

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Table S1: List of the *Origanum* species with locality, altitude, latitude and longitude, collection time**.**

	Species and code	Herbarium number	Locality	Altitude (ft)	Year	Latitude and longitude
Sect. *Majorana*	*Origanum syriacum* subsp. *bevanii* **(OS)**	T.D. 4001	Between Zorkun Plateau - Erzin	1181	2013	N36 º 54' 557" E36 º 15' 668"
	Origanum majorana **(OM)**	T.D. 3984	Mersin : Güzeldere	827	2013	N36 º 52' 472" E34 º 30' 351"
	Origanum onites **(OO)**	T.D. 4032	Between Antalya, Gazipaşa-Anamur, 25. km	1300	2013	-

S1: LC-MS Conditions

Experiments were implemented by a Zivak® HPLC and Zivak® Tandem Gold Triple quadrupole (Istanbul, Türkiye) mass spectrometry equipped with a Troyasil C18 column (150 x 3 mm i.d., 3µm particle size). The mobile phase was made up of water (A, 0.1% formic acid) in methanol (B, 0.1% formic acid), the gradient programme of which was 0-1.00 minute 55% A and 4 % B, 1.01-20.00 minutes 100% B and finally 20.01-23.00 55% A and 45% B. The flow rate of the mobile phase was 0.25 mL/min, and the column temperature was set to 30 ºC. The injection volume was 10 µL.

Ionization technique and collision energies of the experiments are the most important parameters in quantitative mass spectrometry analyses. The three-part quad-pole mass spectrometry system was chosen to use triple quadrupole mass spectrometry because it is widely used for fragmented ion stability. The optimum ESI parameters were determined as 2.40 mTorr CID gas pressure, 5000 V ESI needle voltage, 600 V ESI shield voltage, 300.00 °C drying gas temperature, 50 °C API housing temperature, 55 psi Nebullizer gas pressure and 40 psi drying gas pressure.

S2: Method validation

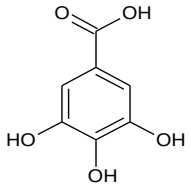
LOD (limit of detection) and LOQ (limit of quantification) of the LC-MS/MS methods for the above compounds were calculated to be 0.5-50 mg/L. The LODs were determined to be 3 times bigger than standart deviation while LOQs were determined to be 10 times bigger than.

The concentration of each analyte within the linear range and concentration of the reported method was obtained from the calibration curve. The linearity for each compound for the reported method was determined by the analysis of the corresponding standard solutions. Peak areas versus the analyte concentrations in mg/kg were plotted to obtain the calibration curves for phenolic acids. Linearity was evaluated using linear regression analysis of a six-point linear plot. The plot was consisted of three replicates per point and squared correlation coefficients, r2 was estimated for each analyte. The correlation coefficients (r2) for all analytes were found to be ≥0.98.

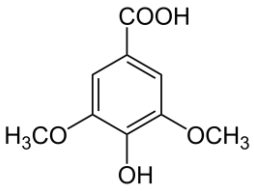
Finally, the calculated concentrations were converted to mg/kg of crude sample by the below equation.

$$Amount\ \ (mg/kg) = \frac{C_a\ x\ V_{final}}{m\ x\ V_{initial}}\ x1000$$

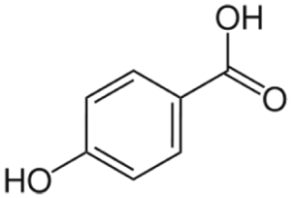
Where C_a is the analyte concentration obtained by calibration curve (mg/L), m for the amount of extract in gram and where as V_{final} and $V_{initial}$ for the final diluted volume before the analysis and the initial sample volume respectively. The EURACHEM/CITAC guide was used for evaluation of sources and quantification of uncertainty of LC-MS/MS method. The maximum contribution comes from the calibration curve.



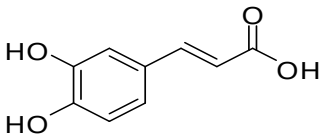
Gallic acid **(1)**



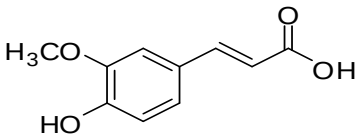
Syringic acid **(2)**



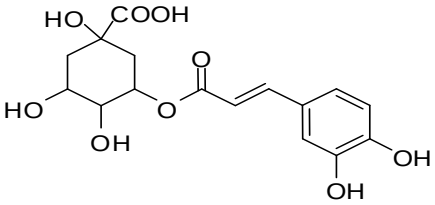
p-Hydroxy benzoic acid **(3)**



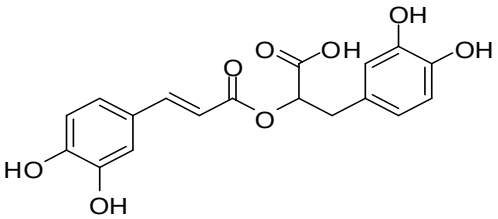
Caffeic acid **(4)**



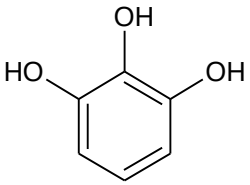
(*E*)-ferulic acid **(5)**



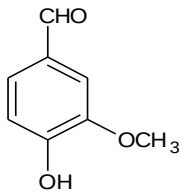
Chlorogenic acid **(6)**



Rosmarinic acid **(7)**



Pyrogallol **(8)**



Vanillin **(9)**

Figure S1: Chemical structure of the determined phenolics