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Phytochemical Characterization of *Rhus coriaria* L. Extracts by Headspace Solid-Phase Micro Extraction Gas Chromatography, Comprehensive Two-Dimensional Liquid Chromatography, and Antioxidant Activity Evaluation

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Abstract: *Rhus coriaria* L. (Anacardiaceae), commonly known as sumac, has been used since ancient times for many different applications, and nowadays is used mostly as a spice obtained from its in the Mediterranean and the Middle ground fruits and employed for flavoring and garnishing food, predominantly Eastern regions. Traditionally, sumac has been also used in popular medicine for the treatment of many ailments including hemorrhoids, wound healing, diarrhea, ulcers, and eye inflammation. Sumac drupes are indeed rich in various classes of phytochemicals including organic acids, flavonoids, tannins, and others, which are responsible of their powerful antioxidant capacity, from which treatment of many common diseases such as cardiovascular disease, diabetes, and cancer could benefit. In this work we evaluated the influence of fruit ripeness, conservation, and processing. To this aim, a phytochemical characterization of six different samples of *Rhus coriaria* L. was carried out. Specifically, headspace solid-phase micro extraction gas chromatography coupled to mass spectrometry and comprehensive two-dimensional liquid chromatography coupled to photodiode array and mass spectrometry detection, were employed. A total of 263 volatile compounds, including terpene hydrocarbons, acids, and aldehydes, as well as 83 polyphenolic compounds, mainly gallic acid derivatives, were positively identified. All samples showed a significant antioxidant activity by means of oxygen radical absorbance capacity, in line with their polyphenolic content and composition. Such findings set a solid ground to support the utilization of this plant as an attractive target for novel nutraceutical approaches and for drug discovery.

Keywords: *Rhus coriaria* L.; sumac; volatiles; polyphenols; LC×LC; GC; mass spectrometry; antioxidant activity

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1. Introduction

Rhus coriaria L. (*R. coriaria*), commonly known as sumac, belongs to the Anacardiaceae family. According to "The Plant List" it is one of the 131 currently accepted species names of the very large and still under evaluation *Rhus* genus (The Plant List (2013). Version 1.1. published on the Internet http://www.theplantlist.org/) accessed on 7 January 2022 [1], to which are usually attributed more than 200 species by most authors [2–4].

Native to the Mediterranean and the Middle East regions, where it is a fairly common species, sumac has a wide distribution range in temperate and subtropical regions, extending from the Canary Islands, Azores, and Madeira in the west to Tadzhikistan and Afghanistan in the east [5]. Since ancient times, distinct parts of the plant have found several applications with significant technological value; tannins extracted from young stems, as well as from leaves, were utilized for tanning hides during leather preparation and in the past centuries the most extensive plantations have been indeed established for this purpose. Sumac has also counted as a source of natural dyes for the textile industry, yellow dye coming from young stems, brown from roots, black from leaves, and red from fruits. Especially bark and fruit preparations have been extensively used in popular medicine to obtain natural remedies against different affections such as eye and urinary tract infections, ulcer, diarrhea, and hepatic disorders [4,6,7]. Recently, *R. coriaria* has also gained some interest for its ornamental features that could be of value in urban landscaping and gardening [8]. Nonetheless, the most famous employment of sumac is to flavor and garnish food. In fact, dry drupes ground to powder are a typical spice that goes by the same plant common name: sumac. It is very popular in several Mediterranean and Middle East countries where it is used as a seasoning, flavoring, and acidulant ingredient in numerous traditional recipes and many significant biological activities have been ascribed to fruit-derived extracts, the most prominent being antioxidant, antimicrobial, and anticancer [7].

In terms of chemical characterization, as reported in the previous investigations, gas chromatography (GC) is the technique of choice for a reliable determination of volatile fingerprints and numerous are the sample preparation procedures that can be applied among these, headspace solid-phase microextraction (HS-SPME) coupled with GC has been widely accepted to the analysis of volatile components in various food matrices, due to its simplicity, selectivity, and sensitivity [9,10]. On the other hand, the polyphenolic content of natural products is usually assessed by liquid chromatography (LC) methods coupled to either a photodiode array (PDA) and/or mass spectrometry (MS) detection [11,12].

Sumac extracts have been characterized in terms of phytochemical composition: one of the earliest works was carried out in 1896 highlighting the presence of gallic acid and myricetin as a component of the leaf extract [13]. Afterwards, many other components were identified in different parts of the plant [7]; recently, more than 211 phytoconstituents including (iso)-flavonoids, tannins, terpenoids, anthocyanins, and others have been determined [14]. In this respect, complex mixtures of natural products are indeed very attractive for the potential of the synergistic beneficial effects of the components within the mixture, but they also pose a challenge concerning the variability of their composition in the starting plant material, due to factors such as geographical origin, environmental conditions, stages of fruit, and plant development and harvest. Therefore, the adoption of improved analytical tools is a mainstay for a precise characterization in which a solid proof of efficacy, together with the definition of a general mechanism of action, must stand.

In this work, the volatile profile and the polyphenolic content of six samples of sumac was carried out: samples one to four were obtained from fruits harvested in Sicily in different seasons and subjected to specific treatments, samples five and six were commercially available processed spices. Specifically, the volatile and non-volatile fraction of the fresh and dried Sicilian drupes and the commercial samples were compared in order to study, in detail, the influence of fruit ripeness, conservation, and processing on the phytochemical composition. As far as the analytical techniques are concerned, headspace solid-phase micro extraction (HS-SPME) gas chromatography (GC), and comprehensive two-dimensional liquid chromatography (LC×LC) were employed. Further, nutraceutical

relevance of the characterized samples was assessed by oxygen radical absorbance capacity (ORAC); antioxidant activity is in fact one of the most prominent biological properties associated with sumac fruit and, in particular, with its primary derived food product, the sumac spice [7].

2. Results and Discussion

2.1. Volatile Fraction Analysis

Despite that, in the literature, there are several studies on *R. coriaria* fruits concerning their non-volatile metabolites, the volatile composition has been less investigated. Recently, Farag et al. reported the flavor profile results on sumac from Palestine, Jordan, and Egypt and its food products, analyzed via solid-phase microextraction (SPME) [15]. Brunke et al. identified over 120 constituents in the essential oil of *R. coriaria* fruits, among which terpene hydrocarbons, oxygenated terpenes, and aliphatic aldehydes were the most abundant [16]. The investigations of Giovannelli et al. on the aroma profile and essential oil composition of *R. coriaria* fruits from four Sicilian sites of collection allowed the identification of 106 compounds by SPME analysis and 169 in the essential oils by GC/MS, and the main constituents were revealed as being *p*-anisaldehyde, (*Z*)-2-heptenal, (*E*)-2-decenal, β-caryophllene, and cembrene [3].

The analysis carried out on the six samples led to the identification of 263 volatile compounds (Table S1), and to the best of our knowledge, this is the first time that the sumac flavor profile has been characterized so thoroughly. In particular, Sample 4 (99.47 ± 10.66) was the most abundant in terms of volatile compounds, whereas Sample 3 (86.71 ± 9.29) was the least abundant one. In terms of chemical classes, Sample 1 was the richest one in terpenes hydrocarbons, whereas it turned out to be the poorest in furans (Figure 1).

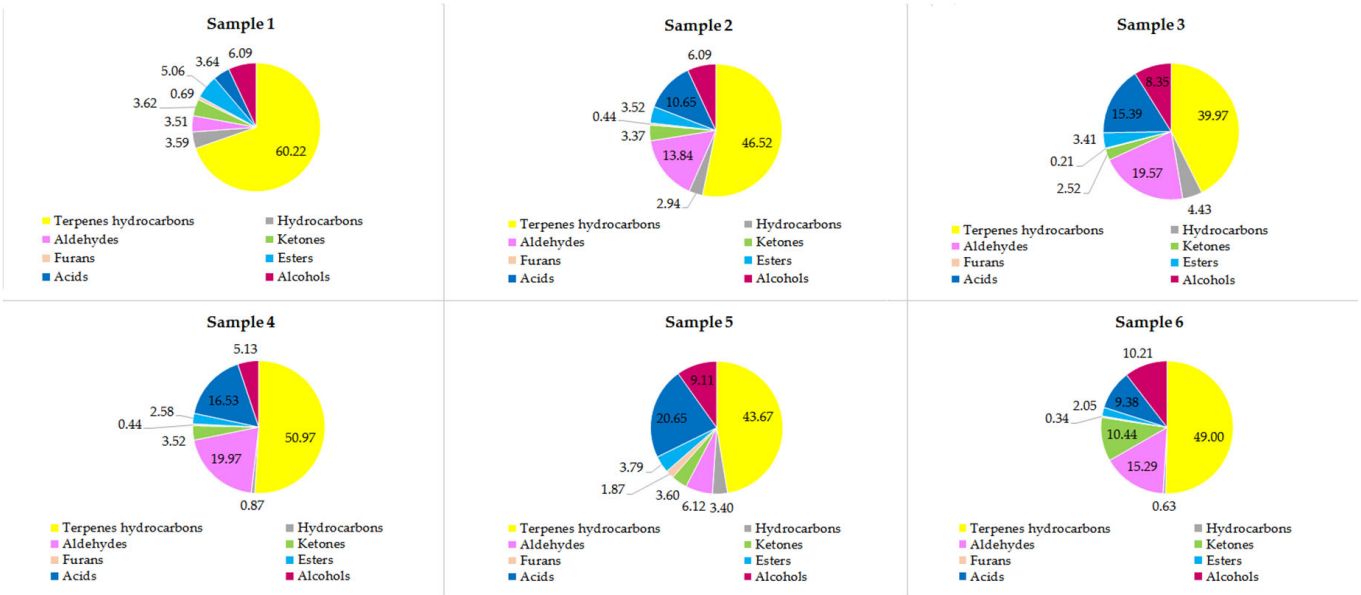

Figure 1. Percentage abundance of the compounds classes present in the analyzed samples. For samples description refer to Section 3.1.

Specifically in the fresh fruits, among the terpenes hydrocarbons, the most abundant compounds identified were α-pinene, (*E*)-caryophyllene, limonene, γ-muurolene, α-copaene, myrcene, *p*-cymene, β-pinene, δ-cadinene, methyl acetate, α-humulene, γ-terpinene, and α-phellandrene, followed by acids (ethanoic, formic, isovaleric) and aldehydes (*n*-nonanal, *n*-hexanal, *n*-octanal, (*E*)-2-heptenal). The sample harvested in the optimal ripening period featured a great relative area percentage for (*E*)-ß-Ocimene, (*Z*)-ß-Ocimene, *neo*-allo-ocimene, and (*Z*)-3-hexenyl-2-methylbutanoate. Instead, a very little amount of the same compounds has been encountered in the sample harvested in October. As shown in

Figure 2, the fruits dried in the stove (Sample 4) exhibited a remarkable quantity of ethanoic acid, (*E*)-2-heptenal, myrcene, *n*-nonanal, α-copaene, (*E*)-caryophyllene, α-humulene and cembrene with respect to those not subjected to the drying process (Sample 3).

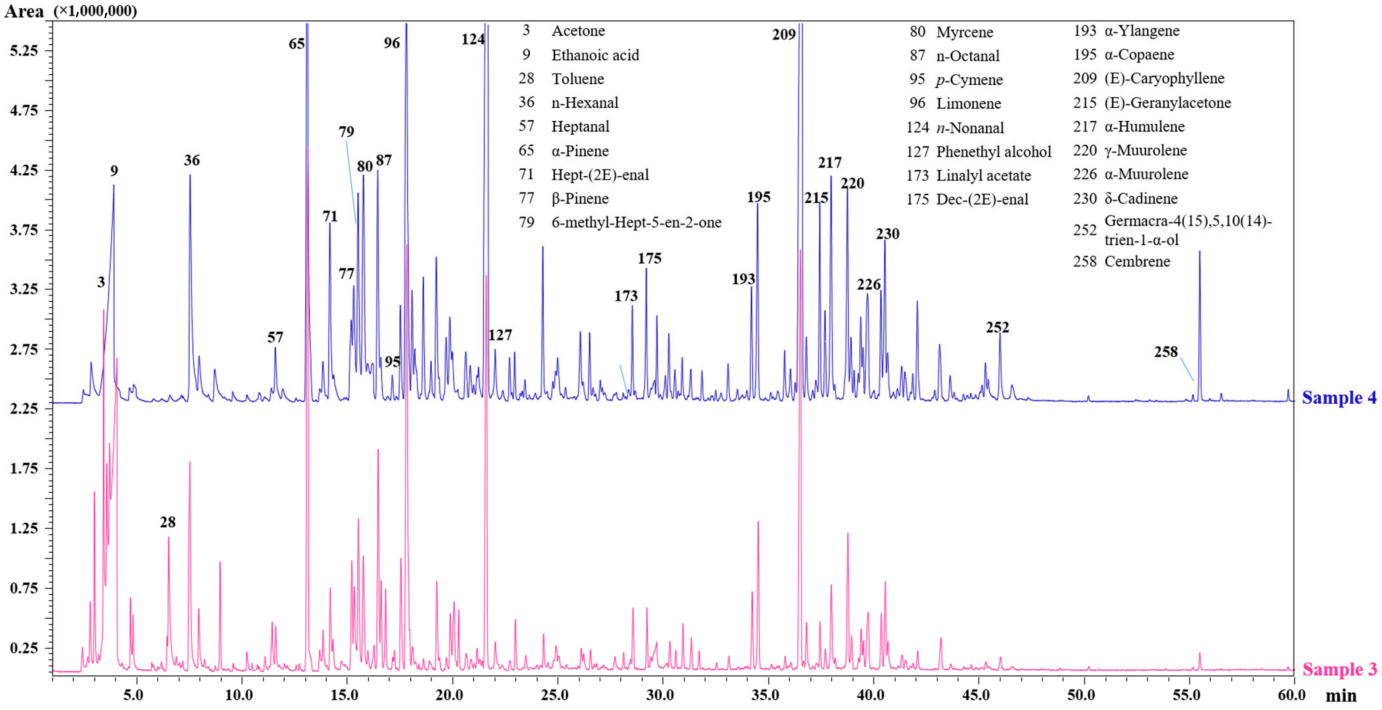

Figure 2. GC-MS analysis of the volatile profile for Sample 3 (fresh, collected in October) and Sample 4 (fresh and air-dried, collected in October).

2.2. Polyphenols Analysis

The polyphenolic fraction of *R. coriaria* fruits has been so far carried out by HPLC coupled with a photodiode array (PDA) and/or MS detection [17,18]. A comprehensive work on the phytochemical components of sumac fruit epicarp from Palestine by using HPLC-PDA-ESI-MS was reported by Abu-Reidah et al. [14], where a tentative identification of 211 phenolic and other phyto-constituents, most of which never reported before in *R. coriaria* fruits, were described. However, in none of these works was a quantification of the individual polyphenolic content reported due to the presence of overlapping peaks and matrix interferences. In this work the analysis of the polyphenolic compounds in *R. coriaria* samples was carried out by HILIC×RP-LC-PDA-ESI/MS. So far, most of the applications on polyphenols in food and natural products have been carried out on RP-LC×RP-LC [19–27], despite applications of HILIC×RP-LC also being reported [28–30]. Prior to either RP-LC×RP-LC or HILIC×RP-LC analysis, an optimization of the single separations must be carried out [31–35]. Normally a low mobile phase flow rate is used in the ^{1}D separation to decrease the fraction volume onto the ^{2}D and increase the ^{1}D sampling rate; as a consequence, a microcolumn is used in the ^{1}D. Since most commercial LC pumps are not capable of delivering a stable and repeatable flow rate, a higher flow rate is commonly employed and split up before entering the ^{1}D column. In this work, an easy-to-use micropump with a completely new direct-drive engineering was employed and was capable of delivering stable micro- to semi-micro flow rates [25]. Notably when HILIC is hyphenated to RP, such coupling is not straightforward due to solvent incompatibility. To overcome such an issue, a modulation procedure called "active modulation" was reported [36,37]. Such an approach is based on the introduction of a make-up flow of a weaker solvent (water) after the ^{1}D separation and before the entrance to the valves. In such a way, a reduction in the solvent strength is achieved, increasing the retention of the trap columns towards the compounds separated in the ^{1}D. Afterwards, when the valve is

actuated, the retained analytes are eluted in narrow bands thanks to the ^{2}D mobile phase. Figure 3 reports the HILIC×RP-LC-PDA-ESI/MS plots of the polyphenolic fraction of *R. coriaria* for Samples 3 and 4. For MS detection, a triple quadruple MS analyzer was used, equipped with an electrospray interface working on both positive and negative ionization mode. The list of the compounds identified is reported in Table S2.

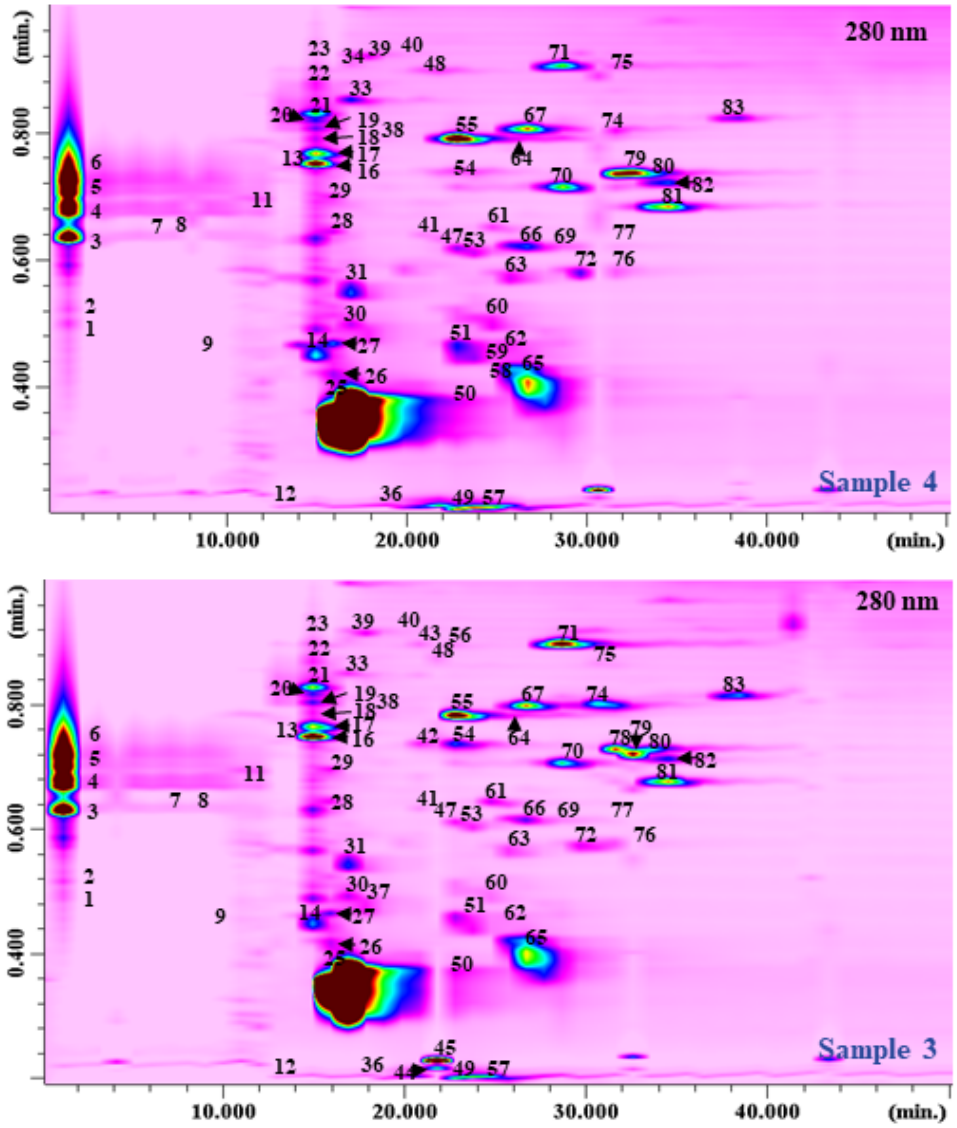

Figure 3. HILIC×RP-LC-PDA contour plots (280 nm) of the polyphenolic profile for Sample 3 (fresh, collected in October) and Sample 4 (fresh and air-dried, collected in October).

A total of 83 polyphenolic compounds were positively identified in the investigated samples by combining the information coming from PDA absorption (λ_{max}), mass-to-charge ratio (m/z), and literature data [17,18]. Among them, the majority were represented by gallic acid and derivates (37), as well as quercetin derivates (11). The rest were represented by cyanidin, luteolin, myricetin, and apigenin derivates. Concerning the performance of the developed HILIC×RP-LC system, Table 1 reports the values attained for both peak capacity and orthogonality [38].

Table 1. Peak capacity and orthogonality calculated for the HILIC×RP-LC focusing modulation set-up of the investigate samples.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
^{1}D peak capacity, $^{1}n_c$	67	73	68	61	55	59
^{2}D peak capacity, $^{2}n_c$	43	39	44	55	48	46
Theoretical peak capacity, $^{2D}n_c$	2875	2829	2971	3381	2673	2691
Effective peak capacity, $^{2D}n^{I}_{c}$	1085	986	1114	1382	1181	1130
Orthogonality, A_O	0.79	0.82	0.90	0.84	0.79	0.72
Corrected peak capacity, $^{2D}n_{corr}$	858	814	1004	1161	934	817

The highest theoretical peak capacity values, resulting from the product of the peak capacity, n_c of the two single dimensions [39], were attained for Sample 4 (3381), whereas the lowest one was attained for Sample 5 (2673). The orthogonality, $A_{O,}$ values ranged from 0.72 to 0.90% for Sample 6 and Sample 3, respectively. With regards to corrected peak capacity $^{2D}n_{corr}$ values, incorporating under-sampling [40] and A_O values [38], the highest values were obtained for Samples 4 (1161) and 3 (1004), respectively. When comparing these values with previously reported ones, these were undoubtedly higher than RP-LC×RP-LC set-ups (695 in Wong et al. [22], 461–633 in Arena et al. [23], 404–639 in Arena et al. [26]), despite slightly lower than similar HILIC×RP-LC set-up with active flow modulation (1605–1830 in Toro-Uribe et al. [29]).

In terms of quantification, a semi-quantification approach was applied, taking into account the chemical classes of the identified compounds (Figure 4). Samples 1, 3, and 4 were the richest ones in terms of bioactive content, accounting for roughly 2608.28, 2367.25 and 2489.56 mg/100 g FW respectively; on the other hand, the poorest ones were represented by Sample 5 and 6, which were relative to commercial ones (253.28 and 338.86 mg/100 g FW, respectively). Notably, gallic acid derivatives were the most abundant ones in all samples investigated, ranging from 219.92 to 2317.46 mg/100 g FW.

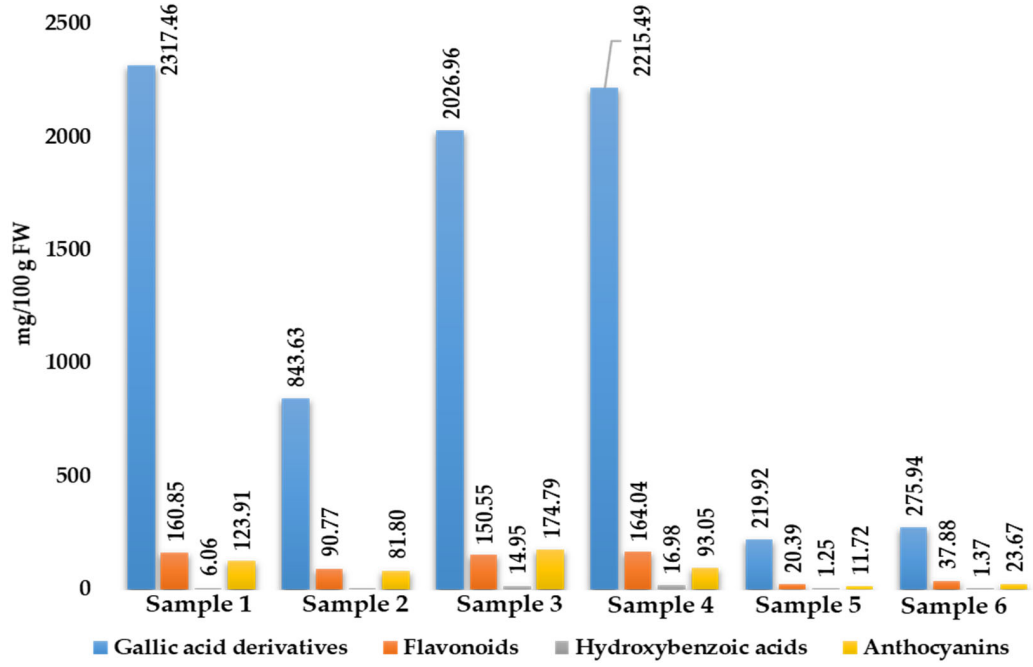

Figure 4. Quantitative content of the six *R. coriaria* samples investigated. For samples description refer to Section 3.1.

2.3. Antioxidant Activity

Several studies reported a wide range of biological properties associated with *R. coriaria* fruit extracts such as antimicrobic, antiproliferative, antidiabetic, and, most prominently, antioxidant activity [7]. In this light, all samples were investigated by ORAC assay, one of the most common methods used to estimate the antioxidant capacity in food. Results, expressed as Trolox equivalents (µmol TE/100 g of extract), are presented in Figure 5a. Among extracts, Sample 3 (226,661.42 ± 22,867.89 µmol TE/100 g) and Sample 4 (225,836.14 ± 23,427.64 µmol TE/100 g) showed the highest antioxidant capacity, followed by Sample 1, Sample 2, Sample 5, and Sample 6 (respectively 208,709.88 ± 22,104.72, 181,393.61 ± 28,287.22, 44,978.42 ± 4717.30, and 34,321.05 ± 4456.08 µmol TE/100 g).

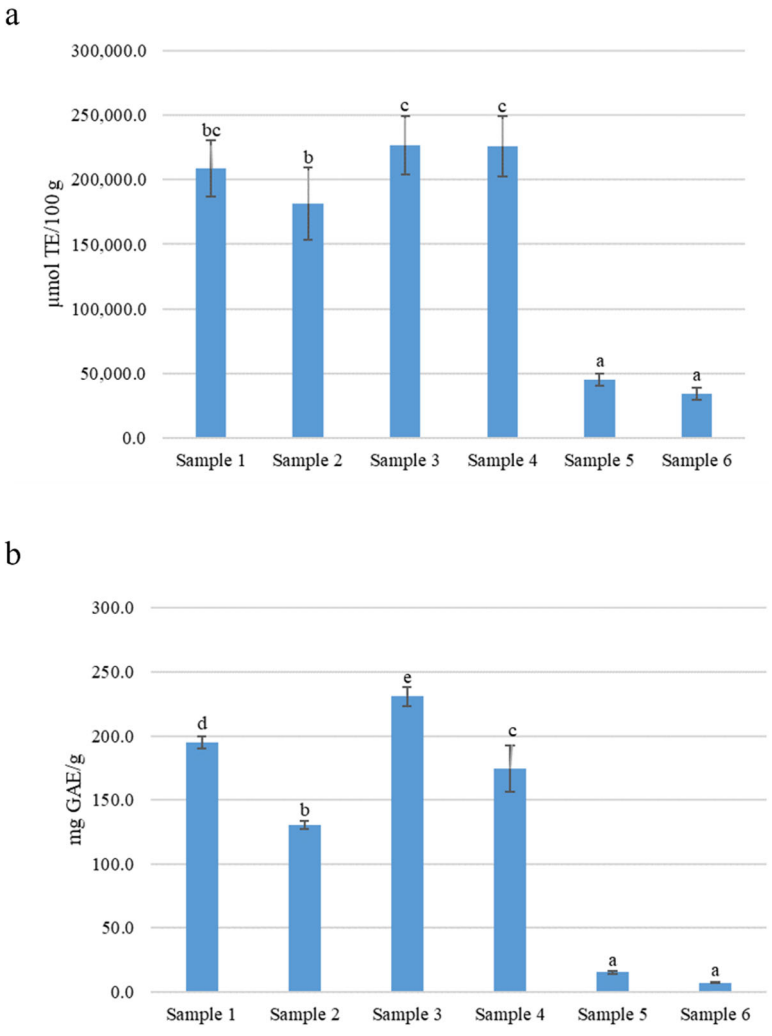

Figure 5. Antioxidant activity (**a**) and total phenolic content (**b**) of *R. coriaria* extracts. Antioxidant activity and total phenolic content were assessed by ORAC and Folin-Ciocalteau methods respectively; results are the average of three independent experiments and are expressed as µmol TE/100 g of extract (**a**) and as milligrams of gallic acid equivalents per gram of extract (mg GAE/g, (**b**). Letters labels indicate significant statistical differences among samples ($p < 0.05$) according to analysis of variance (ANOVA) and the Tukey's (HSD) multiple range test. For samples description refer to Section 3.1.

Furthermore, the total phenolic content (TPC) of *R. coriaria* extracts was determined by the Folin-Ciocalteau method. Results, expressed as milligrams of gallic acid equivalents (GAE) per gram of extract (mg GAE/g), are shown in Figure 5b. TPC of *R. coriaria* extracts well correlate with the antioxidant capacity. In general, the oven dried samples collected in

Sicily, Sample 4, Sample 2, (respectively 174.24 ± 18.10, 130.28 ± 2.65 mg GAE/g), had a lower TCP when compared to their undried counterparts: Sample 3 (230.85 ± 7.37 mg GAE/g) and Sample 1 (194.72 ± 4.79 mg GAE/g). The lowest TCP was reported for the commercial samples, Sample 5 and Sample 6 (15.38 ± 1.40 and 7.25 ± 0.57 mg GAE/g, respectively).

3. Materials and Methods

3.1. Samples

A total of six sumac samples were analyzed. Samples 1 to 4 were collected in the territory of Licodia Eubea Municipality (37°09′ N, 14°42′ E), Sicily region (Italy), at an altitude of about 600 m above sea level from wild plants growing on soils belonging to the association 'Regosols on sandy and conglomeratic rocks [41], the climate of this area, according to the Koppen and Geiger classification [42], is defined as 'Csa, Hot-summer Mediterranean Climate' with an average annual rainfall of 575 mm and an average annual temperature of 16.1 °C. Sample 1 consists of drupes harvested fresh in July, the most appropriate period as far as the ripening stage is concerned; Sample 2 were harvested at the same time but subsequently dried in a vacuum stove at the temperature of 40 °C. Sample 3 and 4 were collected in October (overripe stage), with the difference that also in this case Sample 4 was subjected to the same drying process previously reported.

Sample 5 and 6 were purchased as fruit dry powders on the internet (sumac spice), Sample 5 coming from the Mediterranean area without NaCl addition, and Sample 6 from Iran and with the addition of NaCl as a preservative.

3.2. Standard and Reagents

A C7-C40 Saturated Alkanes (1000 g/mL) standard mixture in hexane (49452-U) supplied by Merck Life Science (Merck KGaA, Darmstadt, Germany) was utilized for ALKANEs linear retention indices (LRIs) calculation.

Trolox (6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid), gallic acid, AAPH (2,20-azobis(2-amidinopropane) dihydrochloride), fluorescein sodium salt, Folin-Ciocalteu reagent, sodium phosphate monobasic (NaH_2PO_4) and potassium phosphate dibasic (K_2HPO_4) were purchased from Merck Life Science (Merck KGaA, Darmstadt, Germany).

LC-MS-grade water, methanol, acetonitrile, and acetic acid were obtained from Merck Life Science (Merck KGaA, Darmstadt, Germany). Gallic acid, protocatechuic acid, isoquercetin, myricetin, and cyanidin were purchased from Merck Life Science (Merck KGaA, Darmstadt, Germany). Stock solutions of 1000 mg L^{-1} were prepared for each standard by dissolving 10 mg in 10 mL of methanol.

3.3. Sample Preparation

For the extraction method optimization, different sample weights, different solvents type and volumes, both pure and in mixture were tested for the polyphenol extraction. The highest yield was obtained, weighing 20 g of grinded sample (fresh or dried) in 100 mL of water as solvent and using an extraction temperature of 40 °C for 1 h.

In order to produce dry extract for HPLC analysis and examination antioxidant properties, liquid extracts were lyophilized. The aqueous samples were frozen at −80 °C for 1 h. Drying was carried out in a freeze dryer LyoQuest-55 (Telstar, Spain) at −50 °C and pressure of 0.011 mbar for 72 h. The yield of polyphenols was 13% *w*/*w*.

For both total phenolic content (TPC) and ORAC assays, lyophilized samples were dissolved in phosphate buffer (PBS, 75 mM, pH 7.0) (10 mg/mL) and filtered. Filtrate has been used straight away for analyses.

3.4. HS-SPME Extraction Conditions for the Detrmination of Volatiles

For the method optimization, a Carboxen/Polydimethylsiloxane (CAR/PDMS) 75 µm fiber 1 cm long (57343-U) and a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30 µm fiber 1 cm long (57329-U), both purchased by Merck Life Science (Darmstadt, Germany), were tested. The fibers were conditioned before the initial use

according to manufacturer's instructions, and a cleaning step of 20 min at 10 °C below the fiber's recommended maximum temperature was applied between consecutive analyses. Furthermore, sample conditioning times of 5 and 10 min were evaluated at the same temperature (37, 50, or 60 °C) employed for the extraction stage, and the analytical repeatability was excellent in both conditions. Different stirring rates (200 and 300 rpm) for sample conditioning and extraction have been also investigated. GC analyses were carried out using for each test using a 10 mL vial with 0.1, 0.2, and 0.5, g samples respectively, and the best results were obtained for a 0.2 g sample weight.

Three different fiber exposure times were also tested: 20, 30, and 40 min. The highest volatile extraction yield was achieved after an exposure time of 40 min, and most of the heavier molecular weight volatiles remained substantially stable thereafter.

In this investigation, the (DVB/CAR/PDMS) 50/30 µm fiber resulted in being the most useful in covering the wide range of volatile analytes; a conditioning time of 5 min and an extraction temperature of 60 °C resulted the best compromise between equilibration time and method sensitivity. Furthermore, a time of 40 min at the same temperature and stirring rate of 300 rpm have proven to be the best choice for an exhaustive extraction of the volatile components.

After the extraction, the analytes were thermally desorbed for 1 min at 260 °C in the GC injector port, in splitless mode.

3.5. GC–MS and GC-FID Analysis

The GC-MS and GC-FID analysis were carried out for qualitative and quantitative purposes, respectively.

GC-MS analyses were carried out on a GC-QP2010 system (Shimadzu, Kyoto, Japan). For the separation, an SLB-5ms fused-silica capillary column (30 m × 0.25 mm *i.d.* × 0.25 µm *df*) (29804-U) (Merck Life Science, Merck KGaA, Darmstadt, Germany) was applied. Helium was used as carrier gas at a constant linear velocity of 30.0 cm/s, which corresponded to an inlet pressure of 24.2 kPa. The temperature program was the following: 40 °C held for 1 min to 350 °C at 3 °C/min, held for 5 min. The interface and ion source temperatures were 250 and 200 °C, respectively. The acquisition was made in full scan mode in the mass range of 40–500 *m/z*, with a scanning rate interval of 0.2 s. Data handling was supported by GCMS solution ver. 4.30 software (Shimadzu, Kyoto, Japan). For the characterization, the following databases were used: W11N17 (Wiley11-Nist17, Wiley, Hoboken, NJ, USA, and FFNSC 4.0 (Shimadzu, Kyoto, Japan). The identification was performed applying two filters, namely spectral similarity match over 85% and linear retention index (LRI) match calculated using a C7–C40 saturated *n*-alkane homologue series with a filter window of ±10 LRI units.

GC-FID analyses were carried out on a GC2010 system (Shimadzu, Kyoto, Japan). Oven temperature program and injection parameters were the same as for MS applications. Helium was used as carrier gas, at a constant linear velocity of 30.0 cm/s, which corresponded to an inlet pressure of 97.4 kPa. The injector temperature was set at 260 °C. The FID temperature was set at 280 °C (sampling rate 200 ms), hydrogen and air flows were 40 and 400 mL/min, respectively. Data were collected by LabSolution software ver. 5.92 (Shimadzu, Kyoto, Japan). Quantitative results were determined as peak area percentage without any correction. Samples were analyzed in triplicates.

3.6. LC×LC-PDA/ESI-MS Analysis

LC×LC analyses were performed on a Shimadzu LC×LC instrument (Kyoto, Japan), consisting of a CBM-20A controller, one LC-Mikros binary pump, one LC-40BX3 dual-plunger parallel-flow pumps, one LC-30AD as make-up pump, a CTO-40C column oven, a SIL-40CX3 autosampler, and an SPD-M40 photo diode array (PDA) detector (1.0 µL detector flow cell volume). In order to connect the two dimensions, two high speed/high pressure two-position, six-ports switching valves with a micro-electric actuator (model FCV-32 AH, 1.034 bar; Shimadzu, Kyoto, Japan), equipped with two C18 guard columns,

were employed. A third LC pump (LC-30AD) was connected through a t-piece between the outlet of the ^{1}D and the inlet of switching valve. The LC×LC instrument was hyphenated to an LCMS-8050 mass spectrometer, through an ESI source (Shimadzu, Kyoto, Japan).

Separations were carried out on a ^{1}D SEQuant ZIC-HILIC column (150 × 1.0 mm *I.D.*, 3.5 µm *dp*) (Merck Life Science, Merck KGaA, Darmstadt, Germany) and a ^{2}D Ascentis Express C18 column (50 × 4.6 mm *I.D.*, 2.7 µm *dp*). (Merck Life Science, Merck KGaA, Darmstadt, Germany).

Two identical C18 guard columns (5 × 4.6 mm *I.D.*, 5 µm *dp*) (Merck Life Science, Merck KGaA, Darmstadt, Germany); were used to collect and transfer the fractions from the ^{1}D into the ^{2}D.

^{1}D mobile phases: (A) 0.1% formic acid in ACN, (B) 0.1% formic acid in water (pH 3). Gradient: 0 min, 30% B; 40 min, 60% B; 50 min, 100% B; 60 min, 100% B; 61 min, 30% B. Flow rate: 10 µL min^{-1}. Column oven: 30 °C. Injection volume: 20 µL.

^{2}D mobile phases: employed were (A) 0.1 % formic acid in water (pH 3), (B) 0.1% formic acid in ACN. Segmented-in-fraction conditions: (^{1}D 0–12 min), 0.01 min, 10% B; 0.89 min, 40% B; 0.90 min, 10% B; (^{1}D 13–17 min) 0.01 min, 0% B; 0.89 min, 40% B; 0.90 min, 0% B; (^{1}D 18–51 min) 0.01 min, 0% B; 0.89 min, 25% B; 0.90 min, 0% B; Flow rate: 3 mL min^{-1}. Modulation time: 1.00 min. Column oven: 30 °C. PDA conditions were in the range from 200 to 550 nm. Sampling rate was set to 40 Hz, whereas the time constant was acquired at 0.08 s.

ESI-MS conditions: mass spectral range: *m/z* 100–2000; event time: 1 s; nebulizing gas (N_2) flow: 3 L min^{-1}; drying gas (N_2) flow: 10 L min^{-1}; heating gas flow (air): 10 L min^{-1}; heat block temperature: 400 °C; desolvation line (DL) temperature: 250 °C; interface temperature: 300 °C; interface voltage 3.50 kV; detector voltage: 1.80 kV.

The LC×LC-LCMS-8050 system and the switching valves were controlled by the Shimadzu Labsolution software (ver. 5.93). The LC×LC data were visualized and elaborated into two and three dimensions using Chromsquare ver. 2.3 software (Shimadzu, Kyoto, Japan).

Samples were diluted 1:4 with 0.1% formic acid in MeOH:ACN solution (70:30 *v/v*) prior to LC×LC-PDA/ESI-MS analysis.

For the quantitative analysis of polyphenolic compounds, gallic acid, protocatechuic acid, isoquercetin, myricetin, and cyanidin were employed. Standard calibration curves were prepared in a concentration range 10–500 mg L^{-1} with seven different concentration levels, run in triplicate.

3.7. Determination of Total Phenolic Content

TPC was determined by the Folin-Ciocalteau method, and the absorbance was measured using a microplate reader (Infinite®, 200 PRO multimode reader, Tecan, Männedorf, Switzerland) [43]. Extracts obtained were properly diluted and subsequently analyzed according to the literature [44]. Firstly, 20 µL of each extract, as well as standard (gallic acid) or blank (PBS), were mixed with 100 µL of Folin–Ciocalteau reagent in 1580 µL of PBS and incubated at room temperature for 8 min, in the dark. Then, 300 µL of Na_2CO_3 solution (0.2 g mL^{-1}) were added and incubated at room temperature for 2 h, in the dark. Samples were centrifugated (20,817× *g* for 5 min at room temperature) and 200 µL of supernatants were transferred to a clear 96-well microplate; the absorbance was read at 765 nm.

The TPC was determined using a gallic acid standard curve (0−1000 µg/mL) ($y = 0.0008x + 0.0031$; $R^2 = 0.996$). Analyses were performed in triplicate and results are expressed as milligrams of gallic acid equivalents (GAE) per gram of extract (mg GAE/g).

3.8. ORAC Assay

ORAC was determined as described by Zulueta et al. [45] using a multifunctional microplate reader (Infinite®, 200 PRO multimode reader, Tecan, Männedorf, Switzerland). The measurements were made in 96-well microplates with black sides and clear bottoms

(BRANDplates®, Wertheim, Germany). Fluorescence was read with an excitation wavelength of 485 nm and an emission wavelength of 535 nm.

A stock solution of fluorescein (FL) was prepared dissolving 22 mg of FL in 50 mL of phosphate buffer (PBS, 75 mM, pH 7.0). FL solution was stored in complete darkness under refrigeration conditions. The FL working solution (7.7 μM) was prepared by diluting 0.167 mL of the stock solution in 25 mL of PBS. The AAPH solution (221 mM) was prepared by dissolving 600 mg of AAPH in 10 mL of PBS.

Samples obtained were properly diluted. In each well, 60 μL of FL working solution and 60 μL of sample, blank (PBS) or standard (Trolox) were mixed and incubated for 15 min at 37 °C. Then, 30 μL of AAPH solution was added. Fluorescence was measured immediately after the AAPH addition, and measurements were then taken every 5 min for 24 cycles at an incubation temperature of 37 °C.

The area under the curve (AUC), referred to by the fluorescence decay curve of each sample, blank, and Trolox, were calculated applying the following formula:

$$AUC = (0.5 + f5/f0 + f10/f0 + \ldots + fn + 5/f0) \times 5 \quad (1)$$

where f0 is the initial fluorescence, f5 is the fluorescence after 5 min, and fn is the fluorescence at time n. The net AUC was calculated by subtracting the AUC of the blank from the AUC of the sample. The antioxidant capacity of samples was determined using a Trolox calibration curve (6.25–100 μM) ($y = 0.5926x$; $R^2 = 0.996$). Analyses were performed in triplicate and results are expressed as μmol TE/100 g of extract.

4. Conclusions

In this study, the phytochemical profile and antioxidant activity of six different fruit extracts of *R. coriaria* are reported. The volatile chemical profile was thoroughly investigated, revealing the presence of 263 volatile compounds; among them, the sample collected in October (overripe stage and dried in vacuum stove) was the most abundant in such compounds (99.47 ± 10.66), whereas the same sample, not subjected to the drying process, represented the least abundant one (86.71 ± 9.29). Moreover, a total of 83 polyphenolic compounds were positively identified in the investigated samples and among them, the majority were represented by gallic acid and its derivates (37). All samples showed an antioxidant activity consistent with polyphenolic content and composition. The obtained results highlight the importance of *R. coriaria* as a promising source of functional ingredients and boost its potential use in the food, nutraceutical, and pharmaceutical industries.

Supplementary Materials: The following are available online. Table S1. Most abundant volatile compounds contained in the samples analysed, expressed in area% as average of three measurements by GC-FID analysis, Table S2. Identification of the polyphenolic compounds in *R. coriaria* extracts by using HILIC×RP-LC-PDA/MS in positive and negative ionization mode.

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Sample Availability: Samples of the compounds are available from the authors.

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Supplementary Materials.

Table S1. Most abundant volatile compounds contained in the samples analysed, expressed in area% as average of three measurements by GC-FID analysis.

	Compounds	LRI_{ex}	LRL_{rif}	Simil. %	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
1	Acetic aldehyde	457	-	90	0.14 ± 0.02	0.03 ± 0.00	0.05 ± 0.01	0.06 ± 0.01	0.03 ± 0.00	0.02 ± 0.00
2	Ethanol	475	-	97	0.85 ± 0.09	0.36 ± 0.04	0.78 ± 0.08	0.14 ± 0.02	0.18 ± 0.02	0.20 ± 0.02
3	Acetone	491	-	97	0.32 ± 0.03	0.11 ± 0.01	0.21 ± 0.02	0.78 ± 0.08	0.10 ± 0.01	0.03 ± 0.00
4	Formic acid	529	480	90	0.67 ± 0.07	3.69 ± 0.40	3.18 ± 0.34	3.79 ± 0.41	0.23 ± 0.02	0.01 ± 0.00
5	Methyl acetate	566	633	90	0.06 ± 0.01	0.25 ± 0.03	0.98 ± 0.10	-	0.38 ± 0.04	0.01 ± 0.00
6	2,3-Butanedione	581	561	90	0.11 ± 0.01	0.05 ± 0.01	0.10 ± 0.01	-	0.02 ± 0.00	0.01 ± 0.00
7	3-Methyl-2-pentanone	578	745	90	0.06 ± 0.01	0.16 ± 0.02	0.04 ± 0.00	-	0.03 ± 0.00	0.04 ± 0.00
8	2-Methylfuran	583	588	92	0.06 ± 0.01	-	-	-	1.21 ± 0.13	0.12 ± 0.01
9	Ethanoic acid	638	661	98	0.60 ± 0.06	10.47 ± 1.12	5.09 ± 0.55	11.16 ± 1.20	16.13 ± 1.73	8.19 ± 0.88
10	Isobutyl alcohol	735	621	94	0.01 ± 0.00	0.04 ± 0.00	-	0.03 ± 0.00	0.04 ± 0.00	0.12 ± 0.01
11	(E)-2-Butenal	641	650	91	tr	0.03 ± 0.00	0.06 ± 0.01	0.10 ± 0.01	-	-
12	Butyl alcohol	658	653	90	tr	0.11 ± 0.01	0.13 ± 0.01	0.03 ± 0.00	-	-
13	3-Hydroxy-pentene	681	691	97	0.02 ± 0.00	0.01 ± 0.00	0.06 ± 0.01	0.10 ± 0.01	-	-
14	Propyl methyl ketone	685	682	90	tr	0.01 ± 0.00	0.58 ± 0.06	0.16 ± 0.02	-	-
15	3-Pentanone	699	697	94	0.06 ± 0.01	-	-	0.10 ± 0.01	-	-
16	*n*-Pentanal	701	696	90	0.10 ± 0.01	0.08 ± 0.01	0.04 ± 0.00	0.07 ± 0.01	-	0.16 ± 0.02
17	Pyruvic acid	704	696	96	0.03 ± 0.00	0.05 ± 0.01	0.04 ± 0.00	0.06 ± 0.01	0.05 ± 0.01	tr
18	Ethyl propanoate	711	708	90	0.01 ± 0.00	-	-	0.02 ± 0.00	-	tr
19	3-Hydroxy-2-butanone	716	716	91	0.35 ± 0.04	-	-	0.03 ± 0.00	-	0.03 ± 0.00
20	Isoprenol	730	724	93	0.09 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	-	0.01 ± 0.00
21	Isopentyl alcohol	734	729	97	0.06 ± 0.01	-	0.07 ± 0.01	0.05 ± 0.01	0.07 ± 0.01	0.07 ± 0.01
22	*sec*-Butyl-carbinol	737	733	92	0.03 ± 0.00	-	0.08 ± 0.01	-	0.10 ± 0.01	-
23	Isopropyl ethyl ketone	746	742	90	0.02 ± 0.00	0.01 ± 0.00	0.06 ± 0.01	0.03 ± 0.00	-	-
24	3-Hexanone	746	782	90	0.03 ± 0.00	-	0.11 ± 0.01	-	-	-
25	(Z)-2-Pentenal	754	-	90	tr	-	0.03 ± 0.00	-	-	-
26	(E)-2-Pentenal	754	751	90	0.01 ± 0.00	0.02 ± 0.00	0.23 ± 0.02	-	-	-
27	Isobutyric acid	755	774	90	-	-	-	0.03 ± 0.00	0.05 ± 0.01	-
28	Toluene	764	763	94	1.04 ± 0.11	0.04 ± 0.00	1.99 ± 0.21	0.09 ± 0.01	-	-
29	Pentyl alcohol	767	763	95	0.03 ± 0.00	0.07 ± 0.01	0.16 ± 0.02	-	0.03 ± 0.00	0.16 ± 0.02
30	(E)-2-Penten-1-ol	769	761	90	0.02 ± 0.00	-	0.05 ± 0.01	-	0.02 ± 0.00	-
31	Prenol	776	772	90	0.01 ± 0.00	-	0.19 ± 0.02	-	0.09 ± 0.01	-
32	Butanoic acid	784	818	90	0.02 ± 0.00	-	0.11 ± 0.01	0.08 ± 0.01	0.06 ± 0.01	0.01 ± 0.00
33	α-Octene	791	788	90	0.18 ± 0.02	0.12 ± 0.01	0.10 ± 0.01	0.04 ± 0.00	0.02 ± 0.00	0.03 ± 0.00
34	3-Methyl-crotonaldehyde	789	780	90	0.01 ± 0.00	0.02 ± 0.00	-	-	-	0.01 ± 0.00
35	*n*-Octane	800	800	96	0.03 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	-	-	-
36	*n*-Hexanal	802	801	96	0.07 ± 0.01	0.53 ± 0.06	2.88 ± 0.31	2.72 ± 0.29	0.10 ± 0.01	0.93 ± 0.10
37	1,3-Octadiene	820	827	90	0.02 ± 0.00	0.12 ± 0.01	-	0.10 ± 0.01	0.01 ± 0.00	0.04 ± 0.00
38	Furfural	831	845	98	0.02 ± 0.00	0.43 ± 0.05	-	-	1.09 ± 0.12	0.16 ± 0.02
39	Isovaleric acid	835	842	90	0.14 ± 0.01	0.28 ± 0.03	0.88 ± 0.09	-	-	0.02 ± 0.00
40	(E)-Ethyl crotonate	843	839	93	0.01 ± 0.00	0.30 ± 0.03	0.02 ± 0.00	0.07 ± 0.01	0.09 ± 0.01	-
41	Ethyl 2-methylbutyrate	847	842	90	0.02 ± 0.00	0.08 ± 0.01	0.04 ± 0.00	0.03 ± 0.00	0.08 ± 0.01	0.01 ± 0.00
42	(E)-2-Hexenal	844	850	90	-	0.39 ± 0.04	0.01 ± 0.00	0.14 ± 0.02	0.07 ± 0.01	-
43	(E)-3-Hexenol	851	847	90	0.01 ± 0.00	0.14 ± 0.02	0.07 ± 0.01	-	-	0.15 ± 0.02
44	(Z)-3-Hexenol	854	853	96	0.52 ± 0.06	0.64 ± 0.07	0.04 ± 0.00	-	0.04 ± 0.00	-
45	(E)-2-Hexenol	866	864	90	0.01 ± 0.00	0.01 ± 0.00	-	-	-	-
46	*n*-Hexanol	869	867	96	0.12 ± 0.01	0.10 ± 0.01	0.17 ± 0.02	0.10 ± 0.01	0.26 ± 0.03	0.13 ± 0.01
47	Isoamyl acetate	875	871	97	0.03 ± 0.00	0.04 ± 0.00	0.03 ± 0.00	0.04 ± 0.00	0.30 ± 0.03	-
48	2-Methylbutyl acetate	881	873	90	0.02 ± 0.00	0.04 ± 0.00	0.07 ± 0.01	0.01 ± 0.00	0.22 ± 0.02	0.15 ± 0.02
49	*n*-Pentanoic acid	882	911	90	0.02 ± 0.00	-	-	0.02 ± 0.00	0.01 ± 0.00	0.15 ± 0.02
50	3-Methyl-3-buten-1-yl-acetate	884	878	90	0.02 ± 0.00	0.12 ± 0.01	0.03 ± 0.00	0.10 ± 0.01	-	0.08 ± 0.01
51	1-Buten-1-one	885	-	90	0.02 ± 0.00	-	0.03 ± 0.00	0.17 ± 0.02	-	-
52	Styrene	886	891	90	0.01 ± 0.00	-	0.16 ± 0.02	-	0.33 ± 0.04	-
53	Pentyl methyl ketone	890	887	90	0.01 ± 0.00	0.14 ± 0.02	-	-	-	-
54	Ethylbenzene	859	857	90	-	0.05 ± 0.01	0.02 ± 0.00	-	-	-
55	(E)-4-Heptenal	894	901	90	0.02 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	-	-	-
56	*n*-Nonene	895	890	90	tr	0.08 ± 0.01	-	-	-	-
57	Heptanal	903	906	94	0.04 ± 0.00	0.40 ± 0.04	0.52 ± 0.06	0.67 ± 0.07	0.14 ± 0.02	0.59 ± 0.06
58	2-Acetyl furan	907	913	90	0.01 ± 0.00	0.12 ± 0.01	-	0.11 ± 0.01	-	-
59	Tricyclene	908	923	90	0.01 ± 0.00	0.06 ± 0.01	0.03 ± 0.00	-	-	-

60	γ-Butyrolactone	911	910	90	0.03 ± 0.00	-	0.10 ± 0.01	-	-	0.15 ± 0.02
61	(E)-3-Nonene	913	886	90	0.01 ± 0.00	0.06 ± 0.01	-	-	0.03 ± 0.00	-
62	Pentyl acetate	915	915	93	0.02 ± 0.00	-	0.01 ± 0.00	-	0.23 ± 0.02	-
63	3-Methyl-apopinene	923	927	94	0.04 ± 0.00	-	0.06 ± 0.01	0.03 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
64	α-Thujene	927	927	91	0.01 ± 0.00	-	0.08 ± 0.01	0.02 ± 0.00		0.04 ± 0.00
65	α-Pinene	935	933	95	6.52 ± 0.70	3.64 ± 0.39	10.82 ± 1.16	6.94 ± 0.74	0.24 ± 0.03	1.61 ± 0.17
66	Dihydromyrcene	943	948	90	0.22 ± 0.02	0.01 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.13 ± 0.01	0.08 ± 0.01
67	α-Fenchene	947	950	91	0.02 ± 0.00	0.02 ± 0.00	0.21 ± 0.02	0.14 ± 0.02	-	0.08 ± 0.01
68	γ-Pentalactone	949	954	92	0.04 ± 0.00	0.10 ± 0.01	-	-	0.27 ± 0.03	0.06 ± 0.01
69	Camphene	951	953	96	0.33 ± 0.04	0.36 ± 0.04	0.48 ± 0.05	0.43 ± 0.05	-	0.10 ± 0.01
70	Thuja-2,4(10)-diene	954	953	93	0.07 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.05 ± 0.01	-	0.02 ± 0.00
71	(E)-2-Heptenal	958	956	94	0.14 ± 0.02	1.05 ± 0.11	0.92 ± 0.10	1.81 ± 0.19	0.25 ± 0.03	1.20 ± 0.13
72	5-Methyl furfural	961	960	92	0.05 ± 0.01	0.03 ± 0.00	0.35 ± 0.04	0.06 ± 0.01	-	-
73	Benzaldehyde	964	960	90	0.08 ± 0.01	0.06 ± 0.01	0.03 ± 0.00	0.12 ± 0.01	0.87 ± 0.09	0.34 ± 0.04
74	*n*-Heptanol	972	970	90	0.05 ± 0.01	0.22 ± 0.02	0.06 ± 0.01	0.05 ± 0.01	0.09 ± 0.01	0.08 ± 0.01
75	Sabinene	973	972	91	-	0.09 ± 0.01	0.05 ± 0.01	-	0.04 ± 0.00	0.07 ± 0.01
76	1-Octen-3-one	974	973	92	-	0.14 ± 0.02	-	0.34 ± 0.04	0.08 ± 0.01	0.11 ± 0.01
77	β-Pinene	978	978	97	1.54 ± 0.17	-	1.16 ± 0.12	0.05 ± 0.01	1.01 ± 0.11	0.04 ± 0.00
78	Vinyl amyl carbinol	982	978	90	0.24 ± 0.03	0.99 ± 0.11	1.09 ± 0.12	-	-	1.58 ± 0.17
79	6-Methyl-hept-5-en-2-one	985	986	90	0.30 ± 0.03	1.28 ± 0.14	1.79 ± 0.19	1.30 ± 0.14	0.75 ± 0.08	1.07 ± 0.11
80	Myrcene	989	991	95	3.69 ± 0.40	2.28 ± 0.24	1.51 ± 0.16	2.14 ± 0.23	0.90 ± 0.10	1.72 ± 0.18
81	2-Pentyl-furan	992	991	90	0.13 ± 0.01	-	-	-	0.24 ± 0.03	-
82	6-Methyl-hept-5-en-2-ol	994	995	90	0.02 ± 0.00	-	0.14 ± 0.02	0.60 ± 0.06	0.24 ± 0.03	-
83	*n*-Hexanoic acid	995	997	90	0.03 ± 0.00	0.29 ± 0.03	0.06 ± 0.01	0.18 ± 0.02	0.09 ± 0.01	0.16 ± 0.02
84	Mesitylene	996	994	90	-	-	-	0.10 ± 0.01	0.10 ± 0.01	0.34 ± 0.04
85	*n*-Decane	1000	1000	93	0.07 ± 0.01	0.66 ± 0.07	0.20 ± 0.02	-	0.19 ± 0.02	0.27 ± 0.03
86	3-Octanol	998	999	90	-	-	-	-	0.16 ± 0.02	0.91 ± 0.10
87	*n*-Octanal	1004	983	93	0.09 ± 0.01	3.37 ± 0.36	2.33 ± 0.25	2.08 ± 0.22	0.37 ± 0.04	1.86 ± 0.20
88	(Z)-3-Hexenyl acetate	1005	1008	97	0.66 ± 0.07	-	-	-	-	0.12 ± 0.01
89	α-Phellandrene	1007	1007	91	0.69 ± 0.07	0.44 ± 0.05	0.86 ± 0.09	0.43 ± 0.05	0.15 ± 0.02	-
90	δ-3-Carene	1010	1009	90	0.08 ± 0.01	0.23 ± 0.02	-	-	0.73 ± 0.08	0.69 ± 0.07
91	Isopentyl isobutyrate	1012	1014	92	0.16 ± 0.02	0.36 ± 0.04	0.05 ± 0.01	-	0.06 ± 0.01	-
92	(E)-2-Hexenyl acetate	1015	1017	93	0.05 ± 0.01	0.05 ± 0.01	0.77 ± 0.08	0.08 ± 0.01	0.45 ± 0.05	0.13 ± 0.01
93	α-Terpinene	1018	1018	94	0.45 ± 0.05	0.22 ± 0.02	0.11 ± 0.01	0.23 ± 0.02	0.21 ± 0.02	0.44 ± 0.05
94	Pelargol	1021	1200	90	0.18 ± 0.02	0.05 ± 0.01	0.17 ± 0.02	0.06 ± 0.01	0.12 ± 0.01	0.13 ± 0.01
95	*p*-Cymene	1025	1025	90	0.54 ± 0.06	0.74 ± 0.08	1.27 ± 0.14	0.87 ± 0.09	2.16 ± 0.23	2.97 ± 0.32
96	Limonene	1021	1030	97	4.71 ± 0.50	3.90 ± 0.42	6.24 ± 0.67	3.96 ± 0.42	3.28 ± 0.35	4.58 ± 0.49
97	ß-Phellandrene	1022	1031	96	1.14 ± 0.12	0.14 ± 0.01	0.19 ± 0.02	0.74 ± 0.08	0.42 ± 0.05	0.54 ± 0.06
98	(Z)-ß-Ocimene	1025	1035	90	2.72 ± 0.29	0.71 ± 0.08	0.08 ± 0.01	0.91 ± 0.10	0.41 ± 0.04	0.71 ± 0.08
99	Oct-3-en-2-one	1033	1036	90	-	0.09 ± 0.01	0.12 ± 0.01	0.15 ± 0.02	0.08 ± 0.01	0.53 ± 0.06
100	2(3H)-Furanone, dihydro-3-hydroxy-4,4-dimethyl-,	1040	1032	92	0.35 ± 0.04	0.05 ± 0.01	0.05 ± 0.01	0.26 ± 0.03	0.35 ± 0.04	0.13 ± 0.01
101	(Z)-2-Octenal	1045	1047	90	0.08 ± 0.01	0.10 ± 0.01	0.02 ± 0.00	0.03 ± 0.00	-	0.22 ± 0.02
102	Phenylacetaldehyde	1046	1045	90	-	0.07 ± 0.01	-	-	0.18 ± 0.02	-
103	(E)-ß-Ocimene	1047	1046	96	5.48 ± 0.59	1.13 ± 0.12	0.10 ± 0.01	0.79 ± 0.08	0.19 ± 0.02	1.22 ± 0.13
104	γ-Hexalactone	1053	1060	90	0.02 ± 0.00	0.14 ± 0.02	0.01 ± 0.00	0.05 ± 0.01	0.16 ± 0.02	0.22 ± 0.02
105	4-Methyl decane	1054	1060	90	0.03 ± 0.00	0.84 ± 0.09	0.13 ± 0.01	0.17 ± 0.02	0.45 ± 0.05	0.14 ± 0.02
106	(E)-2-Octenal	1056	1047	90	0.05 ± 0.01	1.68 ± 0.18	0.02 ± 0.00	1.11 ± 0.12	0.03 ± 0.00	0.28 ± 0.03
107	γ-Terpinene	1057	1058	94	0.67 ± 0.07	0.49 ± 0.05	0.95 ± 0.10	0.76 ± 0.08	0.52 ± 0.06	2.99 ± 0.32
108	(E)-Decahydro-naphthalene	1061	1062	93	0.08 ± 0.01	0.06 ± 0.01	0.13 ± 0.01	0.02 ± 0.00	-	1.20 ± 0.13
109	2-Methyl decane	1062	1064	90	0.17 ± 0.02	0.32 ± 0.03	0.01 ± 0.00	0.14 ± 0.02	0.73 ± 0.08	0.13 ± 0.01
110	(Z)-2-Octenol	1068	1067	94	-	0.55 ± 0.06	0.16 ± 0.02	0.47 ± 0.05	0.19 ± 0.02	0.51 ± 0.05
111	Octanol	1072	1076	90	0.21 ± 0.02	1.82 ± 0.20	0.62 ± 0.07	0.93 ± 0.10	-	1.39 ± 0.15
112	(Z)-Linalool oxide	1075	1169	90	0.05 ± 0.01	1.10 ± 0.12	0.31 ± 0.03	0.52 ± 0.06	1.13 ± 0.12	0.12 ± 0.01
113	Heptanoic acid	1076	1116	92	0.06 ± 0.01	0.05 ± 0.00	0.03 ± 0.00	0.07 ± 0.01		0.13 ± 0.01
114	Terpinolene	1080	1086	94	1.26 ± 0.14	1.30 ± 0.14	0.28 ± 0.03	-	0.08 ± 0.01	0.24 ± 0.03
115	(E)-Linalool oxide	1088	1086	90	-	-	0.04 ± 0.00	0.57 ± 0.06	0.60 ± 0.06	0.23 ± 0.02
116	*p*-Cymenene	1077	1093	90	0.80 ± 0.09	0.85 ± 0.09	0.19 ± 0.02	0.41 ± 0.04	0.50 ± 0.05	0.60 ± 0.06
117	(E)-4-Nonenal	1095	1098	90	0.02 ± 0.00	0.24 ± 0.03	0.08 ± 0.01	0.16 ± 0.02	0.05 ± 0.01	0.02 ± 0.00
118	(3E,5E)-3,5-Octadien-2-one	1096	1073	91	0.22 ± 0.02	-	0.03 ± 0.00	0.10 ± 0.01	0.20 ± 0.02	0.16 ± 0.02
119	*n*-Undecane	1100	1100	90	-	1.18 ± 0.13	0.25 ± 0.03	0.18 ± 0.02	0.98 ± 0.11	0.02 ± 0.00
120	(Z)-3-Hexenyl propanoate	1101	1101	92	0.07 ± 0.01	-	0.02 ± 0.00	-	0.07 ± 0.01	-
121	2-Methylbutyl-2-methyl-butyrate	1102	1104	90	0.76 ± 0.08	-	0.01 ± 0.00	-	-	0.18 ± 0.02
122	Linalool	1103	1101	91	-	0.12 ± 0.01	0.16 ± 0.02	-	0.30 ± 0.03	0.67 ± 0.07

123	3-Methylbutyl-2-methyl-butyrate	1104	1104	92	0.04 ± 0.00	-	0.10 ± 0.01	-	0.12 ± 0.01	-
124	*n*-Nonanal	1105	1107	90	1.05 ± 0.11	5.69 ± 0.61	5.15 ± 0.55	7.84 ± 0.84	1.31 ± 0.14	5.14 ± 0.55
125	2-Methylbutyl isovalerate	1108	1109	92	0.12 ± 0.01	0.13 ± 0.01	-	0.05 ± 0.01	0.06 ± 0.01	0.05 ± 0.01
126	Heptyl acetate	1112	1114	90	0.10 ± 0.01	-	0.04 ± 0.00	0.03 ± 0.00	0.10 ± 0.01	0.11 ± 0.01
127	Phenethyl alcohol	1115	1113	93	0.43 ± 0.05	0.51 ± 0.05	0.43 ± 0.05	0.49 ± 0.05	0.27 ± 0.03	0.10 ± 0.01
128	*endo*-Fenchol	1122	1119	90	0.12 ± 0.01	0.05 ± 0.01	-	0.23 ± 0.02	0.07 ± 0.01	0.06 ± 0.01
129	*dihydro*-Citronellal	1128	1125	90	-	0.01 ± 0.00	0.12 ± 0.01	0.04 ± 0.00	0.06 ± 0.01	0.03 ± 0.00
130	Fenchyl alcohol	1123	1123	90	0.14 ± 0.02	0.18 ± 0.02	0.04 ± 0.00	0.03 ± 0.00	0.05 ± 0.01	0.03 ± 0.00
131	*allo*-(4E,6Z)-Ocimene	1129	1128	90	0.33 ± 0.04	0.23 ± 0.02	0.01 ± 0.00	0.37 ± 0.04	0.25 ± 0.03	0.27 ± 0.03
132	2-Vinyl anisole	1132	1135	91	-	0.06 ± 0.01	-	0.07 ± 0.01	-	-
133	Cosmene	1133	1131	90	0.69 ± 0.07	0.03 ± 0.00	0.01 ± 0.00	-	-	0.04 ± 0.00
134	3-Nonen-2-one	1140	1137	90	0.70 ± 0.08	0.14 ± 0.02	0.02 ± 0.00	0.08 ± 0.01	0.09 ± 0.01	0.02 ± 0.00
135	*neo-allo*-Ocimene	1141	1145	90	1.33 ± 0.14	0.26 ± 0.03	0.01 ± 0.00	0.10 ± 0.01	0.07 ± 0.01	0.04 ± 0.00
136	(E)-Pinocarveol	1142	1141	94	0.23 ± 0.02	0.01 ± 0.00	0.19 ± 0.02	0.23 ± 0.02	0.29 ± 0.03	0.09 ± 0.01
137	(Z)-2-Nonenal	1148	1148	90	0.35 ± 0.04	0.07 ± 0.01	0.02 ± 0.00	0.08 ± 0.01	0.08 ± 0.01	0.06 ± 0.01
138	(Z)-β-Terpineol	1149	1149	91	0.21 ± 0.02	0.12 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.05 ± 0.01	0.12 ± 0.01
139	6-Methyl undecane	1151	1152	90	0.20 ± 0.02	-	0.01 ± 0.00	0.11 ± 0.01	0.14 ± 0.02	0.07 ± 0.01
140	Neomenthol	1155	1170	92	0.38 ± 0.04	0.17 ± 0.02	-	0.03 ± 0.00	0.10 ± 0.01	0.36 ± 0.04
141	Camphene hydrate	1156	1156	90	0.70 ± 0.08	0.03 ± 0.00	0.03 ± 0.00	0.02 ± 0.00	tr	-
142	(E)-2-Nonenal	1162	1163	96	0.11 ± 0.01	0.81 ± 0.09	0.37 ± 0.04	1.12 ± 0.12	0.09 ± 0.01	0.68 ± 0.07
143	Pinocarvone	1166	1164	90	0.56 ± 0.06	0.12 ± 0.01	0.08 ± 0.01	0.13 ± 0.01	0.11 ± 0.01	0.25 ± 0.03
144	3-Methyl undecane	1167	1170	91	0.75 ± 0.08	-	0.02 ± 0.00	0.01 ± 0.00	-	0.08 ± 0.01
145	Isoborneol	1168	1165	94	0.05 ± 0.01	0.14 ± 0.02	0.11 ± 0.01	0.19 ± 0.02	0.34 ± 0.04	0.13 ± 0.01
146	Nonanol	1174	1176	90	0.08 ± 0.01	0.40 ± 0.04	0.30 ± 0.03	0.29 ± 0.03	0.57 ± 0.06	0.04 ± 0.00
147	Borneol	1176	1173	91	0.47 ± 0.05	0.88 ± 0.09	0.19 ± 0.02	0.50 ± 0.05	0.58 ± 0.06	0.12 ± 0.01
148	(Z)-Pinocamphone	1180	1176	92	-	-	0.03 ± 0.00	0.09 ± 0.01	0.11 ± 0.01	0.06 ± 0.01
149	Octanoic acid	1181	1192	91	0.43 ± 0.05	0.11 ± 0.01	-	-	-	0.02 ± 0.00
150	4-Terpinenol	1183	1184	90	-	0.17 ± 0.02	0.04 ± 0.00	0.14 ± 0.02	0.69 ± 0.07	0.52 ± 0.06
151	(Z)-3-Hexenyl-butyrate	1185	1187	91	1.94 ± 0.21	0.05 ± 0.01	-	0.06 ± 0.01	0.17 ± 0.02	0.03 ± 0.00
152	1-Dodecene	1190	1191	90	0.74 ± 0.08	-	-	-	0.18 ± 0.02	0.01 ± 0.00
153	Octyl methyl ketone	1194	1196	91	0.86 ± 0.09	0.26 ± 0.03	0.01 ± 0.00	0.06 ± 0.01	0.05 ± 0.01	0.12 ± 0.01
154	(E)-4-Decenal	1195	1197	92	0.29 ± 0.03	0.11 ± 0.01	0.03 ± 0.00	0.02 ± 0.00	0.11 ± 0.01	0.08 ± 0.01
155	α-Terpineol	1198	1195	95	1.07 ± 0.11	1.85 ± 0.20	0.24 ± 0.03	0.57 ± 0.06	1.18 ± 0.13	1.17 ± 0.13
156	*n*-Dodecane	1200	1200	92	1.02 ± 0.11	0.78 ± 0.08	0.19 ± 0.02	0.21 ± 0.02	-	-
157	1,6-Dihydrocarveol	1201	1203	91	0.86 ± 0.09	0.03 ± 0.00	-	-	3.28 ± 0.35	1.30 ± 0.14
158	(E)-Dihydrocarvone	1204	1204	90	0.24 ± 0.03	-	-	-	0.58 ± 0.06	0.15 ± 0.02
159	Decanal	1207	1208	93	0.07 ± 0.01	0.52 ± 0.06	0.18 ± 0.02	0.51 ± 0.05	-	0.87 ± 0.09
160	Verbenone	1208	1205	90	0.38 ± 0.04	0.05 ± 0.01	-	-	-	0.08 ± 0.01
161	Octyl acetate	1210	1214	90	0.01 ± 0.00	0.09 ± 0.01	0.05 ± 0.01	0.14 ± 0.02	0.36 ± 0.04	0.10 ± 0.01
162	2,5-Dimethyl-undecane	1211	1210	90	0.21 ± 0.02	0.08 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.18 ± 0.02	0.02 ± 0.00
163	(2E,4E)-Nonadienal	1218	1218	91	0.04 ± 0.00	0.13 ± 0.01	0.02 ± 0.00	0.18 ± 0.02	0.09 ± 0.01	0.40 ± 0.04
164	Fenchyl acetate	1220	1219	90	0.01 ± 0.00	0.08 ± 0.01	0.05 ± 0.01	0.11 ± 0.01	-	0.09 ± 0.01
165	Citronellyl nitrile	1221	1221	90	0.13 ± 0.01	0.24 ± 0.03	-	0.11 ± 0.01	0.08 ± 0.01	0.25 ± 0.03
166	(E)-*p*-Mentha-1(7),8-dien-2-ol	1226	1230	91	0.09 ± 0.01	0.07 ± 0.01	-	-	0.14 ± 0.02	0.08 ± 0.01
167	Decane, 5-ethyl-5-methyl-	1229	-	92	0.13 ± 0.01	0.08 ± 0.01	0.04 ± 0.00	0.01 ± 0.00	0.16 ± 0.02	0.22 ± 0.02
168	(Z)-3-Hexenyl-2-methylbutanoate	1230	1231	90	1.06 ± 0.11	0.32 ± 0.03	0.08 ± 0.01	0.05 ± 0.01	0.06 ± 0.01	0.03 ± 0.00
169	6-Ethyl-undecane	1231	1230	93	0.47 ± 0.05	0.24 ± 0.03	0.16 ± 0.02	0.07 ± 0.01	0.10 ± 0.01	0.15 ± 0.02
170	Cuminaldehyde	1240	1243	90	0.57 ± 0.06	0.03 ± 0.00	0.01 ± 0.00	0.14 ± 0.02	0.21 ± 0.02	0.27 ± 0.03
171	Carvone	1245	1246	90	0.09 ± 0.01	0.05 ± 0.01	0.04 ± 0.00	0.01 ± 0.00	1.61 ± 0.17	7.55 ± 0.81
172	(Z)-2-Decenal	1248	1250	91	0.09 ± 0.01	0.17 ± 0.02	0.03 ± 0.00	0.04 ± 0.00	0.14 ± 0.02	0.06 ± 0.01
173	Linalyl acetate	1250	1250	92	0.86 ± 0.09	0.15 ± 0.02	0.65 ± 0.07	0.68 ± 0.07	0.19 ± 0.02	0.01 ± 0.00
174	Ionane	1253	1246	92	0.47 ± 0.05	0.14 ± 0.02	0.02 ± 0.00	0.10 ± 0.01	0.08 ± 0.01	0.06 ± 0.01
175	(E)-2-Decenal	1264	1265	94	0.56 ± 0.06	2.94 ± 0.32	0.59 ± 0.06	0.95 ± 0.10	0.19 ± 0.02	1.55 ± 0.17
176	Nonanoic acid	1274	1289	95	0.08 ± 0.01	0.04 ± 0.00	0.38 ± 0.04	0.27 ± 0.03	0.30 ± 0.03	0.03 ± 0.00
177	Bornyl acetate	1287	1285	96	0.97 ± 0.10	0.29 ± 0.03	0.32 ± 0.03	0.46 ± 0.05	0.29 ± 0.03	0.28 ± 0.03
178	2-*tert*-Butyl-,(Z)-cyclohexanol acetate	1295	1291	90	0.04 ± 0.00	0.15 ± 0.02	0.20 ± 0.02	0.27 ± 0.03	0.03 ± 0.00	0.71 ± 0.08
179	1-Tridecene	1297	1292	90	0.36 ± 0.04	0.18 ± 0.02	-	0.08 ± 0.01	0.41 ± 0.04	0.01 ± 0.00
180	*n*-Tridecane	1300	1300	91	0.07 ± 0.01	0.36 ± 0.04	0.02 ± 0.00	0.02 ± 0.00	0.83 ± 0.09	0.03 ± 0.00
181	1-Terpinen-4-yl acetate	1301	1296	90	0.13 ± 0.01	0.52 ± 0.06	0.01 ± 0.00	0.27 ± 0.03	-	0.01 ± 0.00
182	Carvacrol	1302	1300	91	0.08 ± 0.01	0.06 ± 0.01	0.38 ± 0.04	0.02 ± 0.00	0.30 ± 0.03	0.80 ± 0.09
183	*n*-Undecanal	1309	1309	90	0.01 ± 0.00	0.42 ± 0.05	0.02 ± 0.00	0.03 ± 0.00	0.56 ± 0.06	0.46 ± 0.05
184	Dihydro citronellol acetate	1312	1319	91	0.09 ± 0.01	0.21 ± 0.02	0.17 ± 0.02	0.08 ± 0.01	0.29 ± 0.03	0.07 ± 0.01
185	(Z)-3-Hexenyl tiglate	1322	1325	93	0.53 ± 0.06	1.04 ± 0.11	0.02 ± 0.00	0.04 ± 0.00	0.22 ± 0.02	0.33 ± 0.04

186	γ-Terpinyl acetate	1349	1358	91	0.16 ± 0.02	0.26 ± 0.03	0.14 ± 0.02	0.28 ± 0.03	0.55 ± 0.06	0.25 ± 0.03
187	5-Methyl tridecane	1350	1348	92	0.07 ± 0.01	0.04 ± 0.00	0.02 ± 0.00	-	0.04 ± 0.00	0.03 ± 0.00
188	Eugenol	1351	1357	90	0.01 ± 0.00	-	0.03 ± 0.00	0.01 ± 0.00	0.23 ± 0.02	0.01 ± 0.00
189	(Z)-Geranyl acetate	1355	1361	91	0.02 ± 0.00	0.03 ± 0.00	0.05 ± 0.01	0.08 ± 0.01	-	-
190	2(3H)-Furanone, dihydro-5-pentyl-	1359	1362	90	0.09 ± 0.01	0.01 ± 0.00	0.04 ± 0.00	0.01 ± 0.00	0.08 ± 0.01	0.09 ± 0.01
191	(Z)-8-Undecenal	1361	1365	93	0.05 ± 0.01	0.13 ± 0.01	0.04 ± 0.00	0.03 ± 0.00	0.19 ± 0.02	0.14 ± 0.02
192	Isoledene	1369	1372	91	0.25 ± 0.03	0.04 ± 0.00	0.01 ± 0.00	0.10 ± 0.01	0.19 ± 0.02	0.08 ± 0.01
193	α-Ylangene	1373	1371	90	0.51 ± 0.05	0.53 ± 0.06	0.79 ± 0.08	0.91 ± 0.10	0.24 ± 0.03	0.52 ± 0.06
194	Cyclosativene	1377	1367	90	0.33 ± 0.04	-	0.02 ± 0.00	-	0.62 ± 0.07	0.04 ± 0.00
195	α-Copaene	1380	1375	92	1.00 ± 0.11	0.98 ± 0.11	1.56 ± 0.17	1.82 ± 0.20	0.06 ± 0.01	0.69 ± 0.07
196	β-Bourbonene	1381	1382	90	0.13 ± 0.01	0.05 ± 0.01	0.01 ± 0.00	0.02 ± 0.00	0.25 ± 0.03	0.32 ± 0.03
197	β-Elemene	1387	1390	90	0.16 ± 0.02	0.20 ± 0.02	0.02 ± 0.00	-	-	0.13 ± 0.01
198	α-Gurjunene	1395	1406	92	-	-	0.04 ± 0.00	0.07 ± 0.01	0.02 ± 0.00	0.01 ± 0.00
199	Sativene	1397	1394	93	0.13 ± 0.01	0.05 ± 0.01	0.02 ± 0.00	0.03 ± 0.00	0.03 ± 0.00	0.04 ± 0.00
200	*n*-Tetradecane	1400	1400	91	0.17 ± 0.02	0.71 ± 0.08	0.04 ± 0.00	-	0.18 ± 0.02	0.06 ± 0.01
201	Decyl methyl ketone	1401	1393	90	0.18 ± 0.02	-	0.04 ± 0.00	0.03 ± 0.00	0.05 ± 0.01	0.02 ± 0.00
202	Dodecanal	1404	1410	91	-	-	-	0.02 ± 0.00	-	0.01 ± 0.00
203	(Z)-Caryophyllene	1410	1413	90	0.47 ± 0.05	0.11 ± 0.01	-	0.47 ± 0.05	0.47 ± 0.05	0.04 ± 0.00
204	β-Longipinene	1416	1405	92	0.14 ± 0.02	-	0.08 ± 0.01	0.34 ± 0.04	0.03 ± 0.00	-
205	Bicyclo [5.2.0]nonane, 2-methylene-4,8,8-trimethyl-4-vinyl-	1418	-	90	0.04 ± 0.00	1.01 ± 0.11	0.15 ± 0.02	0.16 ± 0.02	0.11 ± 0.01	0.43 ± 0.05
206	Bicyclo[5.2.0]nonane, 4-methylene-2,8,8-trimethyl-2-vinyl-	1419	-	90	0.47 ± 0.05	0.24 ± 0.03	0.02 ± 0.00	-	0.06 ± 0.01	0.26 ± 0.03
207	Isocaryophyllene	1420	1419	91	0.23 ± 0.02	-	-	-	0.13 ± 0.01	0.05 ± 0.01
208	γ-Elemene	1421	1432	90	0.05 ± 0.01	0.33 ± 0.04	0.01 ± 0.00	-	-	0.07 ± 0.01
209	(E)-Caryophyllene	1425	1425	96	4.78 ± 0.51	5.73 ± 0.61	8.31 ± 0.89	9.28 ± 0.99	11.62 ± 1.24	12.47 ± 1.34
210	α-Guaiene	1435	1438	93	4.12 ± 0.44	0.01 ± 0.00	0.02 ± 0.00	-	tr	-
211	10,10-Dimethyl-2,6-dimethylenebicyclo[7.2.0]undecane	1433	1440	91	-	0.02 ± 0.00	0.40 ± 0.04	0.58 ± 0.06	0.43 ± 0.05	0.75 ± 0.08
212	Isopentyl benzoate	1442	1439	93	0.38 ± 0.04	0.11 ± 0.01	0.01 ± 0.00	0.11 ± 0.01	0.18 ± 0.02	0.05 ± 0.01
213	(E)-α-Bergamotene	1434	1432	90	-	0.03 ± 0.00	0.03 ± 0.00	-	tr	0.01 ± 0.00
214	Aromadendrene	1451	1438	90	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.03 ± 0.00	-
215	(E)-Geranylacetone	1453	1450	95	0.29 ± 0.03	1.34 ± 0.14	0.41 ± 0.04	1.59 ± 0.17	0.66 ± 0.07	0.45 ± 0.05
216	(E)-9-epi-Caryophyllene	1456	1464	90	0.37 ± 0.04	0.45 ± 0.05	0.24 ± 0.03	0.77 ± 0.08	0.74 ± 0.08	0.69 ± 0.07
217	α-Humulene	1463	1454	95	1.48 ± 0.16	1.05 ± 0.11	0.95 ± 0.10	2.19 ± 0.23	2.52 ± 0.27	2.32 ± 0.25
218	Guaia-6,9-diene	1452	-	91	-	0.01 ± 0.00	0.02 ± 0.00	0.03 ± 0.00	0.02 ± 0.00	-
219	Germacrene D	1479	1480	92	0.05 ± 0.01	0.12 ± 0.01	0.12 ± 0.01	0.14 ± 0.02	0.20 ± 0.02	0.08 ± 0.01
220	γ-Muurolene	1481	1478	94	0.69 ± 0.07	1.11 ± 0.12	1.57 ± 0.17	1.56 ± 0.17	0.98 ± 0.11	0.73 ± 0.08
221	α-Amorphene	1485	1482	90	0.33 ± 0.04	0.37 ± 0.04	0.39 ± 0.04	0.57 ± 0.06	0.52 ± 0.06	0.26 ± 0.03
222	δ-Selinene	1492	1489	96	0.30 ± 0.03	0.49 ± 0.05	0.62 ± 0.07	0.80 ± 0.09	0.35 ± 0.04	0.26 ± 0.03
223	β-Selinene	1495	1492	94	0.17 ± 0.02	0.31 ± 0.03	0.46 ± 0.05	0.43 ± 0.05	0.46 ± 0.05	0.25 ± 0.03
224	ε-Amorphene	1498	1502	91	0.09 ± 0.01	0.27 ± 0.03	0.29 ± 0.03	0.33 ± 0.04	0.30 ± 0.03	0.13 ± 0.01
225	(Z)-β-Guaiene	1499	1498	90	0.19 ± 0.02	-	0.41 ± 0.04	0.65 ± 0.07	-	-
226	α-Muurolene	1502	1497	92	0.46 ± 0.05	0.62 ± 0.07	0.49 ± 0.05	0.70 ± 0.08	0.10 ± 0.01	0.03 ± 0.00
227	α-Selinene	1500	1501	92	-	-	-	-	0.93 ± 0.10	0.63 ± 0.07
228	β-Bisabolene	1511	1511	90	0.14 ± 0.02	0.09 ± 0.01	-	0.06 ± 0.01	0.17 ± 0.02	0.11 ± 0.01
229	2,4-bis(1,1-Dimethylethyl)-phenol	1512	1519	91	0.04 ± 0.00	-	0.01 ± 0.00	0.03 ± 0.00	-	0.18 ± 0.02
230	δ-Cadinene	1523	1518	97	0.84 ± 0.09	0.53 ± 0.06	0.98 ± 0.11	0.91 ± 0.10	0.31 ± 0.03	0.35 ± 0.04
231	(E)-Calamenene	1526	1527	90	0.07 ± 0.01	0.10 ± 0.01	0.30 ± 0.03	0.44 ± 0.05	0.11 ± 0.01	0.10 ± 0.01
232	(E)-Cadina-1,4-diene	1538	1536	91	0.11 ± 0.01	0.11 ± 0.01	0.02 ± 0.00	0.15 ± 0.02	0.13 ± 0.01	0.03 ± 0.00
233	Selina-4(15),7(11)-diene	1543	1540	90	0.29 ± 0.03	-	0.21 ± 0.02	0.36 ± 0.04	0.10 ± 0.01	-
234	α-Calacorene	1546	1547	90	0.04 ± 0.00	0.08 ± 0.01	0.06 ± 0.01	0.17 ± 0.02	0.06 ± 0.01	0.05 ± 0.01
235	Selina-3,7(11)-diene	1548	1546	92	0.16 ± 0.02	0.05 ± 0.01	0.06 ± 0.01	0.09 ± 0.01	0.16 ± 0.02	0.11 ± 0.01
236	Italicene epoxide	1556	1546	90	0.03 ± 0.00	0.12 ± 0.01	0.08 ± 0.01	0.20 ± 0.02	0.19 ± 0.02	0.09 ± 0.01
237	2-Methyl-, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-but-2-enal	1578	1581	92	0.01 ± 0.00	-	-	-	1.14 ± 0.12	0.64 ± 0.07
238	Caryophyllene oxide	1590	1587	90	0.28 ± 0.03	0.35 ± 0.04	0.44 ± 0.05	0.39 ± 0.04	0.18 ± 0.02	0.20 ± 0.02
239	(Z)-3-Hexenyl-benzoate	1593	1573	90	0.21 ± 0.02	0.08 ± 0.01	-	0.01 ± 0.00	0.04 ± 0.00	0.06 ± 0.01
240	Caryolan-8-ol	1594	1575	91	0.03 ± 0.00	0.11 ± 0.01	-	0.02 ± 0.00	0.26 ± 0.03	-
241	Caryophyllene alcohol	1595	1575	95	0.05 ± 0.01	0.18 ± 0.02	0.02 ± 0.00	0.08 ± 0.01	-	0.13 ± 0.01
242	*n*-Hexadecane	1600	1600	90	0.03 ± 0.00	0.14 ± 0.02	0.01 ± 0.00	0.15 ± 0.02	0.22 ± 0.02	0.12 ± 0.01

243	Humulene epoxide I	1602	1604	90	0.04 ± 0.00	0.04 ± 0.00	0.08 ± 0.01	0.21 ± 0.02	0.05 ± 0.01	0.02 ± 0.00
244	n-Tetradecanal	1612	1614	92	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.05 ± 0.01	0.12 ± 0.01	0.02 ± 0.00
245	Isopropyl-laurate	1615	1625	91	0.11 ± 0.01	0.56 ± 0.06	0.03 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.03 ± 0.00
246	Humulene epoxide II	1618	1613	90	0.03 ± 0.00	0.05 ± 0.01	0.04 ± 0.00	0.07 ± 0.01	0.08 ± 0.01	0.01 ± 0.00
247	Muurola-4,10(14)-dien-1-beta-ol	1632	1632	90	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.00	0.02 ± 0.00	0.08 ± 0.01	0.01 ± 0.00
248	*allo*-Aromandendrene epoxide	1640	1644	90	-	-	0.02 ± 0.00	0.03 ± 0.00	0.04 ± 0.00	0.03 ± 0.00
249	Humulenol-II	1644	1650	90	0.08 ± 0.01	-	0.07 ± 0.01	0.10 ± 0.01	0.07 ± 0.01	0.03 ± 0.00
250	Caryophylla-4(12),8(13)-dien-5-beta-ol	1645	1636	93	0.07 ± 0.01	0.05 ± 0.01	0.10 ± 0.01	0.20 ± 0.02	0.05 ± 0.01	0.05 ± 0.01
251	4-Cadinen-10-ol	1659	1659	90	0.03 ± 0.00	0.07 ± 0.01	0.01 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	
252	Germacra-4(15),5,10(14)-trien-1-alpha-ol	1665	1683	90	0.05 ± 0.01	-	0.09 ± 0.01	0.11 ± 0.01	0.16 ± 0.02	0.09 ± 0.01
253	Cadalene	1681	1677	90	0.03 ± 0.00	0.05 ± 0.01	0.01 ± 0.00	0.10 ± 0.01	0.17 ± 0.02	0.01 ± 0.00
254	*n*-Heptadecane	1700	1700	94	0.01 ± 0.00	-	0.02 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.07 ± 0.01
255	Phytone	1843	1841	92	0.02 ± 0.00	0.01 ± 0.00	-	0.03 ± 0.00	0.04 ± 0.00	0.01 ± 0.00
256	(5E,9E)-Farnesyl acetone	1916	1915	90	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.04 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
257	Methyl-hexadecanoate	1923	1925	90	0.01 ± 0.00	-	0.01 ± 0.00	0.05 ± 0.01	0.04 ± 0.00	tr
258	Cembrene	1934	1939	94	0.19 ± 0.02	0.49 ± 0.05	0.17 ± 0.02	1.21 ± 0.13	0.96 ± 0.10	0.91 ± 0.10
259	Cembrene ISOMER	1948	-	90	0.01 ± 0.00	-	-	0.03 ± 0.00	0.03 ± 0.00	0.02 ± 0.00
260	Neocembrene	1965	1960	95	0.02 ± 0.00	0.03 ± 0.00	0.01 ± 0.00	0.07 ± 0.01	0.06 ± 0.01	0.05 ± 0.01
261	Ethyl palmitate	1990	1993	90	0.02 ± 0.00	-	-	0.02 ± 0.00	0.04 ± 0.00	tr
262	Cembrene C	2019	2020	90	0.06 ± 0.01	-	-	-	0.02 ± 0.00	0.01 ± 0.00
	TOTAL				**87.49 ± 9.37**	**96.19 ± 10.30**	**86.71 ± 9.29**	**99.47 ± 10.66**	**90.17 ± 9.66**	**97.20 ± 10.41**

The compounds number is reported in order of elution, considering the total number of compounds eluted. tr-traces

Table S2. Identification of the polyphenolic compounds in *R. coriaria* extracts by using HILIC×RP-LC-PDA/MS in positive and negative ionization mode.

Peak No.	Compound	Chemical family	Tt_r (min) RSD (%) (n=6)	$[M-H]^-$ /$[M+H]^+$	λ_{max} (nm)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
1	Tetragalloyl-hexoside	Gallic acid derivate	1.515 (0.57)	787/-	277	x	x	x	x	x	-
2	Pentagalloyl-hexoside	Gallic acid derivate	1.61 (0.47)	939/-	277	x	x	x	x	x	-
3	Hexagalloyl-hexoside	Gallic acid derivate	1.64 (0.66)	1091/-	278	x	x	x	x	x	x
4	Heptagalloyl-hexoside	Gallic acid derivate	1.70 (0.75)	1243/-	276	x	x	x	x	x	x
5	Octagalloyl-hexoside	Gallic acid derivate	1.73 (0.73)	1395/-	276	x	x	x	x	x	x
6	Nonagalloyl-hexoside	Gallic acid derivate	1.78 (0.60)	1547/-	275	x	x	x	x	x	x
7	Galloyl-valoneic acid bilactone I	Gallic acid derivate	5.64 (0.04)	621/-	279	-	-	x	x	-	-
8	Galloyl-valoneic acid bilactone II	Gallic acid derivate	7.64 (0.06)	621/-	278	-	-	x	x	-	-
9	Chrysoriol	Luteolin derivate	11.42 (0.11)	-/301	277	x	x	x	x	x	x
10	Quercetin rhamnoside I	Quercetin derivate	11.65 (0.07)	447/449	254, 352	x	x	-	-	-	-
11	Quercetin rhamnoside II	Quercetin derivate	12.50 (0.17)	447/449	254, 352	x	x	x	x	-	x
12	Malic acid	Malic acid derivate	13.19 (0.07)	133/-	237	x	x	x	x	x	x
13	Levoglucosan gallate	Gallic acid derivate	13.75 (0.06)	313/315	286	x	x	x	-	-	-
14	Protocatechuic acid hexoside	Protocatechuic acid derivate	15.47 (0.11)	315/-	258	x	x	x	x	x	x
15	Rutin	Quercetin derivate	15.75	609/-	266, 353	x	-	-	-	-	-
16	Quercetin hexoside I	Quercetin derivate	15.76 (0.09)	463/465	259, 350	x	x	x	x	x	x
17	Quercetin hexoside II	Quercetin derivate	15.77 (0.11)	463/465	259, 350	x	x	x	x	x	x
18	Quercetin hexoside III	Quercetin derivate	15.80 (0.10)	463/465	259, 350	-	x	x	x	-	-
19	Methyl digallate I	Gallic acid derivate	15.82 (0.03)	335/-	265	x	x	x	x	-	x
20	Methyl digallate II	Gallic acid derivate	15.83 (0.02)	335/-	265	-	-	x	x	-	-
21	Quercetin rhamnoside III	Quercetin derivate	15.84 (0.11)	447/449	259, 350	x	x	x	x	x	x
22	Apiin	Quercetin derivate	15.88 (0.05)	563/-	267, 332	x	x	x	x	-	-
23	Quercetin hexoside IV	Quercetin derivate	15.91 (0.09)	463/465	259, 350	x	x	x	x	-	-
24	Quercetin	Quercetin derivate	15.92 (0.06)	301/303	259, 350	x	x	-	-	-	x
25	Gallic acid	Gallic acid derivate	16.37 (0.08)	169/-	277	x	x	x	x	x	x
26	Galloyl shikimic acid I	Gallic acid derivate	16.42 (0.07)	325/-	276	x	x	x	x	-	-
27	Gallic acid O-malic acid I	Gallic acid derivate	16.48 (0.08)	285/-	276	x	x	x	x	x	x
28	Peonidin O-glucoside I	Cyanidin derivate	16.65 (0.01)	-/463	282, 515	x	x	x	x	x	-
29	Myricetin	Quercetin derivate	16.69 (0.09)	-/319	260, 359	x	x	x	x	x	x
30	Galloylshikimic acid II	Gallic acid derivate	17.52 (0.15)	325/-	273	x	-	x	x	x	-
31	Gallic acid O-malic acid II	Gallic acid derivate	17.56 (0.13)	285/-	276	x	x	x	x	x	x
32	Apigenin glucoside	Apigenin derivate	17.80	-/433	265, 344	-	-	-	-	x	-
33	Peonidin O-glucoside II	Cyanidin derivate	17.85 (0.02)	-/463	280, 515	x	x	x	x	-	x
34	Myricetin O-rhamnosylglucose	Quercetin derivate	17.92 (0.11)	-/625	262, 357	-	x	x	x	-	x
35	Myricetin O-glucuronide I	Quercetin derivate	17.97 (0.05)	493/495	262, 355	x	x	-	-	-	-
36	Quinic acid	Quinic acid derivate	18.20	191/-	237	x	x	x	x	x	-

			(0.09)								
37	Galloylshikimic acid III	Gallic acid derivate	18.47	325/-	274	-	-	x	-	-	-
38	Peonidin O-pentoside	Cyanidin derivate	18.81 (0.24)	-/433	273, 503	x	x	x	x	-	-
39	Myricetin O-glucuronide II	Quercetin derivate	18.93 (0.06)	493/495	261, 355	x	x	x	x	-	x
40	Quercetin rhamnoside IV	Quercetin derivate	19.94 (0.02)	447/449	262, 354	x	x	-	-	-	-
41	Di-galloyl hexoside I	Gallic acid derivate	21.70 (0.05)	483/-	275	x	x	x	x	x	x
42	Cyanidin O-hexoside I	Cyanidin derivate	21.73	-/449	279, 517	-	-	x	-	-	-
43	O-Methyl cyanidinO(2''galloyl)-galactoside	Cyanidin derivate	21.89	-/615	278, 518	-	-	x	-	-	-
44	Galloyl hexoside I	Gallic acid derivate	22.20 (0.11)	331/-	275	x	-	x	-	-	-
45	Cyanidin O-hexoside II	Cyanidin derivate	22.22	-/449	274, 516	-	-	x	-	-	-
46	Di-galloyl hexoside II	Gallic acid derivate	22.59	483/-	276	x	-	-	-	-	-
47	Di-galloyl hexoside III	Gallic acid derivate	22.70 (0.08)	483/-	276	x	x	x	x	x	x
48	O-Methyl-cyanidin O(2''galloyl)-galactoside II	Cyanidin derivate	22.90 (0.06)	-/615	278, 516	x	x	x	x	-	x
49	Galloylpyrogallol	Gallic acid derivate	23.20 (0.11)	277/-	238	x	x	-	-	-	x
50	Galloyl hexoside II	Gallic acid derivate	23.37 (0.02)	331/-	275	x	-	x	x	-	-
51	O-galloylnorbergenin I	Gallic acid derivate	23.48 (0.11)	-/467	276	x	-	x	x	-	-
52	Digalloyl hexoside malic acid I	Gallic acid derivate	23.58	599/-	276	-	x	-	-	-	-
53	Di-galloyl hexoside IV	Gallic acid derivate	23.63 (0.15)	483/-	276	x	-	x	x	x	-
54	Cyanidin O-hexoside III	Cyanidin derivate	23.74 (0.02)	-/449	279, 518	-	x	x	x	-	-
55	Tri-galloyl-hexoside I	Gallic acid derivate	23.80 (0.14)	635/-	276	x	x	x	x	-	-
56	O-Methyl-cyanidin O(2''galloyl)-galactoside III	Cyanidin derivate	23.89	-/615	278, 516	-	-	x	-	-	-
57	Galloyl hexoside III	Gallic acid derivate	24.21 (0.01)	331/-	275	x	-	x	x	x	-
58	Di-galloyl hexoside V	Gallic acid derivate	24.30 (0.01)	483/-	274	-	-	x	x	x	-
59	O-galloylnorbergenin II	Gallic acid derivate	25.44 (0.24)	-/467	277	x	-	-	x	-	-
60	Digalloyl hexoside malic acid II	Gallic acid derivate	25.52 (0.13)	599/-	277	x	x	x	x	-	-
61	Trigalloyllevoglucosan I	Gallic acid derivate	25.67 (0.10)	-/619	278	x	x	x	x	-	x
62	Digalloyl hexoside malic acid III	Gallic acid derivate	26.48 (0.12)	599/-	277	x	x	x	x	-	-
63	Digalloyl hexoside VI	Gallic acid derivate	26.60 (0.16)	483/-	274	x	x	x	x	x	x
64	Tri-galloyl-hexoside II	Gallic acid derivate	26.80 (0.08)	635/-	276	x	x	x	x	-	x
65	O-galloylnorbergenin III	Gallic acid derivate	27.43 (0.11)	-/467	277	x	x	x	x	-	x
66	O-galloylnorbergenin IV	Gallic acid derivate	27.65 (0.13)	-/467	277	x	-	x	x	-	x
67	Tri-galloyl-hexoside III	Gallic acid derivate	27.83 (0.11)	635/-	276	x	x	x	x	-	x
68	Di-O-galloyl-hexahydroxydiphenoyl-scyllo-quercitol I	Gallic acid derivate	27.95 (0.10)	-/771	278	x	-	-	-	-	x
69	Digalloyl hexoside VII	Gallic acid derivate	28.62 (0.13)	483/-	275	x	x	x	x	-	-
70	Tri-galloyl-hexoside IV	Gallic acid derivate	29.73 (0.14)	635/-	276	x	-	x	x	-	-
71	Di-O-galloyl-hexahydroxydiphenoyl-scyllo-quercitol II	Gallic acid derivate	29.91 (0.04)	-/771	278	-	x	x	x	-	-
72	O-galloylnorbergenin V	Gallic acid derivate	30.62 (0.12)	-/467	275	x	x	x	x	x	x
73	Tri-galloyl-hexoside V	Gallic acid derivate	31.80	635/-	276	x	-	-	-	-	-

			(0.02)								
74	Cyanidin O-(2"-galloyl) galactoside	Cyanidin derivate	31.85 (0.05)	-/601	279, 517	x	-	x	x	-	-
75	Tetra-O-galloylhexoside	Gallic acid derivate	31.89 (0.01)	787/-	277	-	-	x	x	-	-
76	O-galloylnorbergenin VI	Gallic acid derivate	32.58 (0.06)	-/467	276	-	-	x	x	-	-
77	Trigalloyllevoglucosan II	Gallic acid derivate	32.63 (0.05)	-/619	276	-	-	x	x	-	-
78	Tri-galloyl-hexoside VI	Gallic acid derivate	32.75 (0.03)	635/-	276	x	x	x	-	-	x
79	Trigalloyllevoglucosan III	Gallic acid derivate	33.73 (0.04)	-/619	276	-	-	x	x	-	-
80	Trigalloyllevoglucosan IV	Gallic acid derivate	34.74 (0.13)	-/619	276	x	-	x	-	-	-
81	Tri-galloyl-hexoside VII	Gallic acid derivate	35.68 (0.08)	635/-	276	x	x	x	x	x	x
82	Tri-galloyl-hexoside VIII	Gallic acid derivate	35.72 (0.05)	635/-	276	-	-	x	x	-	-
83	Di-O-galloyl-hexahydroxydiphenoyl-scyllo-quercitol III	Gallic acid derivate	38.83 (0.09)	-/771	278	x	x	x	x	-	-