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

Mohamed A Farag Corresp., [1, 2] , **Nesrin M Fayek** [1] , **Ibrahim Abou Reidah** [3]

[1] Pharmacognosy Department, College of Pharmacy, Cairo University, Cairo, Egypt

[2] Department of Chemistry, American University in Cairo, New Cairo, Egypt

[3] Department of Chemistry, An-Najah National University, Nablus, Palestine

Corresponding Author: Mohamed A Farag
Email address: mohamed.alifarag@aucegypt.edu

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.

1 **Volatile profiling in Rhus coriaria fruit (Sumac) from 3 different geographical origins and**

2 **upon roasting as analyzed via solid-phase microextraction**

4 Mohamed A. Farag [1,2*], Nesrin M. Fayek[1], Ibrahim Abou Reidah [3]

6 [1] Pharmacognosy Department, College of Pharmacy, Cairo University, Kasr el Aini st., P.B.

7 11562, Cairo, Egypt

8 [2] Department of Chemistry, School of Sciences & Engineering, The American University in

9 Cairo, New Cairo 11835, Egypt.

10 [3] Department of Chemistry, An-Najah National University, PO Box 7, Nablus 415, Palestine

12 [*]Corresponding author: Mohamed A. Farag, email: Mohamed.farag@pharma.cu.edu.eg

13 **Abstract**

14 *Rhus coriaria* (Sumac) is a fruit grown worldwide for its fruit culinary use as a flavoring agent

15 aside from its health benefits. Despite several reports on *R. coriaria* non-volatile metabolites,

16 much less is known concerning volatiles composition within that genus. In an effort to expand on

17 sumac aroma profile, we report on volatiles profiling from 3 sites of different origins including

18 Palestine, Jordan and Egypt in addition to its cold tea and post roasting *via* headspace solid-phase

19 microextraction (SPME). Under optimized conditions, 74 volatile components were identified

20 belonging to alcohols, aromatics, esters, ethers, furan/aldehyde, hydrocarbons, ketones,

21 monoterpenes, oxides and sesquiterpene hydrocarbons. Major components in different sites

22 included α-pinene, naphthalene and o-cymene in Palestinian, Jordanian and Egyptian Sumac,

23 respectively. Sesquiterpenes amounted for the major volatile class in fresh *R. coriaria* at *ca*. 40-

24 58%, whereas furan/aldehydes were the predominant classes in roasted fruits (58%). The

25 multivariate data analyses revealed that furfural and nonanal were more enriched in roasted fruits

26 compared to both fresh fruits and fruits' cold tea preparation. Seeds exhibited no volatile

27 components which justify for its removal prior to sumac fruit use. The change in volatile

28 composition upon roasting is the key for understanding the olfactory and taste properties of *R.*

29 *coriaria* and its several food products.

30 **1. Introduction**

31 *Rhus coriaria* L., (Family Anacardiaceae) is commonly known as sumac (Peter 2012). Sumac
32 name is derived from 'sumaga', simply means red in Syrian language (Shabbir 2012). Sumac
33 has been traditionally used in many Middle Eastern and Mediterranean countries as a spice,
34 dying agent, and medicinal herb (Reidel et al. 2017). It is widely used as a condiment in Turkey
35 and Iran to enhance the taste of poultry and vegetable dishes (Ravindran et al. 2012). In Arab
36 countries, sumac is mixed with sesame seeds, salt and thyme in the popular spice mixture
37 called *za'atar* (or *dukkah*). With regards to its cosmetic use, oils, phytopigments, and proteins
38 derived from the sumac fruit were used in hair care products as anti-dandruff agents, hair colors,
39 and hair cleaning agents, respectively (Gupta et al. 2010). Additionally, antioxidants from the
40 sumac fruits were applied to stabilize sunflower oil (Rayne & Mazza 2007). In terms of its folk
41 medicinal use, sumac is reported for treating diarrhea and dermatological problems in addition to
42 reduction of blood glucose, uric acid and cholesterol levels (Candan 2003; Mamedov et al. 2005;
43 Mozaffarian 2013). With regards to its health benefits, *R. coriaria* also exerts a myriad of
44 biological effects such as antimicrobial, antiviral, antioxidant, anti-inflammatory, anticancer,
45 hepatoprotective, antihypertensive and cardiovascular protection (Bozan et al. 2003; El Hasasna
46 et al. 2015; Pourahmad et al. 2010; Rayne & Mazza 2007). Bioactive agents reported in *R.*
47 *coriaria* (Abu-Reidah et al. 2014) include organic acids, fatty acids, essential and non-essential
48 amino acids, vitamins (B_1, B_2, B_6, B_{12}, C, PP), carbohydrates (xylose and glucose), minerals (K,
49 Ca, Mg, Na, P, Fe), tannins, phenolic acids, anthocyanins, flavonoids and terpenoids (Abu-
50 Reidah et al. 2015; Demchik et al. 2015; Kossah et al. 2010; Kossah et al. 2009). Although *R.*
51 *coriaria* is not recognized as an aromatic plant, its fruit is enriched in essential oil composed of
52 monoterpenes and/or sesquiterpenes (Bahar & Altug 2009; Giovanelli et al. 2017; Morshedloo et
53 al. 2017). Main aroma compounds include nonanal, limonene, 2-decenal, p-anisaldehyde
54 (Giovanelli et al. 2017; Kurucu et al. 1993), (*E*)-caryophyllene (Bahar & Altug 2009; Brunke et
55 al. 1993; Gharaei et al. 2013) and the diterpene cembrene (Gharaei et al. 2013; Giovanelli et al.
56 2017). Volatile composition in plants is known to be affected by various factors such as
57 geographical origin, harvesting time, processing and agricultural practices (Morshedloo et al.
58 2015). Previous studies have revealed for differences in Sumac volatile composition as affected
59 by its origin i.e. Turkey, Italy and Iran. Nevertheless, no report has been made on assessing to
60 what extent roasting could affect its aroma profile.

61 The main objectives of this study were: 1) to assess volatile composition of sumac fruit from

62 different Middle-Eastern origins *viz*. Egypt, Jordan and Palestine using headspace SPME, 2) to

63 assess roasting impact on its aroma profile and 3) to determine sumac cold tea true aroma

64 profile.   Volatiles abundance data were extracted from chromatograms without prior peak

65 identification in an untargeted manner. Considering the complexity of acquired data,

66 unsupervised and supervised multivariate data analyses viz. principal component analysis (PCA)

67 and orthogonal partial least squares (OPLS), respectively, were employed for classification of

68 fruit samples, and to ensure good analytical rigorousness. To the best of our knowledge, this

69 study provides the first volatiles characterization in *R. coriaria* from the Middle East region and

70 to report roasting impact on the fruit aroma.

71 2. Materials and methods

72   *2.1.Plant material*

73 *Rhus coriaria* fruits were collected manually in the full ripe stage from wild trees grown in

74 Nablus, Palestine in October 2016, and were authenticated by Prof. Dr. Ibrahim Abou Reidah,

75 Department of Chemistry, An-Najah National University, Nablus, Palestine**.** Commercial

76 samples of *R. coriaria* fruits in the full ripe stage were purchased from El Hen herbal company,

77 Amman, Jordan and Haraz Drug store, Cairo, Egypt. Voucher specimens were kept at the

78 Department of Pharmacognosy, Faculty of Pharmacy, Cairo University, Egypt. Cold tea of the

79 Palestinian sample was prepared by percolating 10 g of fresh cut fruits (without seeds) in 100 mL

80 distilled water for 10 min, kept at 25 °C, then filtered on Whatman filter paper to remove plant

81 debris. Roasting of the Palestinian sample was carried out by heating fresh cut fruits (without

82 seeds) in an oven set at 120°C for 20 min. Three replicates were analyzed for each sample. The

83 fruits were stored at -20°C till further analysis.

84 *2.2 Chemicals and Materials*

85 SPME fibers of stableflex coated with divinylbenzene/carboxen/polydimethylsiloxane

86 (DVB/CAR/PDMS, 50/30 μm) (57328-U) or PDMS (polydimethylsiloxane) (57302) were

87 purchased by Supelco (Oakville, ON, Canada).   All other chemicals and standards were

88 purchased from Sigma Aldrich, USA.

89 *2.3 Volatiles analysis of fresh and roasted fruits*

90   The HS-SPME volatile analysis was carried out as stated previously (Farag et al. 2017). Fruits

91   (100 mg) were cut into halves, placed in SPME screw cap vials (1.5 ml) and spiked with (*Z*)-3-

92   hexneyl acetate dissolved in water at a final concentration of 2 µg per vial. The SPME fiber

93   was inserted manually into a vial containing seeds placed in an oven kept at 50°C for 30 min.

94   The fiber was subsequently withdrawn into the needle and then injected into the injection port

95   of the gas chromatography-mass spectrometer (GC-MS). GC-Ms analysis was performed on a

96   Schimadzu GC-17A gas chromatogram (Schimadzu, Tokyo, Japan) equipped with DB-5

97   column (30 m × 0.25 mm i.d. × 0.25 µm film thickness; Supelco) and coupled to Schimadzu

98   QP5050A mass spectrometer. The interface and the injector tempreatures were both set at

99   220°C. The following gradient temperature program was used for volatiles analysis. The oven

100   temperature was kept first at 40°C for 3 min, then increased to 180°C at a rate of 12°C min^{-1},

101   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

102   temperature for 5 min. The carrier gas helium was used at a total flow rate of 0.9 mL/min.

103   Splitless injection mode was used for analysis considering the lower levels of volatiles in

104   samples. SPME fiber was prepared for the next analysis by placing it in the injection port for

105   2 min at 220°C to ensure complete elution of volatiles. Blank runs were made during sample

106   analyses. The HP quadruple mass spectrometer was operated in EI mode at 70 eV. A scan

107   range was set at *m/z* 40–500.

108   *2.4. GC-MS data processing and multivariate analysis*

109   Volatile components were identified by comparing their retention indices (RI) relative to n-

110   alkanes (C6-C20), mass matching to NIST, WILEY library database and with standards

111   whenever available. Peaks were first deconvoluted using AMDIS software

112   (http://www.amdis.net) prior to mass spectral matching. Volatiles abundance data were prepared

113   for multivariate data analysis by extraction using MET-IDEA software (Broeckling et al. 2006)

114   for data extraction. Data were then subjected to principal component analysis (PCA), partial least

115   squares-discriminant analysis (OPLS-DA) using SIMCA-P version 13.0 software package

116   (Umetrics, Umea, Sweden). Markers were subsequently identified by analyzing the S-plot, which

117   was declared with covariance (p) and correlation (pcor). All variables were mean centered and

118   scaled to Pareto variance.

119   **3. Results**

120 *3.1* **Volatiles analysis of fresh *R. coriaria* fruit (Sumac) from three different geographical**

121 **origins**

122 GC-MS analysis (Table 1 & 2, Figure 1) of sumac fruits led to the identification of 74 volatile

123 constituents, categorized in 10 different classes *viz.* alcohols, aromatics, esters, ethers,

124 furan/aldehydes, hydrocarbons, ketones, monoterpene hydrocarbons, oxide and sesquiterpene

125 hydrocarbons. A typical chromatogram of fresh and roasted sumac fruit aroma profiles is

126 represented in Figure 1. Initial detection of volatiles started from zero minutes during

127 chromatographic run but considering that no volatile peaks were detected till 5 minutes and with

128 only one major peak for acetic acid (Fig. S1), MS detection started from 5 minutes for all

129 specimens. Considering our interest in volatile terpenoids and hydrocarbons, five minutes delay

130 is appropriate for this study. Acetic acid in sumac is likely to derive the tartar taste for its fruit.

131 Sesquiterpene hydrocarbons amounted for the most dominant class accounting for *ca.* 40-58% of

132 the fresh Sumac aroma with a total of 26 identified volatile constituents (Table 2). Next to

133 sesquiterpenes, monoterpene hydrocarbons represented the most abundant class (*ca.* 17-34%)

134 among specimens (Table 2). Other 8 volatile classes detected amounted for less than 17% of

135 sumac fruit total volatile blend (Table 2). Naphthalene and α-pinene were the major volatile

136 forms in Jordan and Palestine specimens at *ca.* 15.8 and 16.7%, respectively. Whereas,

137 monoterpene hydrocarbons *viz.*, o-cymene 7.7%, β-ocimene 7.5% and limonene 7.3% were the

138 chief components in fresh sumac fruit aroma derived from Egypt. Volatiles found at comparable

139 levels in all 3 examined specimens included (*E*)-β-famesene and (*Z, Z*)-α-farnesene

140 (sesquiterpene hydrocarbons) detected at ca. 6-8%. With regard to oxides, cineole amounted for

141 7.3% of Egyptian sumac aroma blend, at two fold levels that present in specimens from Jordan

142 (3.2%) and Palestine (2.2%) (Table 1).

143 In contrast, roasted fruit aroma was predominated by furan/aldehydes at *ca.* 58% followed by

144 sesquiterpene hydrocarbons at 27%. A dramatic change in fruits aroma profile was observed

145 upon roasting exemplified in high furan/aldehyde (58.1%) and ketone (6.1%) levels in roasted

146 fruit concurrent with a marked decrease in the other 8 volatile classes (Table 2). Roasted

147 specimens were particularly enriched in furfural (34.3%) and (*E*)-nonanal (12.2%) followed by

148 3-thujanone (5.1%) (Table 1, Fig. 2). Sumac fruits are also used worldwide to prepare cold tea

149 by simply soaking the fruit in cold water. Consequently, it was of interest to characterize the

150   sumac cold tea aroma profile; a weak aroma profile was detected compared to fruit exemplified

151   by much lower number of volatile components totaling 14 peaks (Fig. 2).

152   It should be noted that a relatively high standard deviation was observed for some minor

153   constituents (Table 1) viz., β-linalool, styrene, octanal, nonanal and β-ocimene especially from

154   Jordanian specimen. Whether such large variance is associated with the experimental setup and

155   detection method has yet to be determined, Employing other detectors viz. (Flame Ionization

156   Detector). FID detection or automated SPME in volatiles extraction step can help minimize such

157   variance.

158

159

160   *3.2* **Multivariate PCA and OPLS-DA analyses of fresh, roasted and cold tea of *R. coriaria***

161   **fruit volatiles data**

162   Multivariate PCA (Figures 3, 4 & S2) was carried out to explore the relative variability within

163   the different specimens and to identify geographical origin (viz. Egypt, Jordan and Palestine)

164   impact on fresh sumac fruit aroma in an untargeted manner.   Multivariate data analyses

165   additionally help in identifying potential markers for each fruit origin. Palestinian and Jordanian

166   sumac specimens were found more or less clustered together on the right side of PC1 (positive

167   score values). In contrast, Egyptian sumac was positioned on the left side of PC1 (Fig. 3A). A

168   total of 74 volatiles abundance data were subjected to PCA analysis with two major principle

169   components (PC1/PC2) accounting for 60% of the total variance. PCA loading plot (Fig. 3B)

170   revealed that α-pinene contributed the most positively along PC1 and PC2, being most abundant

171   in Palestinian Sumac in agreement with results presented in (Table 1). In contrast, *o*-cymene and

172   limonene located on the far negative side of PC1 were more enriched in Egyptian specimens.

173   Roasting was found to influence sumac aroma profile more than the growth habitat as revealed

174   from PCA analysis (Figure 4A). Roasted specimens were positioned to the right side of PC1

175   (positive side) being most distant in composition, whereas fresh fruits and cold beverage

176   specimens were all positioned together on the left side of PC1 (negative side). PCA model

177   (Figure 4A) was prescribed by PC1 and PC2 accounting for 45% and 24% of the variance,

178   respectively. Unique aroma compounds found in roasted specimens included furfural and

179   nonanal (Figure 4B). To help identify volatile markers unique for roasted specimens, OPLS-DA

180   (orthogonal projection to latent structures-discriminant analysis) was employed (Figure S2).

181 OPLS-DA score plot of roasted versus unroasted fruit showed a clear segregation between
182 roasted and fresh samples explaining 97% of the total variance (R2) and with a prediction
183 goodness parameter Q2=95%. The respective S-plot (a remarkable parameter that compares the
184 variable magnitude versus its reliability in OPLS) identified furfural and nonanal as markers of
185 roasting process (Figure S2-B) and in agreement with PCA analysis. OPLS-DA model of cold
186 sumac tea modelled against fresh fruit failed to provide a fit model as in roasted specimen case,
187 with lower R2 and Q2 values of 85% and 89% respectively (Figure S2-C). In general, the aroma
188 of sumac cold tea appeared to be more dominated by esters *viz*. bornyl acetate, nerol acetate and
189 s esquiterpenes *viz*. (□)-caryophyllene and □-humulene, as revealed from derived S plot (Figure
190 S2-D).

191 ## 4. Discussion

192 Sumac is commonly used as spice or appetizer, simply by blending its dried grounded fruits with
193 freshly cut onion, or being mixed with plant oil or added to poultry dishes (Kossah et al. 2009;
194 Shabbir 2012) in addition to being incorporated in several nutraceutical products (Wang & Zhu
195 2017). Also, sumac fruits oil and protein were used in hair care products (Gupta et al. 2010).

196 The main objective of this study was to explore the variation in volatile compositions among *R.*
197 *coriaria* from 3 different sites including Palestine, Jordan and Egypt and to assess the impact of
198 roasting on fuits' volatile constituents. With regards to the impact of growth habitat on sumac
199 volatiles profile, fruit specimens derived from Jordan and Palestine appeared to be similar in
200 volatiles composition and being distant from that of Egypt. Such result is expected considering
201 the close geographical location of Jordan and Palestine and similar climatic conditions.
202 Abundance of monoterpenes has been reported in sumac fruit grown in Italy (Giovanelli et al.
203 2017; Reidel et al. 2017), with α-pinene, β-ocimene and fenchone as the main components.
204 Whereas, prevalence of sesquiterpenes was reported in sumac fruit originated from Turkey and
205 Iran (Bahar & Altug 2009; Gharaei et al. 2013; Morshedloo et al. 2018) with β-caryophyllene as
206 the most abundant. It should be noted that nonadecane (Bahar & Altug 2009) and p-anisaldehyde
207 (Giovanelli et al. 2017), previously reported as major components of *R. coriaria* essential oil,
208 were not detected in the current study. Such discrepancy could be attributed to either the
209 different collection methods that is SPME adopted herein involving no heat treatment in contrary
210 to steam distillation or to regional differences owing to agricultural or ecological factors (Bahar
211 & Altug 2009; Giovanelli et al. 2017).

212   Upon roasting, a marked variation in volatiles profile was detected. This variation is exemplified
213   in higher furfural and nonanal levels in roasted samples. Likewise, previous reports (Bahar &
214   Altug 2009; Giovanelli et al. 2017; Morshedloo et al. 2018; Reidel et al. 2017) on fresh sumac
215   fruit analyzed using SPME from Turkey, Italy and Iran reported for furfural and nonanal
216   presence at trace levels, suggesting that these are key markers indicative of the roasting process.
217   Elevated levels of nonanal (23%) were only detected in hydro-distilled Sumac fruit in which
218   heating was applied comparable to that of roasting effect (Morshedloo et al. 2018). Our results
219   suggest that both furural and nonanal can be utilized as markers to distinguish between roasted
220   and fresh Sumac samples or to predict whether degradation has occurred in sumac fruits upon
221   storage at elevated temperature. Sumac fruits are enriched in both reducing sugar (xylose) and
222   amino acids (Demchik et al. 2015), regarded as the precursor compounds for Millard reaction
223   likely to occur in sumac fruits upon roasting (Tamanna & Mahmood 2015). Furfurals are major
224   products of Maillard reaction detected in roasted coffee and cocoa beans (Martins et al. 2000),
225   roselle (Farag et al. 2015) and during processing of soyabeans, pasta and meat (Tamanna &
226   Mahmood 2015). Maillard reaction involves the reaction of amino acid with a reducing sugar in
227   the presence of heat, typical of the roasting process (Nie et al. 2013; Yaylayan 2006). Although,
228   furans are of common occurrence in thermal processed foods, increasing awareness of furans
229   health hazard as a possible carcinogen is recognized (Nie et al. 2013; Reinhard et al. 2004).
230   According to the FDA guidelines, average permitted level of furan should not exceed 170 ng/g
231   (FDA 2004).

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

240   **Conclusion**

241   In the present study, we provide the first comprehensive volatile profile of Sumac fruits from 3

242   different Mid-Eastern countries. A total of 74 different volatile constituents were identified with

243   sesquiterpene hydrocarbons as main class followed by monoterpene hydrocarbons. Egyptian

244   Sumac was more enriched in *o*-cymene, β-ocimene and limonene. Whereas, Jordanian and

245   Palestinian specimens exhibited more close volatile profile being enriched in naphthalene and α-

246   pinene. A significant alteration in sumac aroma profile was observed upon roasting,

247   accompanied by a marked increase in furan/aldehydes viz. furfural, 5-methyl furfural, concurrent

248   with a decrease in sesquiterpene and monoterpene hydrocarbons. The prevalence of furans in

249   roasted sample suggest for a distinct change in fruit aroma upon heating and for moreover the

250   monitoring of its furan levels considering its health hazardless. Our volatiles profiling provided

251   the true aroma profile in Sumac fruit growing in the Middle-East, which can be further applied

252   for investigating other factors such as storage, ripening stage, and analyzing its various

253   commercial food products.

254   **REFERENCES**

255   Abu-Reidah IM, Ali-Shtayeh MS, Jamous RM, Arráez-Román D, and Segura-Carretero A. 2015.
256   HPLC–DAD–ESI-MS/MS screening of bioactive components from Rhus coriaria
257   L.(Sumac) fruits. *Food chemistry* 166:179-191.
258   Abu-Reidah IM, Jamous RM, and Ali-Shtayeh MS. 2014. Phytochemistry, pharmacological
259   properties and industrial applications of Rhus coriaria L.(Sumac). *Jordan Journal of*
260   *Biological Sciences* 7.
261   Bahar B, and Altug T. 2009. Flavour characterization of sumach (Rhus coriaria L.) by means of
262   GC/MS and sensory flavour profile analysis techniques. *International Journal of Food*
263   *Properties* 12:379-387.
264   Bozan B, Kosar M, Tunalier Z, Ozturk N, and Baser K. 2003. Antioxidant and free radical
265   scavenging activities of Rhus coriaria and Cinnamomum cassia extracts. *Acta*
266   *Alimentaria* 32:53-61.
267   Broeckling CD, Reddy IR, Duran AL, Zhao X, and Sumner LW. 2006. MET-IDEA: data
268   extraction tool for mass spectrometry-based metabolomics. *Analytical chemistry*
269   78:4334-4341.
270   Brunke EJ, Hammerschmidt FJ, Schmaus G, and Akgül A. 1993. The essential oil of Rhus
271   coriaria L. fruits. *Flavour and fragrance journal* 8:209-214.
272   Candan F. 2003. Effect of Rhus coriaria L.(Anacardiaceae) on superoxide radical scavenging and
273   xanthine oxidase activity. *Journal of enzyme inhibition and medicinal chemistry* 18:59-
274   62.
275   Demchik S, Rajangam A, Hall J, and Singsaas E. 2015. Fatty Acids, Carbohydrates and total
276   proteins of wild sumac (Rhus typhina L.) drupes from the upper Midwest of the United
277   States. *American Journal of Essential Oils and Natural Products* 3:30-34.
278   El Hasasna H, Athamneh K, Al Samri H, Karuvantevida N, Al Dhaheri Y, Hisaindee S,
279   Ramadan G, Al Tamimi N, AbuQamar S, and Eid A. 2015. Rhus coriaria induces

280   senescence and autophagic cell death in breast cancer cells through a mechanism
281   involving p38 and ERK1/2 activation. *Scientific reports* 5:13013.
282 Farag MA, Ali SE, Hodaya RH, El-Seedi HR, Sultani HN, Laub A, Eissa TF, Abou-Zaid FO,
283   and Wessjohann LA. 2017. Phytochemical profiles and antimicrobial activities of Allium
284   cepa red cv. and A. sativum subjected to different drying methods: a comparative MS-
285   based metabolomics. *Molecules* 22:761.
286 Farag MA, Rasheed DM, and Kamal IM. 2015. Volatiles and primary metabolites profiling in
287   two Hibiscus sabdariffa (roselle) cultivars via headspace SPME-GC-MS and
288   chemometrics. *Food Research International* 78:327-335.
289 FDA U. 2004. Exploratory data on furan in food.
290 Gharaei A, Khajeh M, Ghaffari M, and Choopani A. 2013. Iranian Rhus coriaria (sumac)
291   essential oils extraction. *Journal of Essential Oil Bearing Plants* 16:270-273.
292 Giovanelli S, Giusti G, Cioni PL, Minissale P, Ciccarelli D, and Pistelli L. 2017. Aroma profile
293   and essential oil composition of Rhus coriaria fruits from four Sicilian sites of collection.
294   *Industrial Crops and Products* 97:166-174.
295 Gupta A, Malviya R, Singh TP, and Sharma PK. 2010. Indian medicinal plants used in hair care
296   cosmetics: a short review. *Pharmacognosy Journal* 2:361-364.
297 Kossah R, Nsabimana C, Zhang H, and Chen W. 2010. Optimization of extraction of
298   polyphenols from Syrian sumac (Rhus coriaria L.) and Chinese sumac (Rhus typhina L.)
299   fruits. *Research Journal of Phytochemistry* 4:146-153.
300 Kossah R, Nsabimana C, Zhao J, Chen H, Tian F, Zhang H, and Chen W. 2009. Comparative
301   study on the chemical composition of Syrian sumac (Rhus coriaria L.) and Chinese
302   sumac (Rhus typhina L.) fruits. *Pakistan Journal of Nutrition* 8:1570-1574.
303 Kurucu S, Koyuncu M, Güvenç A, Baser K, and Özek T. 1993. The essential oils of Rhus
304   coriaria L.(Sumac). *Journal of Essential Oil Research* 5:481-486.
305 Mamedov N, Gardner Z, and Craker LE. 2005. Medicinal plants used in Russia and Central Asia
306   for the treatment of selected skin conditions. *Journal of herbs, spices & medicinal plants*
307   11:191-222.
308 Martins SI, Jongen WM, and Van Boekel MA. 2000. A review of Maillard reaction in food and
309   implications to kinetic modelling. *Trends in Food Science & Technology* 11:364-373.
310 Morshedloo MR, Craker LE, Salami A, Nazeri V, Sang H, and Maggi F. 2017. Effect of
311   prolonged water stress on essential oil content, compositions and gene expression
312   patterns of mono-and sesquiterpene synthesis in two oregano (Origanum vulgare L.)
313   subspecies. *Plant Physiology and Biochemistry* 111:119-128.
314 Morshedloo MR, Ebadi A, Maggi F, Fattahi R, Yazdani D, and Jafari M. 2015. Chemical
315   characterization of the essential oil compositions from Iranian populations of Hypericum
316   perforatum L. *Industrial Crops and Products* 76:565-573.
317 Morshedloo MR, Maggi F, Neko HT, and Aghdam MS. 2018. Sumac (Rhus coriaria L.) fruit:
318   Essential oil variability in Iranian populations. *Industrial Crops and Products* 111:1-7.
319 Mozaffarian V. 2013. *Identification of medicinal and aromatic plants of Iran*.
320 Nie S, Huang J, Hu J, Zhang Y, Wang S, Li C, Marcone M, and Xie M. 2013. Effect of pH,
321   temperature and heating time on the formation of furan in sugar–glycine model systems.
322   *Food Science and Human Wellness* 2:87-92.
323 Peter KV. 2012. *Handbook of herbs and spices*: Elsevier.
324 Pojero ML. 1891. *Flora sicula: descrizione delle plante vascolari spontanee o indigenate in*
325   *Sicilia*.

326 Pourahmad J, Eskandari MR, Shakibaei R, and Kamalinejad M. 2010. A search for
327   hepatoprotective activity of aqueous extract of Rhus coriaria L. against oxidative stress
328   cytotoxicity. *Food and Chemical Toxicology* 48:854-858.
329 Ravindran P, Pillai G, and Divakaran M. 2012. Other herbs and spices: mango ginger to wasabi.
330   *Handbook of Herbs and Spices (Second Edition), Volume 2*: Elsevier, 557-582.
331 Rayne S, and Mazza G. 2007. Biological activities of extracts from sumac (Rhus spp.): a review.
332   *Plant foods for human nutrition* 62:165-175.
333 Reidel B, Vanessa R, Cioni PL, Majo L, and Pistelli L. 2017. Evolution of volatile emission in
334   Rhus coriaria organs during different stages of growth and evaluation of the essential oil
335   composition. *Chemistry & biodiversity*.
336 Reinhard H, Sager F, Zimmermann H, and Zoller O. 2004. Furan in foods on the Swiss market-
337   method and results. *Mitteilungen aus Lebensmitteluntersuchung und Hygiene* 95:532-
338   535.
339 Shabbir A. 2012. Rhus coriaria linn, a plant of medicinal, nutritional and industrial importance: a
340   review. *J Anim Plant Sci* 22:505-512.
341 Tamanna N, and Mahmood N. 2015. Food processing and maillard reaction products: effect on
342   human health and nutrition. *International journal of food science* 2015.
343 Wang S, and Zhu F. 2017. Chemical composition and biological activity of staghorn sumac
344   (Rhus typhina). *Food chemistry* 237:431-443.
345 Yaylayan V. 2006. Precursors, formation and determination of furan in food. *Journal für
346   Verbraucherschutz und Lebensmittelsicherheit* 1:5-9.
347
348
349
350
351
352
353
354

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

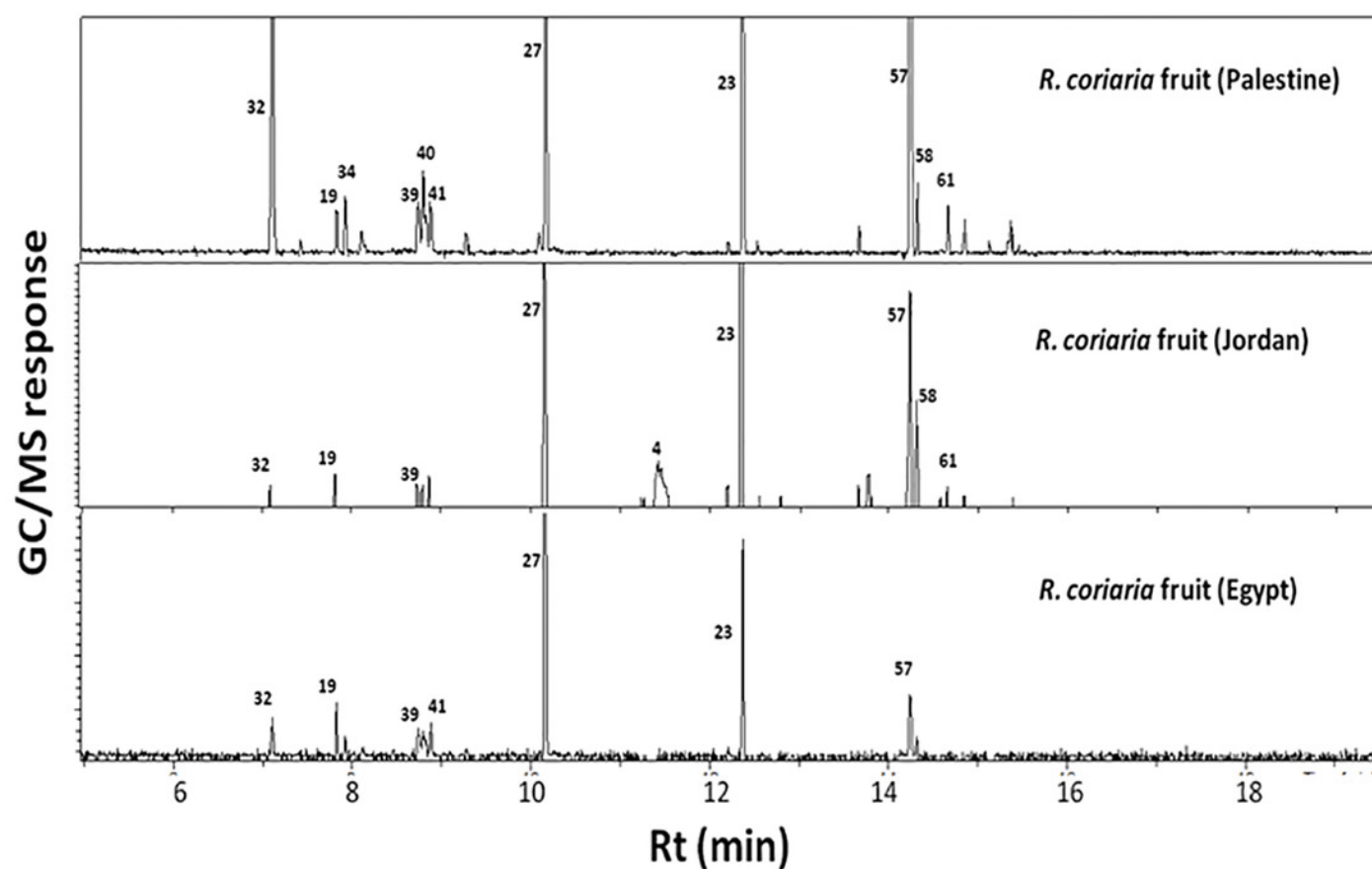



Figure 2

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.

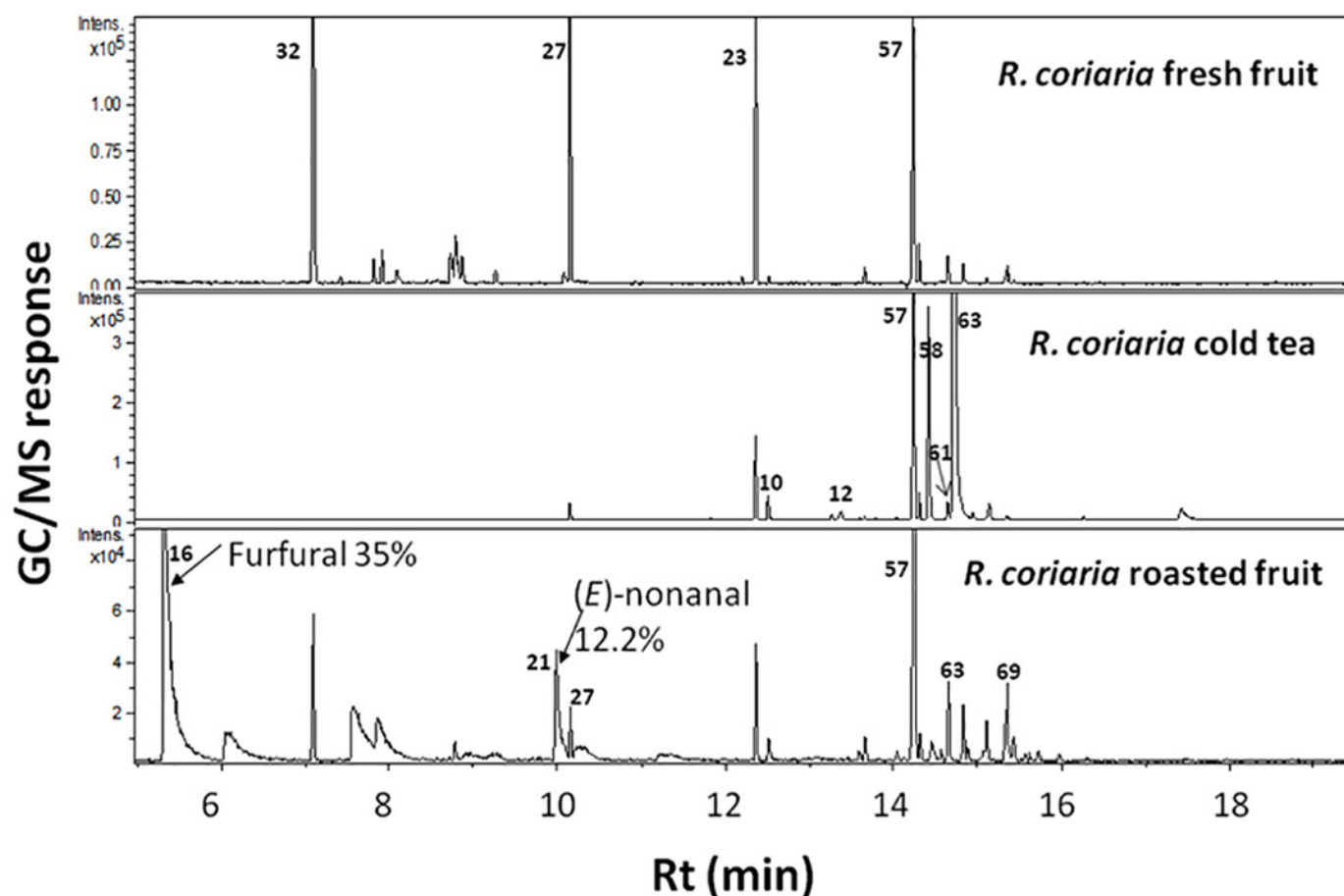



Figure 3

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.

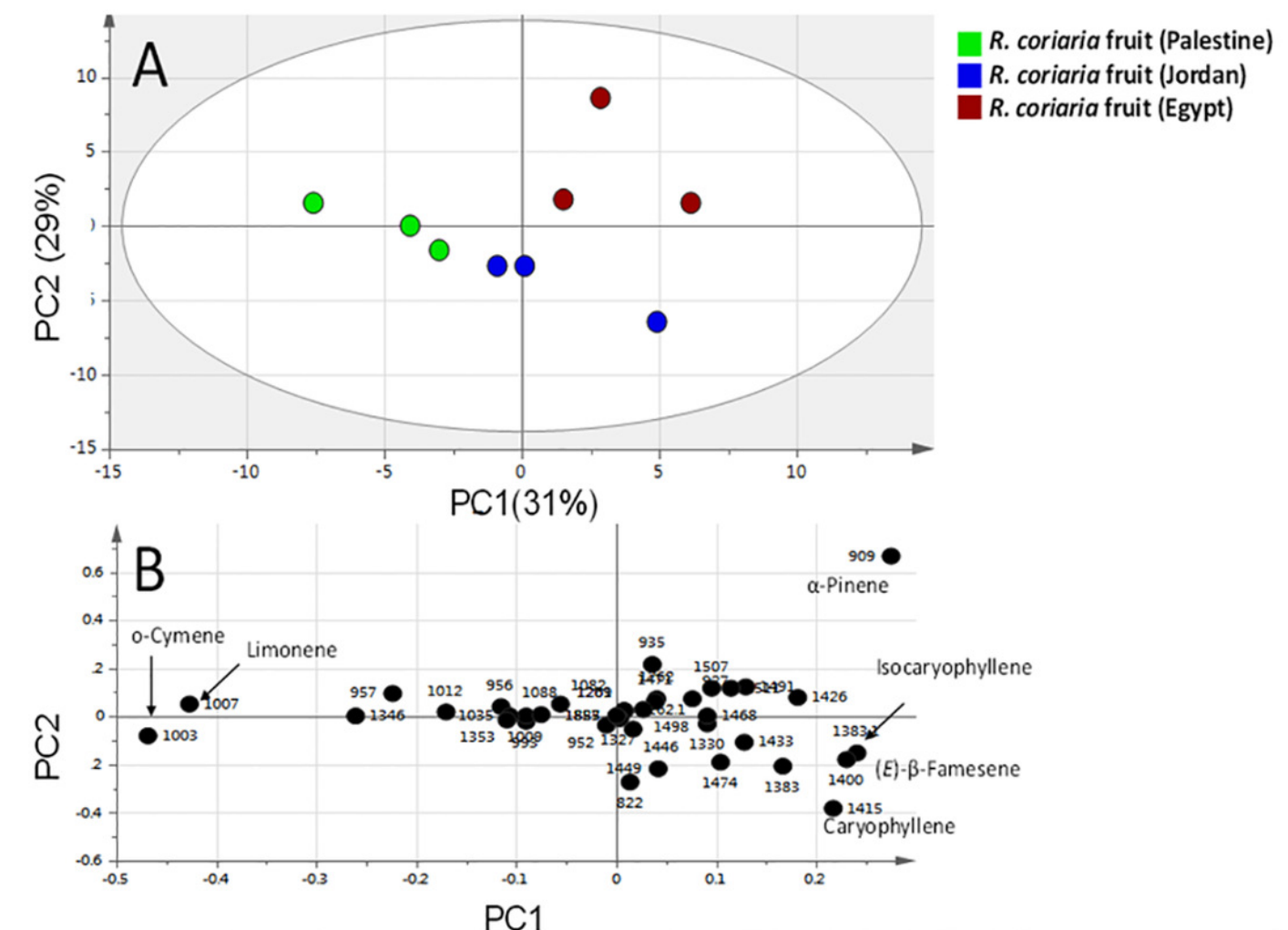
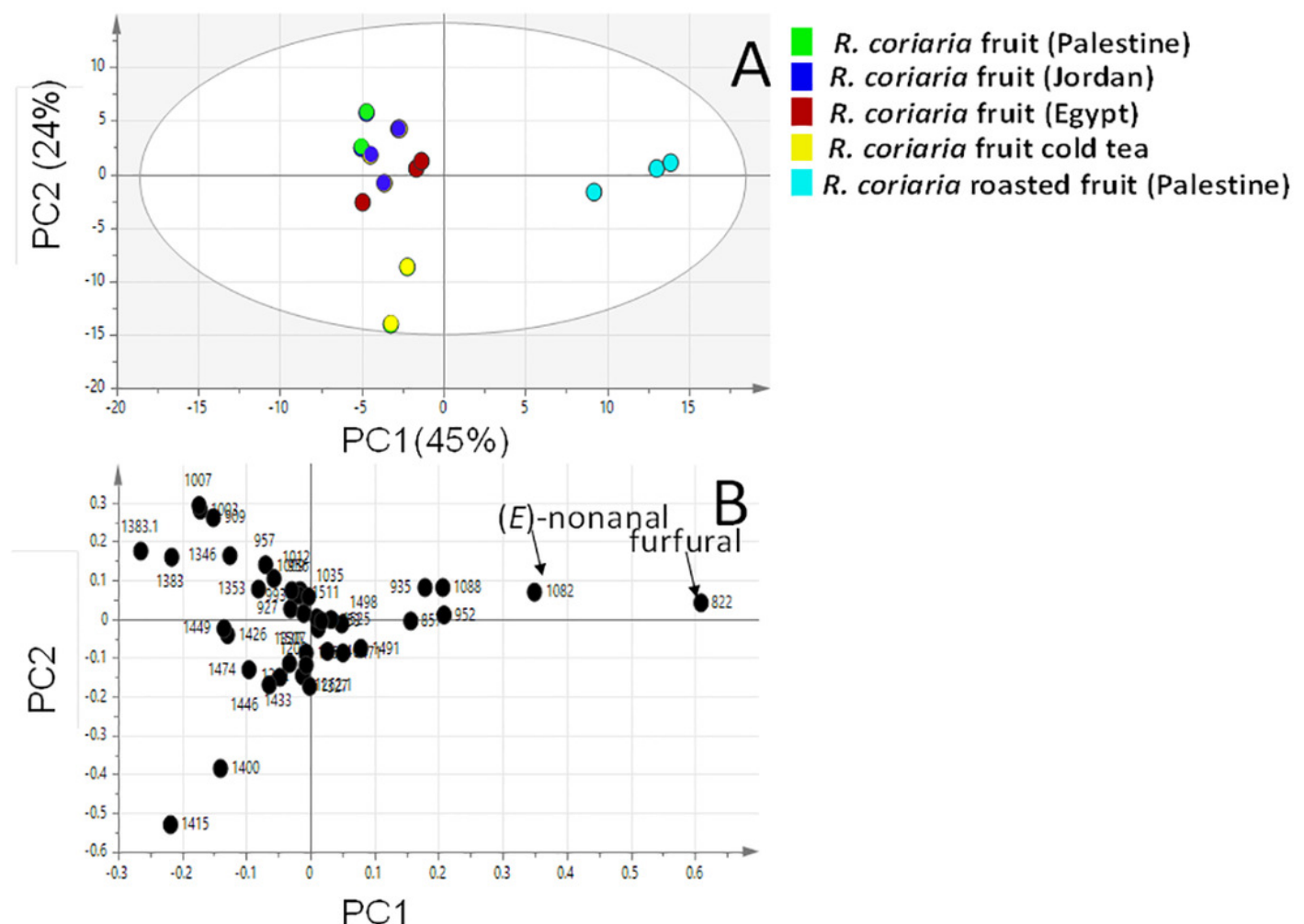



Figure 4

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.

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).

1 **Table 1:** Relative percentage of volatile compounds detected in fresh *R. coriaria* fruit (Sumac) from 3
2 Middle East sites and in response to roasting using SPME-GC–MS measurements (n = 3). The %
3 identified for each class is bolded, while the main component from each site is underlined and bolded.

Volatile constituents	RT	KI	Fresh Sumac						Roasted Sumac	
			Egypt		Jordan		Palestine		Palestine	
			Average (S.D.)							
Alcohols										
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	11.116	1158	0.00	(0.00)	0.06	(0.05)	0.01	(0.02)	0.20	(0.08)
3	4-Terpineol	11.183	1163	0.23	(0.31)	0.52	(0.49)	0.00	(0.00)	0.03	(0.05)
4	α-Terpineol	11.408	1179	0.54	(0.48)	0.03	(0.06)	0.02	(0.03)	0.00	(0.00)
Total alcohols			**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	Dodecane	11.242	1171	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	7.45	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-Terpinene	9.289	1035	0.33	(0.15)	0.17	(0.16)	0.06	(0.11)	0.19	(0.04)
45	Unknown monterpene	9.7171	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-Cubebene	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)

55	(Z,Z)-α-Farnesene	14.119	1389	6.02	(1.98)	7.62	(1.97)	8.60	(1.41)	6.84	(6.42)
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-Famesene 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)	1.75	(0.15)	2.81	(0.97)	0.38	(0.42)
61	α-Humulene	14.662	1433	0.93	(0.50)	1.48	(0.40)	1.49	(0.22)	1.29	(0.90)
62	(Z)-Muurola-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-Muurolene	15.083	1468	0.00	(0.00)	0.27	(0.24)	0.51	(0.79)	0.60	(0.17)
65	α-Muurolene	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**

4 Relative percentage of volatile compounds detected in fresh *R. coriaria* fruit (Sumac) from 3 Middle East
5 sites and in response to roasting using SPME-GC–MS measurements (n = 3). The % identified for each
6 class is bolded, while the main component from each site is underlined and bolded.

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

1   **Table 2:** Relative percentile (%) of the 10 classes of volatile compounds detected in fresh and roasted *R.*
2   *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	Palestine
		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 monoterpene 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**