Volatile profiling in *Rhus coriaria* fruit (Sumac) from 3 different geographical origins and upon roasting as analyzed via solid-phase microextraction

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*Rhus coriaria* (Sumac) is a fruit grown worldwide for its fruit culinary use as flavoring agent and health benefits. Despite several studies on *R. coriaria* non-volatile metabolites, much less is recognized concerning volatiles composition within that genus. In an effort to expand on Sumac flavor profile and in its food products, we report on volatile profiling from 3 accessions of different origins including Palestine, Jordan and Egypt in addition to its cold beverage and post roasting via headspace solid-phase microextraction (SPME). Under optimized conditions, 74 volatile components were identified belonging to alcohols, aromatics, esters, ethers, furan/aldehyde, hydrocarbons, ketones, monoterpenes, oxides and sesquiterpene hydrocarbons. Major identified components included α-pinene, naphthalene and o-cymene in Palestinian, Jordanian and Egyptian Sumac, respectively. Whereas, sesquiterpenes amounted for the major volatile class in fresh *R. coriaria* at ca. 40-58 %, furan/aldehydes were the predominant classes in roasted fruits (58%). Volatiles abundance data was further subjected to multivariate data analyses revealing furfural and nonanal enrichment in roasted compared to fresh fruits and its cold beverage preparation. Seeds exhibited no aroma components which justify for its removal in *R. coriaria* prior to its use as food flavor. Such knowledge is expected to be the key for understanding the olfactory and taste properties of *R. coriaria* and its several food products.
Volatile profiling in Rhus coriaria fruit (Sumac) from 3 different geographical origins and upon roasting as analyzed via solid-phase microextraction

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Abstract

Rhus coriaria (Sumac) is a fruit grown worldwide for its fruit culinary use as a flavoring agent aside from its health benefits. Despite several reports on R. coriaria non-volatile metabolites, much less is known concerning volatiles composition within that genus. In an effort to expand on sumac aroma profile, we report on volatiles profiling from 3 sites of different origins including Palestine, Jordan and Egypt in addition to its cold tea and post roasting via headspace solid-phase microextraction (SPME). Under optimized conditions, 74 volatile components were identified belonging to alcohols, aromatics, esters, ethers, furan/aldehyde, hydrocarbons, ketones, monoterpenes, oxides and sesquiterpene hydrocarbons. Major components in different sites included α-pinene, naphthalene and o-cymene in Palestinian, Jordanian and Egyptian Sumac, respectively. Sesquiterpenes amounted for the major volatile class in fresh R. coriaria at ca. 40-58%, whereas furan/aldehydes were the predominant classes in roasted fruits (58%). The multivariate data analyses revealed that furfural and nonanal were more enriched in roasted fruits compared to both fresh fruits and fruits’ cold tea preparation. Seeds exhibited no volatile components which justify for its removal prior to sumac fruit use. The change in volatile composition upon roasting is the key for understanding the olfactory and taste properties of R. coriaria and its several food products.

1. Introduction
*Rhus coriaria* L., (Family Anacardiaceae) is commonly known as sumac (Peter 2012). Sumac name is derived from ‘sumaga’, simply means red in Syrian language (Shabbir 2012). Sumac has been traditionally used in many Middle Eastern and Mediterranean countries as a spice, dying agent, and medicinal herb (Reidel et al. 2017). It is widely used as a condiment in Turkey and Iran to enhance the taste of poultry and vegetable dishes (Ravindran et al. 2012). In Arab countries, sumac is mixed with sesame seeds, salt and thyme in the popular spice mixture called *za’atar* (or *dukkah*). With regards to its cosmetic use, oils, phytopigments, and proteins derived from the sumac fruit were used in hair care products as anti-dandruff agents, hair colors, and hair cleaning agents, respectively (Gupta et al. 2010). Additionally, antioxidants from the sumac fruits were applied to stabilize sunflower oil (Rayne & Mazza 2007). In terms of its folk medicinal use, sumac is reported for treating diarrhea and dermatological problems in addition to reduction of blood glucose, uric acid and cholesterol levels (Candan 2003; Mamedov et al. 2005; Mozaffarian 2013). With regards to its health benefits, *R. coriaria* also exerts a myriad of biological effects such as antimicrobial, antiviral, antioxidant, anti-inflammatory, anticancer, hepatoprotective, antihypertensive and cardiovascular protection (Bozan et al. 2003; El Hasasna et al. 2015; Pourahmad et al. 2010; Rayne & Mazza 2007). Bioactive agents reported in *R. coriaria* (Abu-Reidah et al. 2014) include organic acids, fatty acids, essential and non-essential amino acids, vitamins (*B*<sub>1</sub>, *B*<sub>2</sub>, *B*<sub>6</sub>, *B*<sub>12</sub>, *C*, *PP*), carbohydrates (*xylose* and *glucose*), minerals (*K*, *Ca*, *Mg*, *Na*, *P*, *Fe*), tannins, phenolic acids, anthocyanins, flavonoids and terpenoids (Abu-Reidah et al. 2015; Demchik et al. 2015; Kossah et al. 2010; Kossah et al. 2009). Although *R. coriaria* is not recognized as an aromatic plant, its fruit is enriched in essential oil composed of monoterpenes and/or sesquiterpenes (Bahar & Altug 2009; Giovanelli et al. 2017; Morshedloo et al. 2017). Main aroma compounds include nonanal, limonene, 2-decenal, p-anisaldehyde (Giovanelli et al. 2017; Kurucu et al. 1993), (E)-caryophyllene (Bahar & Altug 2009; Brunke et al. 1993; Gharaei et al. 2013) and the diterpene cembrene (Gharaei et al. 2013; Giovanelli et al. 2017). Volatile composition in plants is known to be affected by various factors such as geographical origin, harvesting time, processing and agricultural practices (Morshedloo et al. 2015). Previous studies have revealed for differences in Sumac volatile composition as affected by its origin i.e. Turkey, Italy and Iran. Nevertheless, no report has been made on assessing to what extent roasting could affect its aroma profile.
The main objectives of this study were: 1) to assess volatile composition of sumac fruit from different Middle-Eastern origins viz. Egypt, Jordan and Palestine using headspace SPME, 2) to assess roasting impact on its aroma profile and 3) to determine sumac cold tea true aroma profile. Volatiles abundance data were extracted from chromatograms without prior peak identification in an untargeted manner. Considering the complexity of acquired data, unsupervised and supervised multivariate data analyses viz. principal component analysis (PCA) and orthogonal partial least squares (OPLS), respectively, were employed for classification of fruit samples, and to ensure good analytical rigorosity. To the best of our knowledge, this study provides the first volatiles characterization in R. coriaria from the Middle East region and to report roasting impact on the fruit aroma.

2. Materials and methods

2.1. Plant material

Rhus coriaria fruits were collected manually in the full ripe stage from wild trees grown in Nablus, Palestine in October 2016, and were authenticated by Prof. Dr. Ibrahim Abou Reidah, Department of Chemistry, An-Najah National University, Nablus, Palestine. Commercial samples of R. coriaria fruits in the full ripe stage were purchased from El Hen herbal company, Amman, Jordan and Haraz Drug store, Cairo, Egypt. Voucher specimens were kept at the Department of Pharmacognosy, Faculty of Pharmacy, Cairo University, Egypt. Cold tea of the Palestinian sample was prepared by percolating 10 g of fresh cut fruits (without seeds) in 100 mL distilled water for 10 min, kept at 25 °C, then filtered on Whatman filter paper to remove plant debris. Roasting of the Palestinian sample was carried out by heating fresh cut fruits (without seeds) in an oven set at 120°C for 20 min. Three replicates were analyzed for each sample. The fruits were stored at -20°C till further analysis.

2.2 Chemicals and Materials

SPME fibers of stableflex coated with divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50/30 μm) (57328-U) or PDMS (polydimethylsiloxane) (57302) were purchased by Supelco (Oakville, ON, Canada). All other chemicals and standards were purchased from Sigma Aldrich, USA.

2.3 Volatiles analysis of fresh and roasted fruits
The HS-SPME volatile analysis was carried out as stated previously (Farag et al. 2017). Fruits (100 mg) were cut into halves, placed in SPME screw cap vials (1.5 ml) and spiked with (Z)-3-hexenyl acetate dissolved in water at a final concentration of 2 µg per vial. The SPME fiber was inserted manually into a vial containing seeds placed in an oven kept at 50°C for 30 min. The fiber was subsequently withdrawn into the needle and then injected into the injection port of the gas chromatography-mass spectrometer (GC-MS). GC-Ms analysis was performed on a Schimadzu GC-17A gas chromatogram (Schimadzu, Tokyo, Japan) equipped with DB-5 column (30 m × 0.25 mm i.d. × 0.25 µm film thickness; Supelco) and coupled to Schimadzu QP5050A mass spectrometer. The interface and the injector temperatures were both set at 220°C. The following gradient temperature program was used for volatiles analysis. The oven temperature was kept first at 40°C for 3 min, then increased to 180°C at a rate of 12°C min\(^{-1}\), kept at 180°C for 5 min, and finally ramped at a rate of 40°C min\(^{-1}\) to 240°C and kept at this temperature for 5 min. The carrier gas helium was used at a total flow rate of 0.9 mL/min. Splitless injection mode was used for analysis considering the lower levels of volatiles in samples. SPME fiber was prepared for the next analysis by placing it in the injection port for 2 min at 220°C to ensure complete elution of volatiles. Blank runs were made during sample analyses. The HP quadruple mass spectrometer was operated in EI mode at 70 eV. A scan range was set at \(m/z\) 40–500.

### 2.4. GC-MS data processing and multivariate analysis

Volatile components were identified by comparing their retention indices (RI) relative to n-alkanes (C6-C20), mass matching to NIST, WILEY library database and with standards whenever available. Peaks were first deconvoluted using AMDIS software (http://www.amdis.net) prior to mass spectral matching. Volatiles abundance data were prepared for multivariate data analysis by extraction using MET-IDEA software (Broeckling et al. 2006) for data extraction. Data were then subjected to principal component analysis (PCA), partial least squares-discriminant analysis (OPLS-DA) using SIMCA-P version 13.0 software package (Umetrics, Umea, Sweden). Markers were subsequently identified by analyzing the S-plot, which was declared with covariance (p) and correlation (pcor). All variables were mean centered and scaled to Pareto variance.

### 3. Results
3.1 Volatiles analysis of fresh *R. coriaria* fruit (Sumac) from three different geographical origins

GC-MS analysis (Table 1 & 2, Figure 1) of sumac fruits led to the identification of 74 volatile constituents, categorized in 10 different classes viz. alcohols, aromatics, esters, ethers, furan/aldehydes, hydrocarbons, ketones, monoterpenic hydrocarbons, oxide and sesquiterpene hydrocarbons. A typical chromatogram of fresh and roasted sumac fruit aroma profiles is represented in Figure 1. Initial detection of volatiles started from zero minutes during chromatographic run but considering that no volatile peaks were detected till 5 minutes and with only one major peak for acetic acid (Fig. S1), MS detection started from 5 minutes for all specimens. Considering our interest in volatile terpenoids and hydrocarbons, five minutes delay is appropriate for this study. Acetic acid in sumac is likely to derive the tartar taste for its fruit. Sesquiterpene hydrocarbons amounted for the most dominant class accounting for ca. 40-58% of the fresh Sumac aroma with a total of 26 identified volatile constituents (Table 2). Next to sesquiterpenes, monoterpenic hydrocarbons represented the most abundant class (ca. 17-34%) among specimens (Table 2). Other 8 volatile classes detected amounted for less than 17% of sumac fruit total volatile blend (Table 2). Naphthalene and α-pinene were the major volatile forms in Jordan and Palestine specimens at ca. 15.8 and 16.7%, respectively. Whereas, monoterpenic hydrocarbons viz., o-cymene 7.7%, β-ocimene 7.5% and limonene 7.3% were the chief components in fresh sumac fruit aroma derived from Egypt. Volatiles found at comparable levels in all 3 examined specimens included (E)-β-farnesene and (Z, Z)-α-farnesene (sesquiterpene hydrocarbons) detected at ca. 6-8%. With regard to oxides, cineole amounted for 7.3% of Egyptian sumac aroma blend, at two fold levels that present in specimens from Jordan (3.2%) and Palestine (2.2%) (Table 1).

In contrast, roasted fruit aroma was predominated by furan/aldehydes at ca. 58% followed by sesquiterpene hydrocarbons at 27%. A dramatic change in fruits aroma profile was observed upon roasting exemplified in high furan/aldehyde (58.1%) and ketone (6.1%) levels in roasted fruit concurrent with a marked decrease in the other 8 volatile classes (Table 2). Roasted specimens were particularly enriched in furfural (34.3%) and (E)-nonanal (12.2%) followed by 3-thujanone (5.1%) (Table 1, Fig. 2). Sumac fruits are also used worldwide to prepare cold tea by simply soaking the fruit in cold water. Consequently, it was of interest to characterize the
sumac cold tea aroma profile; a weak aroma profile was detected compared to fruit exemplified by much lower number of volatile components totaling 14 peaks (Fig. 2).

It should be noted that a relatively high standard deviation was observed for some minor constituents (Table 1) viz., β-linalool, styrene, octanal, nonanal and β-ocimene especially from Jordanian specimen. Whether such large variance is associated with the experimental setup and detection method has yet to be determined, Employing other detectors viz. (Flame Ionization Detector). FID detection or automated SPME in volatiles extraction step can help minimize such variance.

3.2 Multivariate PCA and OPLS-DA analyses of fresh, roasted and cold tea of R. coriaria fruit volatiles data

Multivariate PCA (Figures 3, 4 & S2) was carried out to explore the relative variability within the different specimens and to identify geographical origin (viz. Egypt, Jordan and Palestine) impact on fresh sumac fruit aroma in an untargeted manner. Multivariate data analyses additionally help in identifying potential markers for each fruit origin. Palestinian and Jordanian sumac specimens were found more or less clustered together on the right side of PC1 (positive score values). In contrast, Egyptian sumac was positioned on the left side of PC1 (Fig. 3A). A total of 74 volatiles abundance data were subjected to PCA analysis with two major principle components (PC1/PC2) accounting for 60% of the total variance. PCA loading plot (Fig. 3B) revealed that α-pinene contributed the most positively along PC1 and PC2, being most abundant in Palestinian Sumac in agreement with results presented in (Table 1). In contrast, o-cymene and limonene located on the far negative side of PC1 were more enriched in Egyptian specimens. Roasting was found to influence sumac aroma profile more than the growth habitat as revealed from PCA analysis (Figure 4A). Roasted specimens were positioned to the right side of PC1 (positive side) being most distant in composition, whereas fresh fruits and cold beverage specimens were all positioned together on the left side of PC1 (negative side). PCA model (Figure 4A) was prescribed by PC1 and PC2 accounting for 45% and 24% of the variance, respectively. Unique aroma compounds found in roasted specimens included furfural and nonanal (Figure 4B). To help identify volatile markers unique for roasted specimens, OPLS-DA (orthogonal projection to latent structures-discriminant analysis) was employed (Figure S2).
OPLS-DA score plot of roasted versus unroasted fruit showed a clear segregation between roasted and fresh samples explaining 97% of the total variance (R²) and with a prediction goodness parameter Q²=95%. The respective S-plot (a remarkable parameter that compares the variable magnitude versus its reliability in OPLS) identified furfural and nonanal as markers of roasting process (Figure S2-B) and in agreement with PCA analysis. OPLS-DA model of cold sumac tea modelled against fresh fruit failed to provide a fit model as in roasted specimen case, with lower R² and Q² values of 85% and 89% respectively (Figure S2-C). In general, the aroma of sumac cold tea appeared to be more dominated by esters *viz.* bornyl acetate, nerol acetate and sesquiterpenes *viz.* (−)-caryophyllene and −humulene, as revealed from derived S plot (Figure S2-D).

4. Discussion

Sumac is commonly used as spice or appetizer, simply by blending its dried grounded fruits with freshly cut onion, or being mixed with plant oil or added to poultry dishes (Kossah et al. 2009; Shabbir 2012) in addition to being incorporated in several nutraceutical products (Wang & Zhu 2017). Also, sumac fruits oil and protein were used in hair care products (Gupta et al. 2010).

The main objective of this study was to explore the variation in volatile compositions among *R. coriaria* from 3 different sites including Palestine, Jordan and Egypt and to assess the impact of roasting on fruits’ volatile constituents. With regards to the impact of growth habitat on sumac volatiles profile, fruit specimens derived from Jordan and Palestine appeared to be similar in volatiles composition and being distant from that of Egypt. Such result is expected considering the close geographical location of Jordan and Palestine and similar climatic conditions. Abundance of monoterpenes has been reported in sumac fruit grown in Italy (Giovanelli et al. 2017; Reidel et al. 2017), with α-pinene, β-ocimene and fenchone as the main components. Whereas, prevalence of sesquiterpenes was reported in sumac fruit originated from Turkey and Iran (Bahar & Altug 2009; Gharaei et al. 2013; Morshedloo et al. 2018) with β-caryophyllene as the most abundant. It should be noted that nonadecane (Bahar & Altug 2009) and p-anisaldehyde (Giovanelli et al. 2017), previously reported as major components of *R. coriaria* essential oil, were not detected in the current study. Such discrepancy could be attributed to either the different collection methods that is SPME adopted herein involving no heat treatment in contrary to steam distillation or to regional differences owing to agricultural or ecological factors (Bahar & Altug 2009; Giovanelli et al. 2017).
Upon roasting, a marked variation in volatiles profile was detected. This variation is exemplified in higher furfural and nonanal levels in roasted samples. Likewise, previous reports (Bahar & Altug 2009; Giovanelli et al. 2017; Morshedloo et al. 2018; Reidel et al. 2017) on fresh sumac fruit analyzed using SPME from Turkey, Italy and Iran reported for furfural and nonanal presence at trace levels, suggesting that these are key markers indicative of the roasting process. Elevated levels of nonanal (23%) were only detected in hydro-distilled Sumac fruit in which heating was applied comparable to that of roasting effect (Morshedloo et al. 2018). Our results suggest that both furfural and nonanal can be utilized as markers to distinguish between roasted and fresh Sumac samples or to predict whether degradation has occurred in sumac fruits upon storage at elevated temperature. Sumac fruits are enriched in both reducing sugar (xylose) and amino acids (Demchik et al. 2015), regarded as the precursor compounds for Maillard reaction likely to occur in sumac fruits upon roasting (Tamanna & Mahmood 2015). Furfurals are major products of Maillard reaction detected in roasted coffee and cocoa beans (Martins et al. 2000), roselle (Farag et al. 2015) and during processing of soyabeans, pasta and meat (Tamanna & Mahmood 2015). Maillard reaction involves the reaction of amino acid with a reducing sugar in the presence of heat, typical of the roasting process (Nie et al. 2013; Yaylayan 2006). Although, furans are of common occurrence in thermal processed foods, increasing awareness of furans health hazard as a possible carcinogen is recognized (Nie et al. 2013; Reinhard et al. 2004). According to the FDA guidelines, average permitted level of furan should not exceed 170 ng/g (FDA 2004).

In order to identify geographical origin (viz. Egypt, Jordan and Palestine) impact on fresh sumac fruit aroma profile in an untargeted manner and to help in identifying potential markers for each fruit origin, PCA was attempted to model the volatiles abundance data. Palestinian and Jordanian sumac specimens clustered together distant from that of Egyptian sumac. In an attempt to evaluate the effect of heat on sumac, roasting was carried out as previously explained (experimental section). The respective S-plot showed a marked increase in furfural and nonanal upon roasting. Such high furan levels (up to 40%) in roasted specimens warrants more for its quantification in sumac heated food products for safety and health issues.

Conclusion
In the present study, we provide the first comprehensive volatile profile of Sumac fruits from 3 different Mid-Eastern countries. A total of 74 different volatile constituents were identified with sesquiterpene hydrocarbons as main class followed by monoterpene hydrocarbons. Egyptian Sumac was more enriched in o-cymene, β-ocimene and limonene. Whereas, Jordanian and Palestinian specimens exhibited more close volatile profile being enriched in naphthalene and α-pinene. A significant alteration in sumac aroma profile was observed upon roasting, accompanied by a marked increase in furan/aldehydes viz. furfural, 5-methyl furfural, concurrent with a decrease in sesquiterpene and monoterpene hydrocarbons. The prevalence of furans in roasted sample suggest for a distinct change in fruit aroma upon heating and for moreover the monitoring of its furan levels considering its health hazardless. Our volatiles profiling provided the true aroma profile in Sumac fruit growing in the Middle-East, which can be further applied for investigating other factors such as storage, ripening stage, and analyzing its various commercial food products.

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Figure 1

Representative SPME-GC-MS chromatogram of fresh *R. coriaria* fruit (Sumac) collected from Egypt, Jordan and Palestine.

Assigned peak numbers follow that listed in Table 1.
Figure 2

Representative SPME-GC-MS chromatogram of fresh, cold tea and roasted *R. coriaria* fruit (Sumac) from Palestine.

Assigned peak numbers correspond to volatiles listed in Table 1.
Figure 3

Principal component analyses of fresh *R. coriaria* fruit (Sumac) from 3 Middle East sites analyzed by SPME-GC-MS (*n* = 3).

Clusters are located at the distinct positions in two-dimensional space described by two vectors of principal component 1 (PC1) = 31% and PC2 = 29%. (A) Score Plot of PC1 vs. PC2 scores. (B) Loading plot for PC1 & PC2 contributing volatile peaks and their assignments, with each volatile denoted by its KI value.
Figure 4

Principal component analyses of fresh, roasted and cold beverage *Rhus coriaria* fruit (Sumac) analyzed by SPME-GC-MS (n = 3).

Clusters are located at the distinct positions in two-dimensional space described by two vectors of principal component 1 (PC1) = 45% and PC2 = 24%. (A) Score Plot of PC1 vs. PC2 scores. (B) Loading plot for PC1 & PC2 contributing mass peaks and their assignments, with each volatile denoted by its KI value.
Table 1 (on next page)

Relative percentage of volatile compounds detected in fresh *R. coriaria* fruit (Sumac) from 3 Middle East sites and in response to roasting using SPME-GC-MS measurements (*n* = 3).
| Volatile constituents | RT  | KI  | Fresh Sumac | Roasted Sumac |
|------------------------|-----|-----|-------------|---------------|
|                        |     |     | Egypt       | Jordan        | Palestine     |
|                        |     |     |            |               |               |
| **Alcohols**           |     |     | Average (S.D.) |                |
| 1 β-Linalool           | 9.93| 1077| 3.38 (1.17) | 1.84 (1.60)   | 0.90 (0.43)   | 0.28 (0.24)   |
| 2 endo-Borneol         | 11.16| 1158| 0.00 (0.00) | 0.06 (0.05)   | 0.01 (0.02)   | 0.20 (0.08)   |
| 3 4-Terpineol          | 11.18| 1163| 0.23 (0.31) | 0.52 (0.49)   | 0.00 (0.00)   | 0.03 (0.05)   |
| 4 α-Terpineol          | 11.40| 1169| 0.54 (0.48) | 0.03 (0.06)   | 0.02 (0.03)   | 0.00 (0.00)   |
| **Total alcohols**     |   11.55| 1179| 4.15        | 2.46          | 0.93          | 0.51          |
| **Aromatics**          |     |     |            |               |               |
| 5 Styrene              | 6.433| 874 | 0.20 (0.30) | 0.69 (0.64)   | 1.08 (0.69)   | 0.03 (0.05)   |
| 6 Naphthalene          | 11.328| 1176| 0.00 (0.00) | 15.88 (4.18)  | 0.00 (0.00)   | 0.00 (0.00)   |
| **Total aromatics**    |     |     | 0.20        | 16.56         | 1.08          | 0.03          |
| **Esters**             |     |     |            |               |               |
| 7 Methyl nonanoate     | 11.608| 1193| 1.30 (2.08) | 0.26 (0.25)   | 0.00 (0.00)   | 0.10 (0.18)   |
| 8 Bornyl formate       | 11.833| 1209| 0.00 (0.00) | 0.00 (0.00)   | 0.01 (0.03)   | 0.07 (0.09)   |
| 9 Linalyl acetate      | 11.958| 1219| 0.24 (0.41) | 0.03 (0.06)   | 0.02 (0.03)   | 0.09 (0.13)   |
| 10 Bornyl acetate      | 12.523| 1261| 0.00 (0.00) | 0.00 (0.00)   | 0.01 (0.03)   | 0.07 (0.09)   |
| 11 Isobornyl formate   | 12.534| 1262| 0.00 (0.00) | 0.00 (0.00)   | 0.01 (0.03)   | 0.07 (0.09)   |
| 12 Nerol acetate       | 13.36| 1327| 0.00 (0.00) | 0.10 (0.09)   | 0.03 (0.05)   | 0.29 (0.21)   |
| **Total esters**       |     |     | 1.54        | 0.39          | 0.09          | 0.68          |
| **Ethers**             |     |     |            |               |               |
| 13 Estragole           | 11.393| 1177| 0.00 (0.00) | 0.00 (0.00)   | 0.00 (0.00)   | 0.00 (0.00)   |
| 14 Allyl p-methylbenzyl ether | 13.598| 1346| 4.46 (1.37) | 0.89 (0.29)   | 2.27 (2.77)   | 0.38 (0.24)   |
| 15 Precocene I         | 14.725| 1439| 1.70 (2.45) | 0.29 (0.25)   | 0.35 (0.27)   | 0.34 (0.56)   |
| **Total ethers**       |     |     | 6.17        | 1.17          | 2.62          | 0.72          |
| **Furan/aldehydes**    |     |     |            |               |               |
| 16 Furfural            | 5.35 | 822 | 0.32 (0.34) | 3.73 (3.26)   | 0.00 (0.00)   | 34.37 (10.55) |
| 17 Maleic anhydride    | 6.092| 857 | 0.00 (0.00) | 0.00 (0.00)   | 0.00 (0.00)   | 2.57 (0.63)   |
| 18 Itaconic anhydride  | 7.599| 935 | 0.90 (0.53) | 0.29 (0.38)   | 1.80 (0.57)   | 4.29 (0.48)   |
| 19 Furfural, 5-methyl- | 7.893| 952 | 0.00 (0.00) | 0.19 (0.33)   | 0.00 (0.00)   | 3.91 (1.13)   |
| 20 Octanal             | 8.408| 982 | 1.22 (0.85) | 0.65 (0.57)   | 0.36 (0.23)   | 0.47 (0.36)   |
| 21 Nonanal             | 10.008| 1082| 1.37 (1.93) | 0.76 (0.84)   | 0.93 (0.86)   | 12.20 (5.08)  |
| 22 Decanal             | 11.418| 1181| 0.00 (0.00) | 0.00 (0.00)   | 0.00 (0.00)   | 0.00 (0.00)   |
| 23 (Z)-2-Decenal       | 12.204| 1237| 0.18 (0.26) | 0.55 (0.47)   | 0.40 (0.19)   | 0.38 (0.46)   |
| **Total furan/aldehydes** |     |     | 3.99        | 6.17          | 3.49          | 58.19         |
| **Hydrocarbons**       |     |     |            |               |               |
| 24 Methylcristal        | 14.242| 1471| 0.00 (0.00) | 0.03 (0.05)   | 0.00 (0.00)   | 0.00 (0.00)   |
| **Total hydrocarbons** |     |     | 0.00        | 0.03          | 0.00          | 0.00          |
|     | Ketones                           |     |     |     |     |     |     |     |
|-----|-----------------------------------|-----|-----|-----|-----|-----|-----|-----|
| 25  | Camphenone, 6-                   | 9.34| 1039| 1.20| (1.16)| 0.29| (0.26)| 0.42| (0.20)| 0.56| (0.22) |
| 26  | Acetophenone                      | 9.549| 1052| 0.18| (0.15)| 0.00| (0.00)| 0.01| (0.02)| 0.00| (0.00) |
| 27  | 3-Thujanone                       | 10.105| 1088| 0.93| (0.59)| 0.89| (0.77)| 0.84| (0.07)| 5.16| (3.74) |
| 28  | Camphor                           | 10.758| 1133| 0.00| (0.00)| 0.00| (0.00)| 0.00| (0.00)| 0.00| (0.00) |
| 29  | p-Menthone                        | 10.822| 1137| 0.00| (0.00)| 0.00| (0.00)| 0.00| (0.00)| 0.00| (0.00) |
| 30  | Pyranone                          | 10.917| 1144| 0.00| (0.00)| 0.00| (0.00)| 0.00| (0.00)| 0.40| (0.68) |
| 31  | Carvone                           | 12.075| 1228| 0.00| (0.00)| 0.03| (0.06)| 0.00| (0.00)| 0.02| (0.03) |
|     | **Total ketones**                 |     |     | **2.30**|     | **1.21**|     | **1.26**|     | **6.14** |

|     | Monoterpene hydrocarbon          |     |     |     |     |     |     |     |
|-----|-----------------------------------|-----|-----|-----|-----|-----|-----|-----|
| 32  | α-Pinene                          | 7.143| 909 | 4.05| (1.55)| 1.98| (0.15)| 16.70| (5.56)| 2.01| (1.81) |
| 33  | α-Fenchene                        | 7.459| 927 | 0.18| (0.16)| 0.00| (0.00)| 0.80| (0.52)| 0.04| (0.04) |
| 34  | β-Pinene                          | 7.948| 957 | 1.79| (1.46)| 0.50| (0.44)| 0.84| (0.52)| 0.11| (0.06) |
| 35  | β-Myrcene                         | 7.95 | 956 | 0.88| (0.54)| 0.18| (0.16)| 0.17| (0.29)| 0.17| (0.12) |
| 36  | β-Thujene                         | 8.483| 986 | 1.06| (0.52)| 0.82| (0.31)| 1.39| (1.84)| 0.59| (0.83) |
| 37  | 4-Carene                          | 8.602| 993 | 0.42| (0.29)| 0.31| (0.27)| 0.08| (0.14)| 0.09| (0.02) |
| 38  | 1,3,8-p-Menthatriene              | 8.745| 1001| 1.42| (0.19)| 0.81| (0.71)| 0.28| (0.33)| 0.02| (0.03) |
| 39  | O-Cymene                          | 8.768| 1003| 7.73| (1.27)| 4.25| (1.87)| 2.40| (0.82)| 0.23| (0.09) |
| 40  | Limonene                          | 8.827| 1007| 7.36| (3.63)| 3.36| (0.73)| 3.90| (1.03)| 0.73| (0.12) |
| 41  | β-Phellandrene                    | 8.849| 1009| 0.47| (0.15)| 0.55| (0.49)| 0.22| (0.38)| 0.08| (0.02) |
| 42  | β-Ocimene                         | 9.042| 1020| 7.50| (0.80)| 3.83| (2.93)| 3.21| (1.63)| 0.85| (0.41) |
| 43  | γ-Terpinene                       | 9.283| 1036| 0.66| (0.43)| 0.29| (0.25)| 0.08| (0.14)| 0.13| (0.09) |
| 44  | β-Terpine                         | 9.289| 1035| 0.33| (0.15)| 0.17| (0.16)| 0.06| (0.11)| 0.19| (0.04) |
| 45  | Unknown monoterpene               | 9.717| 1063| 0.38| (0.17)| 0.17| (0.23)| 0.03| (0.05)| 0.06| (0.00) |
| 46  | p-Cymenene                        | 9.81 | 1069| 0.10| (0.17)| 0.11| (0.10)| 0.00| (0.00)| 0.02| (0.03) |
| 47  | Unknown monoterpene               | 12.533| 1262| 0.00| (0.00)| 0.00| (0.00)| 0.15| (0.15)| 0.18| (0.20) |
|     | **Total monoterpene hydrocarbon**|     |     | **34.33**|     | **17.33**|     | **30.32**|     | **5.51** |

|     | Oxides                            |     |     |     |     |     |     |     |
|-----|-----------------------------------|-----|-----|-----|-----|-----|-----|-----|
| 48  | Cineole                           | 8.908| 1012| 7.27| (2.98)| 3.25| (0.81)| 2.23| (0.15)| 0.53| (0.31) |
|     | **Total oxides**                  |     |     | **7.27**|     | **3.25**|     | **2.23**|     | **0.53** |

|     | Sesquiterpene hydrocarbon         |     |     |     |     |     |     |     |
|-----|-----------------------------------|-----|-----|-----|-----|-----|-----|-----|
| 49  | Unknown sesquiterpene             | 12.631| 1270| 0.00| (0.00)| 0.13| (0.11)| 0.01| (0.02)| 0.06| (0.08) |
| 50  | α-Longipinene                     | 13.393| 1330| 0.00| (0.00)| 0.78| (0.25)| 0.53| (0.46)| 0.17| (0.21) |
| 51  | Copaene                           | 13.662| 1352| 0.00| (0.00)| 0.17| (0.15)| 0.17| (0.22)| 0.12| (0.10) |
| 52  | α-Cubebeene                       | 13.675| 1353| 1.29| (0.40)| 0.60| (0.07)| 0.93| (0.67)| 0.27| (0.22) |
| 53  | Isocaryophyllene                  | 14.042| 1383| 4.42| (0.52)| 5.26| (0.81)| 5.76| (0.81)| 0.50| (0.74) |
| 54  | (E)-β-Famesene                    | 14.05 | 1383| 6.05| (1.69)| 6.58| (1.94)| 8.26| (1.49)| 0.07| (0.03) |
Relative percentage of volatile compounds detected in fresh *R. coriaria* fruit (Sumac) from 3 Middle East sites and in response to roasting using SPME-GC–MS measurements (*n* = 3). The % identified for each class is bolded, while the main component from each site is underlined and bolded.

|   | Compound Description                        | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 6 | Site 7 | Site 8 |
|---|---------------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| 55| (Z,Z)-α-Farnesene                           | 14.119 | 1389   |         |         |        |        |        |        |
| 56| Longifolene                                  | 14.2   | 1396   | 4.42   |        | (0.52)| 5.23   | (0.81)| 5.73   | (0.84)| 4.81   | (3.96)|
| 57| Caryophyllene                                | 14.252 | 1400   | 4.46   |        | (1.37)| 5.29   | (1.33)| 6.21   | (1.13)| 4.21   | (3.11)|
| 58| (E)-β-Farnesene isomer                       | 14.433 | 1415   | 3.72   |        | (2.69)| 6.51   | (2.00)| 5.73   | (5.12)| 0.64   | (0.67)|
| 59| Aromadendrene                                | 14.558 | 1425   | 2.15   |        | (3.04)| 3.70   | (5.72)| 2.74   | (4.10)| 0.45   | (0.30)|
| 60| Farnesene isomer                             | 14.575 | 1426   | 1.29   |        | (0.40)| 0.75   | (0.79)| 1.25   | (0.40)| 0.96   | (0.67)|
| 61| α-Humulene                                   | 14.662 | 1433   | 0.93   |        | (0.50)| 1.48   | (0.40)| 1.49   | (0.22)| 1.29   | (0.90)|
| 62| (Z)-Murola-4(14),5-diene                     | 14.817 | 1446   | 1.29   |        | (0.40)| 0.75   | (0.79)| 1.25   | (0.40)| 0.96   | (0.67)|
| 63| Germacrene D                                 | 14.841 | 1449   | 2.83   |        | (2.38)| 2.46   | (3.56)| 2.34   | (2.71)| 0.82   | (0.61)|
| 64| γ-Murolene                                   | 15.083 | 1468   | 0.00   |        | (0.00)| 0.27   | (0.24)| 0.51   | (0.79)| 0.60   | (0.17)|
| 65| α-Murolene                                   | 15.123 | 1471   | 0.26   |        | (0.23)| 0.17   | (0.22)| 0.37   | (0.32)| 0.90   | (0.58)|
| 66| β-Bisabolene                                 | 15.153 | 1474   | 0.93   |        | (0.50)| 1.64   | (0.27)| 1.29   | (1.16)| 0.39   | (0.32)|
| 67| γ-Cadinene                                   | 15.342 | 1489   | 0.00   |        | (0.00)| 0.00   | (0.00)| 0.35   | (0.32)| 0.82   | (0.55)|
| 68| δ-Cadinene, (+)                              | 15.359 | 1491   | 0.00   |        | (0.00)| 0.28   | (0.27)| 1.04   | (0.91)| 1.79   | (1.18)|
| 69| Calamenene                                   | 15.442 | 1498   | 0.00   |        | (0.00)| 0.17   | (0.15)| 0.17   | (0.20)| 0.50   | (0.29)|
| 70| Naphthalene, 1,2,3,4,4a,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)- | 15.575 | 1507   | 0.00   |        | (0.00)| 0.17   | (0.15)| 0.68   | (0.61)| 0.36   | (0.24)|
| 71| Unknown sesquiterpene                        | 15.628 | 1511   | 0.00   |        | (0.00)| 0.41   | (0.40)| 0.98   | (0.86)| 0.30   | (0.19)|
| 72| α-Calacorene                                 | 15.705 | 1517   | 0.00   |        | (0.00)| 0.03   | (0.05)| 0.03   | (0.04)| 0.30   | (0.11)|
| 73| Unknown sesquiterpene                        | 15.977 | 1525   | 0.00   |        | (0.00)| 0.00   | (0.00)| 0.00   | (0.00)| 0.11   | (0.03)|
| 74| Unknown sesquiterpene                        | 21.707 | 1853   | 0.00   |        | (0.00)| 0.00   | (0.00)| 0.00   | (0.00)| 0.03   | (0.06)|

**Total sesquiterpene hydrocarbon** | 40.06 | 51.44 | 57.98 | 27.71|
**Total volatiles**                 | 100.00| 0.00  | 100.00| 0.00  | 100.00| 0.00  | 100.00| 0.00  |
Table 2 (on next page)

Relative percentile (%) of the 10 classes of volatile compounds detected in fresh and roasted *R. coriaria* fruit (Sumac) from 3 Middle East sites as analyzed using SPME-GC-MS
**Table 2**: Relative percentile (%) of the 10 classes of volatile compounds detected in fresh and roasted *R. coriaria* fruit (Sumac) from 3 Middle East sites as analyzed using SPME-GC–MS.

| No. of volatile constituents | Class                           | Fresh Sumac | Roasted Sumac |
|------------------------------|---------------------------------|-------------|---------------|
|                              |                                 | Egypt       | Jordan        | Palestine     |
|                              |                                 | Average (%) |               | Average (%)   |
| 4                            | Total alcohols                  | 4.15        | 2.46          | 0.93          | 0.51          |
| 2                            | Total aromatics                 | 0.20        | 16.56         | 1.08          | 0.03          |
| 6                            | Total esters                    | 1.54        | 0.39          | 0.09          | 0.68          |
| 3                            | Total ethers                    | 6.17        | 1.17          | 2.62          | 0.72          |
| 8                            | Total furan/aldehyde            | 3.99        | 6.17          | 3.49          | 58.2          |
| 1                            | Total hydrocarbons              | 0           | 0.03          | 0             | 0             |
| 7                            | Total ketones                   | 2.30        | 1.21          | 1.26          | 6.14          |
| 16                           | Total monoterpenes Hydrocarbons | 34.33       | 17.33         | 30.3          | 5.51          |
| 1                            | Total oxide                     | 7.27        | 3.25          | 2.23          | 0.53          |
| 26                           | Total sesquiterpene Hydrocarbon | 40.06       | 51.44         | 58            | 27.7          |