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HPLC–DAD–ESI-MS/MS screening of bioactive components from *Rhus coriaria* L. (Sumac) fruits

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ABSTRACT

Rhus coriaria L. (sumac) is an important crop widely used in the Mediterranean basin as a food spice, and also in folk medicine, due to its health-promoting properties. Phytochemicals present in plant foods are in part responsible for these consequent health benefits. Nevertheless, detailed information on these bioactive compounds is still scarce. Therefore, the present work was aimed at investigating the phytochemical components of sumac fruit epicarp using HPLC–DAD–ESI-MS/MS in two different ionisation modes. The proposed method provided tentative identification of 211 phenolic and other phyto-constituents, most of which have not been described so far in *R. coriaria* fruits. More than 180 phytochemicals (tannins, (iso)flavonoids, terpenoids, etc.) are reported herein in sumac fruits for the first time. The obtained results highlight the importance of *R. coriaria* as a promising source of functional ingredients, and boost its potential use in the food and nutraceutical industries.

1. Introduction

Sumac, *Rhus coriaria* L. (Anacardiaceae), is a wild edible plant growing in the Mediterranean region, has long been used as a seasoning spice, either in pure form or in combination with other spices (Ali-Shtayeh, & Jamous, 2008), sauce, appetizer, drink, and as a souring agent in food recipes. *R. coriaria* L. is an important and the most widely used species of the genus *Rhus* in the Mediterranean region since antiquity. Recently, the consumption of sumac fruits has been increasing around the world as an important economic crop (Kizil, & Turk, 2010).

In folk medicine and traditional Arabic Palestinian herbal medicine, this plant has been used in the treatment of cancer, stroke, diarrhoea, hypertension, dysentery, haematemesis, ophthalmia, stomach ache, diuresis, diabetes, atherosclerosis, measles, smallpox, liver disease, aconuresis, teeth and gum ailments, headaches, animal bites, dermatitis, and liver disease (Ali-Shtayeh, & Jamous, 2008; Shafiei, Nobakht, & Moazzam, 2011). Furthermore, *R. coriaria* is known to possess non-mutagenic, fever-reducing, DNA protective, antiseptic, antifungal, antibacterial, antioxidant, anti-ischaemic, hypouricemic, hypoglycaemic, and hepatoprotective properties, which support its traditional uses (Anwer et al., 2013; Chakraborty et al., 2009; Madihi et al., 2013; Shafiei et al., 2011).

Among 56 Palestinian plants tested, sumac was found to have the greatest antimicrobial effect against *Probionibacterium acnes* (*MIC* 6 mg/ml, *MBC* 6 mg/ml), *Staphylococcus aureus* (*MIC* 4 mg/ml, *MBC* 6 mg/ml), *Escherichia coli* (*MIC* 6 mg/ml, *MBC* 8 mg/ml) and *Pseudomonas aeruginosa* (*MIC* 4 mg/ml and *MBC* 6 mg/ml) (Ali-Shtayeh, Al-Assali, & Jamous, 2013).

The literature lacks detailed information on *R. coriaria* chemical composition. Previous works have reported sumac to contain phenolic compounds, such as hydrolysable tannins, anthocyanins and also organic acids such as malic and citric acids (Kosar, Bozan, Temelli, & Baser, 2007; Kossah, Nsabimana, Zhang, & Chen, 2010). Interestingly, the acidic and astringent tastes, may be due to indigenous organic acids (mainly, malic acid) and tannins. Many compounds have been identified from different parts of sumac, such as phenolics, organic acids, proteins, fibre, volatile oils, fatty acids, vitamins, and minerals (Anwer et al., 2013; Özcan, & Haciseferogullari, 2004). Only a few studies have been carried out on the chemical composition of *R. coriaria* leaves (Regazzoni et al., 2013; Van Loo, De Bruyn, & Verzele, 1988) and little is known about the phytochemical composition of the plant's fruit epicarps.

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Although *R. coriaria* is a particularly rich source of phenolic compounds (Kossah et al., 2010), the phenolic constituents of sumac fruit's epicarp remains so far incompletely investigated. Thus, detailed and extended profiling of the phytochemicals of sumac fruits using high sensitive tools is necessary. Consequently, suitable methods need to be established for the identification of phytochemicals in plant food matrices (Abu-Reidah, Contreras, Arráez-Román, Fernández-Gutiérrez, & Segura-Carretero, 2014). Mass spectrometry coupled to high-performance liquid chromatography (HPLC–MS) has been increasingly used in the structural characterisation of complex matrices and has proved to be the tool of choice to identify phenolic compounds (Abu-Reidah, Arráez-Román, Lozano-Sánchez, Segura-Carretero, & Fernández-Gutiérrez, 2013; Abu-Reidah, Arráez-Román, Segura-Carretero, & Fernández-Gutiérrez, 2013; Lee, Zweigenbaum, & Mitchell, 2013).

Therefore, the objective of the present study was to investigate the phytochemical composition of hydro-methanolic extracts of *R. coriaria* fruits cultivated in Palestine, by using high-performance liquid chromatography-diode array detector-hyphenated with tandem mass spectrometry (HPLC–DAD–ESI-MS/MS) as a potent analytical technique.

2. Materials and methods

2.1. Chemicals

Acetonitrile and methanol of analytical or HPLC grade were purchased from Labscan (Dublin, Ireland). Acetic acid of analytical grade (assay >99.5%) was purchased from Fluka (Switzerland). Water was purified by using a Milli-Q system (Millipore, Bedford, USA).

2.2. Sample preparation

Sumac is commercially obtainable in local markets in ready-to-use ground form. In our present study, for quality control considerations, sumac samples were harvested in their mature stage from the wild habitat mountains of Nablus (Qusra village) in summer of 2012 and were identified by Prof. Mohammad S. Ali-Shtayeh from BERC. Collected sumac samples were dried, and then epicarps of *R. coriaria* L. fruits were liberated from kernels and ground into powder using a household mill and stored at room temperature until they were used for extraction.

2.3. Extraction of phenolic compounds

The extraction procedure was performed following Abu-Reidah, Arráez-Román, Segura-Carretero, and Fernández-Gutiérrez (2013), with some modifications. Portions of the dried and ground Sumac fruit epicarps (0.5 g) were extracted using methanol (80% v/v) and sonicated for 30 min at room temperature. The mixture was centrifuged for 15 min at 3800*g* and the supernatant was collected into a round-bottom flask. The extraction process was repeated three times. To get rid of the non-polar fraction that could be extracted by 80% methanol, the supernatant was mixed twice with 5 mL of *n*-hexane. The solvent was evaporated using a rotary evaporator under vacuum at 40 °C and the dry residue was dissolved in aqueous methanol. Finally, the extract was centrifuged again and the supernatant was filtered through a 0.2-μm syringe filter and stored at −20 °C until analysis.

2.4. HPLC–DAD/QTOF-MS analysis

Separation of phenolic compounds from sumac extract was performed on an Agilent 1200 series Rapid Resolution LC (Agilent Technologies, Santa Clara, CA) consisting of a vacuum degasser, an auto-sampler, a binary pump and diode-array detector (DAD). This instrument was equipped with an Agilent Zorbax C18 column (4.6 × 150 mm, 5 μm) from Agilent Technologies. Acidified water (0.5% acetic acid, v/v) and acetonitrile were used as mobile phases A and B, respectively. The gradient was programmed as follows: 0 min, 0% B; 20 min, 20% B; 30 min, 30% B; 40 min, 50% B; 50 min, 75% B; 60 min, 100% B; 62 min 0% B, and finally, the initial conditions were held for 8 min as a re-equilibration step. The flow rate was set at 0.80 mL/min throughout the gradient. The flow from the HPLC system into the ESI-Q-TOF-MS detector was 0.2 mL/min. The injection volume was 10 μL and the column temperature was maintained at 25 °C.

The HPLC system was coupled to a quadrupole-time-of-flight (micrOTOF-Q™, Bruker Daltonik GmbH, Bremen, Germany) orthogonal accelerated Q-TOF mass spectrometer, equipped with an electrospray ionisation source (ESI). Parameters for analysis were set using negative and positive ion modes, with spectra acquired over a mass range from *m*/*z* 50 to 1100. The optimum values of the ESI-MS parameters were: capillary voltage, −3.5 and +4.0 kV; drying gas temperature, 190 °C; drying gas flow, 9.0 L/min; nebulising gas pressure, 29 psi; collision RF, 150 Vpp; transfer time 70 μs, and pre-pulse storage, 5 μs. Moreover, automatic MS/MS experiments were performed adjusting the collision energy values as follows: *m*/*z* 100, 20 eV; *m*/*z* 500, 30 eV; *m*/*z* 1000, 35 eV, using nitrogen as collision gas. The MS data were processed through Data Analysis 4.0 software (Bruker Daltonics, Bremen, Germany) which provided a list of possible elemental formulas by using the Generate Molecular Formula™ editor. The editor uses a CHNO algorithm, which provides standard functionalities, such as maximum/minimum elemental range, and a sophisticated comparison of the theoretical with the measured isotope pattern (mSigma value), for increasing the confidence in the suggested molecular formula. The widely accepted accuracy for confirmation of elemental compositions has been established as 5 ppm.

At some stage in the HPLC method development, an external apparatus calibration was performed using a Cole Palmer syringe pump (Vernon Hills, IL) directly linked to the interface, passing a solution of sodium acetate. Using this method, an exact calibration curve based on numerous cluster masses each differing by 82 Da ($C_2H_3NaO_2$) was obtained. Due to the compensation of temperature drift in the Q-TOF, this external calibration provided accurate mass values for a complete run without the need for a dual sprayer set up for internal mass calibration.

3. Results and discussion

3.1. Characterisation of the phenolics and other phytochemical derivatives

3.1.1. General

Table 1 shows the list of 211 compounds tentatively identified through HPLC–DAD–ESI-MS/MS experiments along with their retention times (t_R), detected accurate mass (ionisation modes either negative and/or positive, molecular formula, error in ppm (between the mass found and the accurate mass) of each phytochemical, as well as the MS/MS fragment ions and the bibliographic references used in the characterisation process.

In the present work, a qualitative analysis of the phenolic composition from the hydro-methanol extract of sumac fruits (epicarps) has been carried out using HPLC–DAD–ESI-MS/MS in negative and positive ionisation modes. The method was used to detect and characterise 211 phytochemical compounds, of which 188 were tentatively characterised for the first time in sumac (*R. coriaria*) fruits. Fig. 1A–C correspond to the base peak

Table 1
Phytochemical compounds detected and characterised in *R. coriaria* L. fruits by using HPLC–DAD/QTOF-MS in positive and negative ionisation modes.

Peak No.	Tentative assignment	t_R (min.)	$[M+H]^+$ (m/z)	$[M-H]^-$ (m/z)	Error (ppm)	mSigma	Molecular formula	MS2/MS fragment ions[b]	Reference
1	Quinic acid I	2.35	193.0708	191.0566	−2.8	1.4	$C_7H_{12}O_6$	173.0442(4), 109.0302(4)[a]	–
2	Malic acid I	2.69	–	133.0144	−1.2	1.8	$C_4H_6O_5$	115.0034(100)[a]	–
3	Malic acid hexoside I	2.91	–	295.0663	−1.3	7.6	$C_{10}H_{16}O_{10}$	133.0140(100),115.0030(63)[a]	Ley et al. (2006)
4	Malic acid hexoside II	3.16	–	295.0673	−0.8	7.3	$C_{10}H_{16}O_{10}$	133.0137(100),115.0030(41)[a]	Ley et al. (2006)
5	Malic acid hexoside III	3.36	–	295.0671	−0.2	0.9	$C_{10}H_{16}O_{10}$	133.0136(100), 115.0044(48)[a]	Ley et al. (2006)
6	Oxydisuccinic acid	4.32	251.0410	249.0262	−3.9	7.3	$C_8H_{10}O_9$	133.0141(100),115.0036(52)[a]	–
7	Malic acid II	4.37	135.0284	133.0143	−0.4	1.7	$C_4H_6O_5$	115.0024(100)[a]	–
8	Malic acid III	4.82	135.0281	133.0140	1.7	2.9	$C_4H_6O_5$	115.0024(100)[a]	–
9	Quinic acid II	5.71	193.0365	191.0555	3.5	1.8	$C_7H_{12}O_6$	173.0409(100)[a]	–
10	*O*-Succinoyl-di-*O*-caffeoylquinic acid	5.75	–	615.1383	−4.5	10	$C_{29}H_{28}O_{15}$	307.0675(15), 191.0569(100)[a]	–
11	Malic acid derivative	6.52	–	289.0569	−1.5	10.3	$C_{11}H_{14}O_9$	173.0466(26),155.0369(4), 133.0141(100),115.0034(22)[a]	–
12	Caftaric acid	6.75	–	311.0354	8.5	21	$C_{13}H_{12}O_9$	133.0135(100), 115.0031(37)[a]	–
13	Galloylhexose I	7.44	–	331.0647	4.3	3.8	$C_{13}H_{16}O_{10}$	169.0158(100)[a]	Fröhlich et al. (2002)
14	Galloylhexose II	9.09	–	331.0669	0.6	14.8	$C_{13}H_{16}O_{10}$	169.0148(100)[a]	Fröhlich et al. (2002)
15	Levoglucosan gallate I	9.50	315.0717	–	−2	1.3	$C_{13}H_{14}O_9$	153.0196(100),109.0270(6)	–
16	Galloylhexose III	9.86	–	331.0673	−0.8	13.4	$C_{13}H_{16}O_{10}$	271.0470(100),211.0255(47), 169.0142(55)[a]	Fröhlich et al. (2002)
17	Levoglucosan gallate II	10.68	315.0730	–	−6.1	7.5	$C_{13}H_{14}O_9$	153.0186(100),125.0219(6), 109.0252(2)	–
18	Galloylhexose IV	11.00	–	331.0671	−0.1	0.3	$C_{13}H_{16}O_{10}$	271.0462(100),211.0252(46), 169.0144(38)[a]	Fröhlich et al. (2002)
19	O-galloylnorbergenin i	11.01	467.0803	–	3.7	7.2	$C_{20}H_{18}O_{13}$	171.0278(2),153.0184(100)	–
20	Digalloyl-hexoside I	11.40	–	483.0772	1.8	4.7	$C_{20}H_{20}O_{14}$	331.067(25), 169.0143(56)[a]	Fröhlich et al. (2002)
21	Galloylhexose derivative I	11.42	–	505.0606	3.5	10.3	$C_{22}H_{18}O_{14}$	445.0404(6), 331.0665(6), 169.0102(10)[a]	–
22	*O*-galloylnorbergenin ii	11.54	467.0816	–	1	13	$C_{20}H_{18}O_{13}$	171.0291(2),153.0181(100)	–
23	Digalloyl-hexoside II	11.92	–	483.0773	1.2	1.8	$C_{20}H_{20}O_{14}$	331.0671(20),313.0560(6), 169.0144(52)[a]	Fröhlich et al. (2002)
24	Galloylhexose derivative II	11.94	–	505.0625	−0.2	13.4	$C_{22}H_{18}O_{14}$	331.0650(9), 169.0134(11)[a]	–
25	Protocatechuic acid hexoside	12.21	–	315.0717	1.5	10.1	$C_{13}H_{16}O_9$	153.0169(50), 152.0108(100), 109.0286(14), 108.0215(39)[a]	–
26	Gallic acid dihexose	12.56	–	493.1191	1.5	41.8	$C_{19}H_{26}O_{15}$	313.0561(100)[a]	–
27	Galloylhexose malic acid I	12.73	–	447.0777	0.8	8.2	$C_{17}H_{20}O_{14}$	331.0666(100),271.0481(10), 169.0153(14)[a]	–
28	Galloylhexose V	12.86	–	331.0672	−0.5	7.1	$C_{13}H_{16}O_{10}$	169.0146(100),125.0244(11)[a]	Fröhlich et al. (2002)
29	Galloylhexose malic acid II	13.00	–	447.0782	−0.4	4.8	$C_{17}H_{20}O_{14}$	331.0673(100),169.0147(19), 133.0146(6)[a]	–
30	Unknown	13.33	309.0632	307.0469	−3.3	7.5	$C_{14}H_{12}O_8$	289.0339(50), 245.0457(35), 201.0571(100)[a]	–
31	Protocatechoic acid	13.47	–	153.0194	−0.6	4.1	$C_7H_6O_4$	109.0293(100)[a]	Shabana et al. (2011)
32	Galloylshikimic acid I	13.49	–	325.0567	−0.6	2.4	$C_{14}H_{14}O_9$	169.0145(100),153.0200(13), 125.0244(20)[a]	–
33	Digalloyl-hexose-malic acid I	13.55	–	599.0901	−2	14.4	$C_{24}H_{24}O_{18}$	483.0794(48),465.0621(6), 447.0773(8),313.0548(3), 169.0142(22)[a]	–
34	Gallic acid hexose derivative	13.62	–	487.1082	2.2	27	$C_{20}H_{24}O_{14}$	331.0618(28),169.0152(70)[a]	–
35	Syringic acid hexoside	13.77	–	359.0977	1.7	12.8	$C_{15}H_{20}O_{10}$	197.0425(7)[a]	–
36	Gallic acid *O*-malic acid	13.80	–	285.0261	−3.1	1.8	$C_{11}H_{10}O_9$	169.0153(5),133.0141(100)[a]	Zhang et al. (2004)
37	Galloylshikimic acid II	13.94	–	325.0572	−2.2	5.4	$C_{14}H_{14}O_9$	169.0152(100),125.0236(14)[a]	–
38	Digalloyl-hexose malic acid II	14.26	–	599.0891	−0.1	11.4	$C_{24}H_{24}O_{18}$	483.0779(39),447.0756(21), 313.0680(1),169.0146(19)[a]	–
39	Unknown	14.46	583.0937	–	−1.3	14.1	$C_{24}H_{22}O_{17}$	171.0332(3),154.0203(9), 127.0371(13),109.0265(6), 97.0286(21)	–
40	Galloylquinic acid I	14.71	–	343.0691	−5.8	45.8	$C_{14}H_{16}O_{10}$	191.0626(12), 169.0156(83)[a]	–
41	*O*-galloylnorbergenin iii	15.04	467.0828	–	−1.7	31.4	$C_{20}H_{18}O_{13}$	153.0191(100)	–
42	Digalloyl-hexose malic acid III	15.35	–	599.0881	1.5	5.2	$C_{24}H_{24}O_{18}$	599.0875(100),483.0771(12), 447.0772(14),169.0143(11)[a]	–
43	Coumaryl-hexoside	15.77	–	325.0924	1.5	10.8	$C_{15}H_{18}O_8$	163.0398(100), 119.0491(60)[a]	–
44	Digalloyl-hexoside III	16.10	485.0949	483.0793	−2.6	12	$C_{20}H_{20}O_{14}$	423.0570(37), 331.0665(12), 169.0143(17)[a]	Fröhlich et al. (2002)
45	*O*-galloylnorbergenin iv	16.25	476.0837	–	−3.6	11.8	$C_{20}H_{18}O_{13}$	303.0561(20),153.0193(100)	–
46	Digalloyl-hexoside IV	16.49	485.0809	483.0774	1.2	4.9	$C_{20}H_{20}O_{14}$	423.0581(3), 331.0699(6), 169.0149(25)[a]	Fröhlich et al. (2002)
47	Galloylquinic acid II	16.62	–	343.0675	−1.3	16.6	$C_{14}H_{16}O_{10}$	191.0570(33), 169.0139(100)[a]	–
48	Trigalloyllevoglucosan I	16.67	619.0961	–	−5	2.2	$C_{27}H_{22}O_{17}$	153.0183(100),109.0309(1)	Chen, and Bergmeier (2011)

(*continued on next page*)

Table 1 (*continued*)

Peak No.	Tentative assignment	t_R (min.)	$[M+H]^+$ (*m/z*)	$[M-H]^-$ (*m/z*)	Error (ppm)	mSigma	Molecular formula	MS2/MS fragment ions[b]	Reference
49	Digalloyl-hexose malic acid IV	16.68	–	599.0884	1	5.5	$C_{24}H_{24}O_{18}$	483.0784(40), 447.0757(6), 331.0664(5), 313.0537(2), 169.0138(18)[a]	–
50	Kaempferol hexoside or Luteolin hexoside I	16.92	449.1048	–	6.8	65	$C_{21}H_{20}O_{11}$	287.0571(100)	Buziashvili, Komissarenko, and Kolesnikov (1970) and Shrestha, et al. (2012)
51	Tri-galloyl-hexoside I	16.94	637.1110	635.0896	−0.9	4.1	$C_{27}H_{24}O_{18}$	483.0759(23), 465.0699(9), 169.0128(9)[a]	Regazzoni et al. (2013)
52	Penstemide	17.16	–	443.1917	1.3	7.1	$C_{21}H_{32}O_{10}$	101.0229(2)[a]	Rodríguez-Pérez et al. (2013)
53	Digallic acid I	17.18	323.0403	321.0260	−2.4	6.4	$C_{14}H_{10}O_9$	169.0139(100), 125.0240(18)[a]	El Sissi et al. (1972)
54	Digalloyl-hexoside V	17.50	–	483.0775	1.1	3.5	$C_{20}H_{20}O_{14}$	331.0681(4), 169.0144(19)[a]	Fröhlich et al. (2002)
55	Kaempferol hexoside or Luteolin hexoside II	17.55	449.1082	–	−0.9	4.7	$C_{21}H_{20}O_{12}$	287.0576(100)	Buziashvili, Komissarenko, and Kolesnikov(1970) and Shrestha et al. (2012)
56	*O*-galloylnorbergenin v	17.75	467.0826	–	−1.1	15.8	$C_{20}H_{18}O_{13}$	153.0187(100)	–
57	Methyl gallate	18.24	185.0441	183.0302	−1.5	1.7	$C_8H_8O_5$	168.0076(28), 140.0112(64), 124.0170(39)[a]	Shabana et al. (2011)
58	Trigalloyllevoglucosan II	18.40	619.0945	–	−2.4	3.3	$C_{27}H_{22}O_{17}$	303.0531(3),153.0180(100)	Chen, and Bergmeier (2011)
59	Tri-galloyl-hexoside II	18.57	637.1106	635.0886	0.6	2.7	$C_{27}H_{24}O_{18}$	331.0699(1), 169.0128(8)[a]	Regazzoni et al. (2013)
60	Digallic acid II	18.71	323.0408	321.0257	−1.1	2.7	$C_{14}H_{10}O_9$	169.0164(100),125.0243(18)[a]	El Sissi et al. (1972)
61	Coumaric acid	18.72	–	163.0403	−1.3	3.9	$C_9H_8O_3$	119.0507(100)[a]	Min-Young, Ill-Min, Deog-Cheon, and Hee-Juhn (2009)
62	Trigalloyllevoglucosan III	18.81	619.0950	–	−2.4	3.3	$C_{27}H_{22}O_{17}$	153.0186(100)	Chen, and Bergmeier (2011)
63	Galloylpyrogallol	18.82	279.0512	–	−4.5	5.8	$C_{13}H_{10}O_7$	153.0190(100)	–
64	Isorhamnetin hexoside I	18.94	479.1167	–	3.5	13	$C_{22}H_{22}O_{12}$	317.0671(100)	–
65	Apigenin glucoside I	18.96	433.1149	–	−4.6	13.4	$C_{21}H_{20}O_{10}$	271.0617(100)	Shabana et al. (2011)
66	Tri-galloyl-hexoside III	19.04	637.1100	635.0882	1.3	2	$C_{27}H_{24}O_{18}$	483.0774(7), 465.0658(4), 169.0147(3)[a]	Regazzoni et al. (2013)
67	Isorhamnetin hexoside II	19.14	479.1189	–	−1.1	7.6	$C_{22}H_{22}O_{12}$	317.0664(100)	–
68	Kaempferol-hexose malic acid I	19.16	565.1194	–	−1.1	14	$C_{25}H_{24}O_{15}$	287.0558(100)	Perestrelo et al. (2012)
69	Hydroxy-methoxyphenyl-*O*-(*O*-galloyl)-hexose	19.45	–	453.1053	−3.1	40.4	$C_{20}H_{22}O_{12}$	313.0573(15), 179.0414(9), 169.0153(13)[a]	–
70	Cyanidin-3-*O*-(2″galloyl)-galactoside	19.65	601.1186	599.1039	0.6	30	$C_{28}H_{24}O_{15}$	285.0405(100)[a]	Kirby et al. (2013)
71	Trigalloyllevoglucosan IV	20.23	619.0935	–	−0.9	3.4	$C_{27}H_{22}O_{17}$	153.0183(100)	Chen, and Bergmeier (2011)
72	Tri-galloyl-hexoside IV	20.37	–	635.0895	−0.8	4.4	$C_{27}H_{24}O_{18}$	483.0777(7), 465.0675(4), 169.0147(3)[a]	Regazzoni et al. (2013)
73	7-*O*-Methyl-delphinidin-3-*O*-(2″ galloyl)-galactoside I	20.38	631.1301	–	−1.3	17	$C_{29}H_{26}O_{16}$	317.0650(100), 233.0448(3), 153.0195(27)	Kirby et al. (2013)
74	Kaempferol-hexose malic acid II	20.39	565.1193	–	−0.8	41	$C_{25}H_{24}O_{15}$	287.0549(100)	Perestrelo et al. (2012)
75	7-*O*-Methyl-delphinidin-3-*O*-(2″ galloyl)-galactoside II	20.57	631.1304	–	−1.3	17	$C_{29}H_{26}O_{16}$	317.0665(100), 233.0425(2), 153.0183(10)	Kirby et al. (2013)
76	Spinochrome A	20.92	265.1465	263.0217	−7.4	13.2	$C_{12}H_8O_7$	245.0085(30), 235.0277(30), 219.0267(24), 207.0309(22), 191.0391(19)[a]	–
77	Apigenin-7-*O*-(6″-*O*-galloyl)-β-D-glucopyranoside	20.97	585.1241	–	6	20.6	$C_{28}H_{24}O_{14}$	271.0618(100), 153.0187(10)	Tian et al., 2010
78	*O*-Galloyl arbutin	21.04	425.1066	–	2.8	30.5	$C_{19}H_{20}O_{11}$	273.0707(4)	Shi & Zuo, (1992)
79	Coumaryl-hexose malic acid	21.06	–	441.1037	0.3	8.5	$C_{19}H_{22}O_{12}$	325.0926(13), 163.0405(100), 119.0509(5)[a]	–
80	Methyl-dihydroquercetin hexoside	21.64	–	479.1190	1	4.2	$C_{22}H_{24}O_{12}$	317.0701(26), 299.0574(100)[a]	–
81	7-*O*-Methyl-cyanidin-3-*O*-galactoside	21.66	463.1231	461.1090	−0.1	11.8	$C_{22}H_{22}O_{11}$	299.0562(61), 298.0480(100)[a]	Kirby et al. (2013)
82	Caffeoylquinic acid	21.88	355.1040	–	−4.6	48	$C_{16}H_{18}O_9$	193.0494(100)	–
83	Trigalloyllevoglucosan V	22.03	619.0959	–	−4.7	12	$C_{27}H_{22}O_{17}$	153.0183(100)	Chen, and Bergmeier (2011)
84	Chrysoriol-hexose	22.08	579.1361	–	−2.8	4.2	$C_{26}H_{26}O_{15}$	301.0705(100)	–

Table 1 (*continued*)

Peak No.	Tentative assignment	t_R (min.)	$[M+H]^+$ (m/z)	$[M-H]^-$ (m/z)	Error (ppm)	mSigma	Molecular formula	MS2/MS fragment ions[b]	Reference
	malic acid								
85	Myricetin hexose-malic acid I	22.13	–	595.1297	1.3	12.6	$C_{26}H_{28}O_{16}$	479.1180(100), 369.0832(29), 317.0687(7), 299.0570(34)[a]	–
86	Tri-galloyl-hexoside V	22.15	–	635.0888	0.2	12	$C_{27}H_{24}O_{18}$	465.0620(21), 483.0748(12), 169.0147(4)[a]	Regazzoni et al. (2013)
87	Eriodictyol hexoside or Dihydrokaempferol hexoside I	22.18	–	449.1087	0.5	21	$C_{21}H_{22}O_{11}$	287.0570(86), 269.0448(54), 259.0603(66)[a]	–
88	Ampeloptin	22.27	–	319.0470	−3.4	13.6	$C_{15}H_{12}O_8$	193.0153(100), 179.0005(35), 153.0181(45), 125.0251(68)[a]	–
89	Myricetin galloyl-hexoside	22.72	–	631.1306	−0.2	6.8	$C_{29}H_{28}O_{16}$	317.0675(100)[a]	–
90	7-*O*-Methyl-cyanidin-3-*O*-(2″galloyl)-galactoside	22.74	615.1358	613.1196	0.5	2.5	$C_{29}H_{26}O_{15}$	299.0568(100)[a]	Kirby et al. (2013)
91	Myricetin-hexose malic acid II	22.85	–	595.1303	0.2	16.5	$C_{26}H_{28}O_{16}$	479.1181(100), 369.0824(28), 317.0683(35), 299.0572(42)[a]	–
92	Di-*O*-galloyl-3,4-(S)-hexahydroxydiphenoyl protoquercitol I	23.00	619.0950	–	−3.3	8.1	$C_{27}H_{22}O_{17}$	301.0716(100)	Nishimura, Nonaka, and Nishioka (1984)
93	Di-*O*-galloyl-2,3-(S)-hexahydroxydiphenoyl-scyllo-quercitol II	23.05	771.1092	–	−6.8	4.8	$C_{34}H_{26}O_{21}$	153.0177(100)	Nishimura et al. (1984)
94	Tetra-*O*-galloylhexoside I	23.07	789.1208	787.1008	−1	4.9	$C_{34}H_{28}O_{22}$	635.0872(8), 169.0109(1)[a]	Regazzoni et al. (2013)
95	Eriodictyol xyloyl-deoxyhexose	23.41	–	565.1197	0.4	18.7	$C_{25}H_{26}O_{15}$	287.0553(76)[a]	–
96	Umbelliferone	23.46	163.0391	161.0241	2.2	9.4	$C_9H_6O_3$	133.0299(100), 117.0341(61), 105.0332(10)[a]	–
97	Trigalloyllevoglucosan VI	23.62	619.0945	–	−2.4	33	$C_{27}H_{22}O_{17}$	301.0713(37), 153.0182(100)	Chen, and Bergmeier (2011)
98	Isorhamnetin hexoside III	23.66	–	477.1030	1.7	32	$C_{22}H_{22}O_{12}$	314.0576(8),313.0561(50)[a]	–
99	Tetra-*O*-galloyl-scyllo-quercitol	23.74	731.1477	–	−3.2	2.8	$C_{33}H_{30}O_{19}$	301.0716(100),153.0179(7)	Nishimura et al. (1984)
100	Glycitein 7-*O*-glucoside	23.76	447.1282	–	0.8	23.7	$C_{22}H_{22}O_{10}$	285.0768(100)	–
101	Myricetin *O*-rhamnosylglucose	23.86	627.1577	625.1409	0.3	6.1	$C_{27}H_{30}O_{17}$	317.0311(3), 316.0198(5)[a]	Regazzoni et al. (2013)
102	Ampelopsin glucoside	23.88	–	481.0995	−1.6	16.7	$C_{21}H_{22}O_{13}$	319.0460(65), 301.0360(40), 193.0144(100)[a]	Yeom et al. (2003)
103	Quercetin glucoside I	24.09	465.1017	–	2.3	13.8	$C_{21}H_{20}O_{12}$	303.0512(100)	Regazzoni et al. (2013)
104	Myricetin-hexose malic acid III	24.11	597.1081	–	0.9	18.8	$C_{25}H_{24}O_{17}$	319.0454(100)	–
105	Myricetin-3-*O*-glucuronide	24.20	495.0766	493.0625	−0.2	3.2	$C_{21}H_{18}O_{14}$	317.0308(100)[a]	Regazzoni et al. (2013)
106	Myricitin derivative	24.21	–	515.0451	3.2	11	$C_{23}H_{16}O_{14}$	339.0125(23), 317.0307(100)[a]	–
107	Myricitin derivative	24.23	657.1317	–	5.9	19.8	$C_{27}H_{28}O_{19}$	319.0478(100)	–
108	Myricetin-3-*O*-glucoside	24.40	481.0970	479.0826	1.1	6.6	$C_{21}H_{20}O_{13}$	317.0291(28), 316.0243(76), 169.0144(26)[a]	Regazzoni et al. (2013)
109	Trigallic acid	24.43	–	473.0362	−0.2	2.4	$C_{21}H_{14}O_{13}$	321.0262(22), 169.0147(100)[a]	Nishimura et al. (1984)
110	Myricetin-hexose malic acid IV	24.48	597.1077	–	1.5	18.9	$C_{25}H_{24}O_{17}$	319.0466(100)	–
111	Trigalloyllevoglucosan VII	25.12	619.0945	–	−2.4	33	$C_{27}H_{22}O_{17}$	301.0707(3), 153.0185(100)	Chen, and Bergmeier (2011)
112	Benzoic acid, 3,4,5–trihydroxy-2-oxo-1,3-propanediyl ester	25.14	–	393.0449	3.6	41.9	$C_{17}H_{14}O_{11}$	317.0402(49), 241.0355(100), 169.0144(76), 125.0240(9)[a]	–
113	Tetra-*O*-galloylhexoside II	25.15	789.1224	787.0992	0.9	2.3	$C_{34}H_{28}O_{22}$	635.0871(5), 169.0130(1)[a]	Regazzoni et al. (2013)
114	Horridin	25.25	595.1669	–	−2	38	$C_{27}H_{30}O_{15}$	433.1152(48), 301.0714(100)	–
115	Pentagalloyl-hexoside I	25.39	941.1328	939.1081	3	9.5	$C_{41}H_{32}O_{26}$	787.1001(4), 617.0767(6), 465.0660(4), 393.0444(81), 317.0402(100), 241.0367(24), 169.0148(27)[a]	Regazzoni et al. (2013)
116	Trigalloyllevoglucosan VIII	25.47	619.0973	617.0833	−7.9	41.6	$C_{27}H_{22}O_{17}$	465.0710(6), 393.0458(73), 317.0407(100), 241.0356(22), 169.0150(33)[a]	Chen, and Bergmeier (2011)
117	Mingjinianuronide B	25.55	563.1402	–	−1.1	25.8	$C_{26}H_{26}O_{14}$	301.0720(100)	Tan and Zuo (1994)
118	Apiin I	25.74	565.1577	563.1385	3.7	13.0	$C_{26}H_{28}O_{14}$	443.1033(8),413.0890(100)[a]	Abu-Reidah et al. (2013)
119	Trigalloyllevoglucosan IX	25.77	619.0961	–	−5.1	6.7	$C_{27}H_{22}O_{17}$	301.0698(14),237.0422(4), 153.0186(100)	–
120	Apigenin neohesperidoside I	25.82	579.1710	–	−0.2	45.6	$C_{27}H_{30}O_{14}$	433.1151(100),271.0606(4)	Matsuda (1966)

(*continued on next page*)

Table 1 (*continued*)

Peak No.	Tentative assignment	t_R (min.)	$[M+H]^+$ (m/z)	$[M-H]^-$ (m/z)	Error (ppm)	mSigma	Molecular formula	MS2/MS fragment ions[b]	Reference
121	Quercetin-3-*O*-(6″-3-hydroxy-3-methylglutaroyl)-â-galactoside	25.84	593.1552	–	−8.5	45.0	$C_{27}H_{28}O_{15}$	301.0721(100)	Sari, Heikki, Sampo, and Ari (2006)
122	Spicoside E	25.86	615.1353	–	−1.3	168.3	$C_{29}H_{26}O_{15}$	303.0516(100),153.0196(70)	Albach, Grayer, Kite, and Jensen (2005)
123	Apiin II	25.97	565.1577	–	−4.4	8.9	$C_{26}H_{28}O_{14}$	433.1116(99),271.0643(6)	Abu-Reidah et al. (2013)
124	Rutin	26.01	611.1627	609.1441	3.3	6.1	$C_{27}H_{30}O_{17}$	303.0512(100)	Olchowik et al. (2012)
125	Pentagalloyl-hexoside II	26.19	941.1325	939.1095	1.4	37.1	$C_{41}H_{32}O_{26}$	787.1003(5),393.0445(42), 169.0154(2)[a]	–
126	Isovitexin	26.23	433.1116	–	3	37	$C_{21}H_{20}O_{10}$	415.1022(6),343.0762(10), 313.0719(100)	–
127	Petunidin-3-*O*-glucoside pyruvate	26.30	–	545.0892	8	30	$C_{21}H_{20}O_{12}$	463.0878, 316.0227(100)[a]	Sáenz-navajas et al. (2010)
128	Myricetin-3-*O*-rhamnoside	26.38	465.1027	–	0.1	5.6	$C_{21}H_{20}O_{12}$	319.0460(100)	Regazzoni et al. (2013)
129	Digalloyl-hexoyl-ellagic acid	26.43	767.1437	765.0955	−1.3	11.1	$C_{35}H_{26}O_{20}$	463.0869(25), 300.9994(100)[a]	Wu et al. (2013)
130	Ellagic acid	26.44	303.0158	–	−7.6	5.1	$C_{14}H_6O_8$	303.0149(42),285.0055(39), 275.0207(69),257.0087(100), 247.0288(35), 229.0161(51), 201.0187(33), 173.0241(12)	El Sissi et al. (1972)
131	Chrysoeriol-6-*O*-acetyl-4′-β-d-glucoside	26.51	505.1331	–	1.8	30.7	$C_{24}H_{24}O_{12}$	301.0732(100)	Chandrashekar et al. (2005)
132	Trigalloyllevoglucosan IX	26.53	619.0966	–	3.7	24.8	$C_{20}H_{26}O_{22}$	301.0692(2), 153.0187(100)	–
133	Quercetin-hexose malic acid I	26.56	581.1153	579.0984	1.3	7.2	$C_{25}H_{24}O_{16}$	463.0864(100), 301.0339(6)[a]	Shabana et al. (2011) and Regazzoni et al. (2013)
134	Eriodictyol hexoside or Dihydrokaempferol hexoside II	26.68	–	449.1076	2.9	59.3	$C_{21}H_{22}O_{11}$	287.0560(100), 151.0029(30)[a]	–
135	Quercetin glucoside II	26.71	465.1026	–	0.4	4.7	$C_{21}H_{20}O_{12}$	303.0511(100)	Regazzoni et al. (2013)
136	Quercetin glucuronide	26.88	479.0825	477.0670	0.9	6.6	$C_{21}H_{18}O_{13}$	301.0358(100)[a]	Al Sayed et al. (2010)
137	Kaempferol hexoside or Luteolin hexoside I	27.03	449.1086	447.0928	1.1	16.2	$C_{21}H_{20}O_{11}$	285.0415(50)[a]	Buziashvili et al. (1970)
138	Quercetin-hexose malic acid II	27.05	581.1151	579.0982	1.7	10	$C_{25}H_{24}O_{16}$	463.0879(100), 301.0360(9)[a]	Shabana et al. (2011) and Regazzoni et al. (2013)
139	Quercetin glucoside III	27.12	465.1028	–	−0.2	21.4	$C_{21}H_{20}O_{12}$	303.0514(100)	Regazzoni et al. (2013)
140	Pentagalloyl-hexoside III	27.13	941.1320	939.1096	1.4	34.5	$C_{41}H_{32}O_{26}$	769.0887(6), 617.0777(11), 447.0572(7), 393.0444(22), 317.0402(25), 169.0142(100)[a]	Regazzoni et al. (2013)
141	Kaempferol rutinoside I	27.45	595.1660	–	−0.4	52.6	$C_{27}H_{30}O_{15}$	287.0567(100)	Ding et al. (2009)
142	Kaempferol-hexose malic acid III	27.49	565.1208	563.1031	2.1	11.1	$C_{25}H_{24}O_{15}$	447.0930(100), 285.0409(4)[a]	Perestrelo et al. (2012)
143	Chrysoriol derivative	27.64	657.1482	–	−4.8	11.5	$C_{31}H_{28}O_{16}$	301.0726(100)	–
144	Mangiferitin	27.84	261.0394	259.0240	3.3	82.1	$C_{13}H_8O_6$	191.0312(30)[a]	–
145	Pentagalloyl-hexoside IV	27.86	939.1098	–	1.2	9.8	$C_{41}H_{30}O_{26}$	393.0376(1), 169.0142(100)	Regazzoni et al. (2013)
146	1,5-di-*O*-galloyl-3,4-(*S*)-hexahydroxydiphenoyl protoquercitol	27.89	771.1085	–	−5.9	4.8	$C_{34}H_{26}O_{21}$	153.0186(100)	Nishimura et al. (1984)
147	Myricetin-rhamnose malic acid	28.16	581.1149	579.0990	2.6	19	$C_{25}H_{24}O_{16}$	463.0873(100), 316.0223(3), 301.0345(1)[a]	–
148	Dihydroxybenzoic acetate-digallate I	28.18	–	545.0544	5.3	42.7	$C_{24}H_{18}O_{15}$	393.0454(100), 317.0408(11), 169.0136(3)[a]	Hahn and Fekete, 1954
149	Pentagalloyl-hexoside V	28.30	941.1317	939.1088	2.3	9.5	$C_{41}H_{32}O_{26}$	393.0443(22), 169.0135(3)[a]	Regazzoni et al. (2013)
150	Kaempferol rutinoside II	28.31	595.1640	–	2.9	15.7	$C_{27}H_{30}O_{15}$	287.0581(100), 153.0223(8)	Ding et al. (2009)
151	Methyl digallate I	28.33	–	335.0403	−0.4	7.2	$C_{15}H_{12}O_9$	183.0302(100)[a]	Shabana et al. (2011)
152	Kaempferol hexoside or Luteolin hexoside II	28.38	449.1086	447.0930	0.5	9.6	$C_{21}H_{20}O_{11}$	285.0381(29), 284.0318(77)[a]	Buziashvili et al. 1970 and Shrestha et al. (2012)
153	Quercetin arabinoside	28.40	435.0942	433.0760	3.6	18.8	$C_{20}H_{18}O_{11}$	301.0324(39), 300.0261(100)[a]	Buziashvili et al. (1970)
154	Apigenin neohesperidoside II	28.43	579.1717	577.1534	5.1	37.5	$C_{27}H_{30}O_{14}$	269.0452(44)[a]	Matsuda (1966)
155	Methyl digallate II	28.75	337.0578	335.0412	−1	1.8	$C_{15}H_{12}O_9$	183.0303(100)[a]	Shabana et al. (2011)
156	Kaempferol-hexose malic acid IV	28.96	565.1210	563.1010	5.8	21.2	$C_{25}H_{24}O_{15}$	447.0904(100),285.0426(12)[a]	Perestrelo et al. (2012)
157	Kaempferol 3-glucuronide	29.25	463.0902	–	−6.7	10.0	$C_{21}H_{18}O_{12}$	287.0574(100)	Al Sayed et al. (2010)

Table 1 (*continued*)

Peak No.	Tentative assignment	t_R (min.)	$[M+H]^+$ (m/z)	$[M-H]^-$ (m/z)	Error (ppm)	mSigma	Molecular formula	MS2/MS fragment ions[b]	Reference
158	Quercetin rhamnoside	29.30	449.1097	447.0925	1.9	3.5	$C_{21}H_{20}O_{11}$	301.0350(100)[a]	Regazzoni et al. (2013)
159	Dihydroxybenzoic acetate-digallate II	29.32	–	545.0546	5	32.1	$C_{24}H_{18}O_{15}$	469.0489(100), 393.5454(21), 169.0144(44)[a]	Hahn and Fekete, 1954
160	Hexagalloyl-hexoside	29.42	–	1091.1192	2.4	3.9	$C_{48}H_{36}O_{30}$	939.0980(1), 769.0780(12), 617.0649, 393.0443(39), 169.0140(34)[a]	Regazzoni et al. (2013)
161	Kaempferol-hexose malic acid V	29.58	565.1152	–	−3.7	11.0	$C_{25}H_{24}O_{15}$	287.0549(100)	Perestrelo et al. (2012)
162	Dihydroxybenzoic acetate-digallate III	29.62	–	545.0556	3.2	38.7	$C_{24}H_{18}O_{15}$	469.0493(100), 393.5466(15), 169.0147(34)[a]	Hahn and Fekete, 1954
163	Apigenin glucuronide	29.90	447.0928	445.0765	−1.5	143.0	$C_{21}H_{20}O_{11}$	271.0613(100)[a]	–
164	Apigenin glucoside II	29.92	433.1143	431.0953	−3.2	62.8	$C_{21}H_{22}O_{10}$	271.0618(100)[a]	Shabana et al. (2011)
165	Camellianin A	30.81	621.1855	–	−6.7	28	$C_{29}H_{32}O_{15}$	433.1153(100), 313.0726(63), 271.0648(8)	–
166	Genistein-hexose malic acid	31.08	549.1265	–	1.7	177.0	$C_{25}H_{24}O_{14}$	271.0605(100)	–
167	Galloyl-valoneic acid bilactone	31.11	623.1887	621.0596	−2.4	26.6	$C_{22}H_{22}O_{21}$	469.5507(46), 393.5454(2), 169.0139(3)[a]	Sanz et al. (2010)
168	Quercetin-rhamnose malic acid I	31.13	565.1089	563.1024	3.3	4.2	$C_{25}H_{24}O_{15}$	447.0917(100), 301.0354(10)[a]	–
169	Quercetin-rhamnose malic acid II	31.40	565.0903	–	−4.4	9.0	$C_{28}H_{20}O_{13}$	303.0520(100)	–
170	Myricetin	31.41	319.0457	317.0300	0.8	28.3	$C_{15}H_{10}O_8$	287.0218(38), 271.0222(4), 178.9985(85), 151.0036(87), 137.0240(34)[a]	Regazzoni et al. (2013)
171	Dihydroxybenzoic acetate-digallate IV	31.42	–	545.0542	5.7	46.3	$C_{24}H_{18}O_{15}$	393.0465(100), 169.0151(94)[a]	Hahn and Fekete, 1954
172	Quercetin glucoside IV	31.48	465.1026	–	0.3	9.3	$C_{21}H_{20}O_{12}$	303.0520(100), 129.0545(32)	Regazzoni et al. (2013)
173	Quercetin-hexose malic acid III	31.62	581.1151	–	−2.4	45.4	$C_{25}H_{24}O_{16}$	303.0691(100)	–
174	Myricitrin *O*-gallate	31.80	617.1164	615.0988	0.6	30.5	$C_{28}H_{24}O_{16}$	469.5507(33), 393.0439(10), 317.0299(2), 169.0134(3)[a]	Moharram et al. (2006)
175	Kaempherol rhamnoside	31.92	433.1153	–	−5.6	15.7	$C_{21}H_{20}O_{10}$	287.0571(100)	Shabana et al. (2011)
176	Quercetin I	32.14	-	301.0346	2.5	12.8	$C_{15}H_{10}O_7$	217.0060(2), 191.0389(1), 151.0054(2)[a]	Shabana et al. (2011) and Kosar et al. (2007)
177	Quercetin-hexose malic acid IV	32.20	581.1132	–	0.8	46.4	$C_{25}H_{24}O_{16}$	303.0524(100)	–
178	Isorhamentin hexose-malic acid	33.60	595.1376	–	−13	49	$C_{26}H_{26}O_{16}$	317.0700(100)	–
179	Kaempferol rhamnose-malic acid	33.80	–	547.1060	6.1	31.0	$C_{25}H_{24}O_{14}$	431.0974(100), 285.0396(43)[a]	–
180	Homoprotocatechuic acid	34.15	169.0497	–	−1.2	6.0	$C_8H_8O_4$	141.0615(36), 126.0261(56), 108.0218(100), 95.0393(50)	–
181	Unknown	34.52	–	593.1327	−4.4	31.3	$C_{30}H_{26}O_{13}$	513.1687(18), 441.1239(36)[a]	–
182	Quercitrin 2″ *O*-gallate	34.77	–	599.1008	5.8	25.0	$C_{28}H_{24}O_{15}$	301.0358(100)[a]	Moharram et al. (2006)
183	Isorhamnetin hexoside IV	34.81	–	477.1012	5.6	14.7	$C_{22}H_{22}O_{12}$	315.0506(58), 314.0438(80)[a]	–
184	Di-benzopyrano-furanacetic acid deriv.	35.31	–	515.0429	7.4	52.0	$C_{23}H_{16}O_{14}$	469.0477(34), 384.0422(42), 303.0118(38), 169.0129(100)[a]	–
185	Luteolin	36.30	287.0562	285.0406	−0.6	7.1	$C_{15}H_{10}O_6$	217.0486(2), 199.0418(2), 175.0387(1), 151.0038(3), 133.0288(3)[a]	Kim, Chung, Choi, and Park (2009)
186	Quercetin II	36.57	303.0520	301.0352	0.6	2.3	$C_{15}H_{10}O_7$	273.0399(13), 229.0504(3), 178.9983(48), 151.0029(100), 121.0292(15)[a]	Shabana et al. (2011) and Kosar et al. (2007)
187	Quercetin dimer	36.59	–	603.0760	3.4	25	$C_{30}H_{20}O_{14}$	301.0354(100)[a]	–
188	Isorhamnetin hexoside V	36.60	–	477.1030	1.8	22.4	$C_{22}H_{22}O_{12}$	315.0517(100), 271.0590(26)[a]	–
189	Afzelin *O*-gallate	37.11	585.1265	583.1072	3.7	17.2	$C_{28}H_{24}O_{14}$	297.0596(40), 285.0411(100), 169.0108(7)[a]	Moharram et al. (2006)
190	Butein	38.91	273.0773	–	−5.7	13.0	$C_{15}H_{12}O_5$	142.9542(28), 163.0369(16), 137.0232(100)	Lee et al. (2008)
191	Chrysoriol	40.16	301.0692	–	3.0	49.2	$C_{16}H_{12}O_6$	286.0470(100), 258.0545(81)	–
192	Kaempferol	40.22	287.0556	285.0404	0.3	10.0	$C_{15}H_{10}O_6$	257.0437(1), 229.0526(1), 213.0525(1), 201.0348(1), 151.0027(2)[a]	Shabana et al. (2011)
193	Hinokiflavone or Amenthoflavone or Agathisflavone I	41.46	539.0992	537.0822	1.1	4.7	$C_{30}H_{18}O_{10}$	541.2242(13), 425.2128(14), 417.0566(3), 375.0507(13)[a]	Van Loo et al. (1988)
194	Ascorbyl monomyristate	41.60	387.2393	–	−4	5.8	$C_{20}H_{34}O_7$	121.1006(100)	–
195	Dihydroxypalmitic acid	41.92	289.2393	287.2231	−6.7	11.1	$C_{16}H_{34}O_4$	147.1175(49), 133.1016(73), 121.1025(67), 109.1001(100)[a]	–

(*continued on next page*)

Table 1 (*continued*)

Peak No.	Tentative assignment	t_R (min.)	$[M+H]^+$ (*m/z*)	$[M-H]^-$ (*m/z*)	Error (ppm)	mSigma	Molecular formula	MS2/MS fragment ions[b]	Reference
196	Hexadecadienoic acid	41.94	253.2180	–	−7	1.6	$C_{16}H_{28}O_2$	142.9508(100), 132.9601(58), 109.1001(45), 95.0848(88)	–
197	Deacetylforskolin	42.12	369.2284	–	−3.3	1.3	$C_{20}H_{32}O_6$	253.2123(12), 235.2088(14), 217.1924(18)	Zhang et al. (2009)
198	Hinokiflavone or Amenthoflavone or Agathisflavone II	42.33	539.0996	537.0818	1.7	12	$C_{30}H_{18}O_{10}$	425.2064(13)[a]	Van Loo et al. (1988)
199	Rhamnetin I	42.43	–	315.0505	0.5	17	$C_{16}H_{12}O_7$	179.0352(100),164.0099(32)[a]	Wollenweber (1974)
200	Unknown	42.54	405.2497	403.2315	−3.4	5.8	$C_{20}H_{38}O_8$	323.2266(13), 305.2146(8), 253.2189(100), 235.2055(87), 217.1956(53)[a]	–
201	Rhamnetin II	43.29	317.0675	315.0511	−0.1	6.1	$C_{16}H_{12}O_7$	300.0279(27), 193.0141(17), 165.0195(100), 121.0285(17)[a]	Wollenweber (1974)
202	Hinokiflavone or Amenthoflavone or Agathisflavone III	46.86	539.0998	–	−4.8	30.5	$C_{30}H_{18}O_{10}$	–	Van Loo et al. (1988)
203	Vapiprost	50.57	478.2952	–	0.0	35	$C_{30}H_{39}NO_4$	337.2748(100),306.2805(29)	–
204	Sespendole	50.77	520.3416	–	0.9	36.4	$C_{33}H_{45}NO_4$	184.0743(100),104.1077(31)	–
205	Linoleic acid amide	51.17	280.2647	–	−4.4	10.4	$C_{18}H_{33}NO$	109.1001(59),95.0837(100)	–
206	Unknown	52.67	522.3587	–	−0.7	33	$C_{33}H_{47}NO_4$	184.0736(100)	–
207	Linoleylhydroxamate I	53.04	296.2598	–	−4.7	3.2	$C_{18}H_{33}NO_2$	169.1235(100),95.0840(75)	–
208	Unknown	53.17	522.3581	–	−0.7	33	$C_{18}H_{33}NO_4$	184.0743(100),104.1076(29)	–
209	Linoleylhydroxamate II	53.44	296.2584	–	−4.7	3.4	$C_{18}H_{33}NO_2$	169.1235(100),95.0840(75)	–
210	Betunolic acid I	55.12	455.3518	–	0.4	27.8	$C_{30}H_{46}O_3$	437.3483(12), 419.3347(17), 295.2454(12), 189.1606(45), 139.1118(100),121.0998(54)	Shabana et al. (2011)
211	Triterpenoid derivative	55.44	663.4616	–	0.5	51.7	$C_{42}H_{62}O_6$	551.3333(80), 495.2626(100), 439.2103(35)	–
212	Moroctic acid	55.66	277.2177	–	−5.4	50.8	$C_{18}H_{28}O_2$	149.0229(100)	–
213	Vebonol	57.17	453.3384	–	−4.7	9.1	$C_{30}H_{44}O_3$	435.3301(32), 213.1652(27), 201.1641(100)	–
214	Betunolic acid II	57.97	455.3535	–	−3.3	2.5	$C_{30}H_{46}O_3$	201.1633(100),187.1465(66), 161.1301(87), 133.1010(81), 121.1001(79), 109.1015(55)	Shabana et al. (2011)
215	Deoxycorticosterone glucoside	58.73	493.2809	––	−2.7	5.3	$C_{27}H_{40}O_8$	337.2781(43), 263.2339(31), 109.0987(70), 95.0850(100)	–
216	Dihydroisovaltrate	59.17	425.2170	–	0.0	15.6	$C_{22}H_{32}O_8$	425.2103(38), 365.1975(64), 281.1337(24)	–
217	Oxoglycyrrhetinic acid	59.70	469.3320	–	−1.7	13.6	$C_{30}H_{44}O_4$	337.2849(3), 221.1595(3), 137.0970(100), 175.1419(8)	–

Rt: retention time. I, II, III... stand for isomers.
[a] Fragmentation pattern in negative ionization mode.
[b] Between parenthesis (relative intensity %).

chromatogram (BPC) in positive and negative ionisation modes together with the UV chromatogram at 280 nm in aqueous methanol extract of *R. coriaria* L.

The compounds detected in this work were tentatively characterised by means of MS data, together with the interpretation of the observed MS/MS spectra in comparison with those found in the literature. The formerly identified phytochemicals from the same botanical family or species have been also utilised in the identification when applicable. In the identification process, the following public databases were consulted: ChemSpider (http://www.chemspider.com), SciFinder Scholar (https://scifinder.cas.org), Kegg Ligand Database (http://www.genome.jp/kegg/ligand.html), and Phenol-Explorer (www.phenol-explorer.eu). Commercial standards were not available for all the sumac phenolics and phytochemical compounds detected in this work.

3.1.2. Organic acids

At the beginning of analysis, several very polar compounds such as malic acid isomers and derivatives have been detected, in accordance with the literature; malic acid was reported to be the most abundant organic acid in *R. coriaria* (Kossah, Nsabimana, Zhang, Chen, 2010). Thus, compounds **2**, **7** and **8** were proposed as malic acid isomers, while **3**, **4**, and **5** were suggested as glycosides of malic acid (Ley et al., 2006).

3.1.3. Phenolic acids and derivatives

In the present work we were able to characterise 9 phenolic acid derivatives, 3 of which (**25**, **35**, **43)** were detected in negative ionisation mode and show the neutral loss of a hexose moiety. Based on QTOF-MS analysis and MS/MS fragmentation pattern, these compounds were proposed as protocatechuic acid hexoside, syringic acid hexoside and coumaryl-hexoside, respectively. In positive ionisation mode a compound with a major fragment at *m/z* 355.1040 was assigned as caffeoylquinic acid (Fig. 2a), relying on the neutral loss of caffeic acid moiety (−162 Da) and the a product ion at *m/z* 193.0494 (quinic acid). Compound **12** (t_R 6.75 min), is suggested as caftaric acid.

3.1.4. Phenolic compounds conjugated with malic acid derivatives

For the first time, in the present work, the methodology used allowed us to identify 26 unusual phenolics conjugated with glycoside-malic acid. This fragmentation pattern was previously described by Perestrelo et al. (2012). From MS and MS/MS fragmentation pattern data, a dominant neutral loss of 287 Da was observed, which may be attributed to the loss of hexose-malic acid moiety in all 26 detected compounds in both positive and negative ionisation modes. Compounds **27** and **29,** with a precursor ion $[M-H]^-$ at *m/z* 447.0777 and with the identical formula $C_{17}H_{19}O_{14}$, have been assigned as galloyl-hexose-malic acid

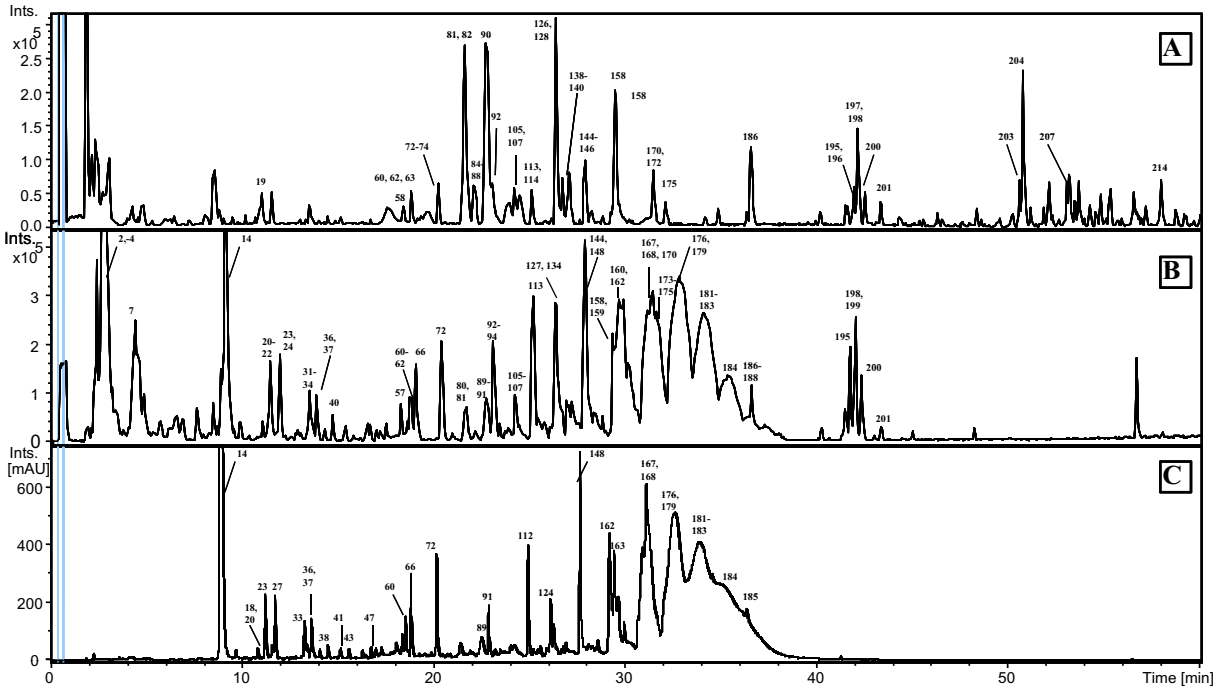

Fig. 1. HPLC–DAD/QTOF-MS base peak chromatograms (BPC) of: (A) MS in positive ion mode, (B) MS in negative ion mode, and (C) UV at 280 nm, for the hydro-methanol extract of sumac fruits.

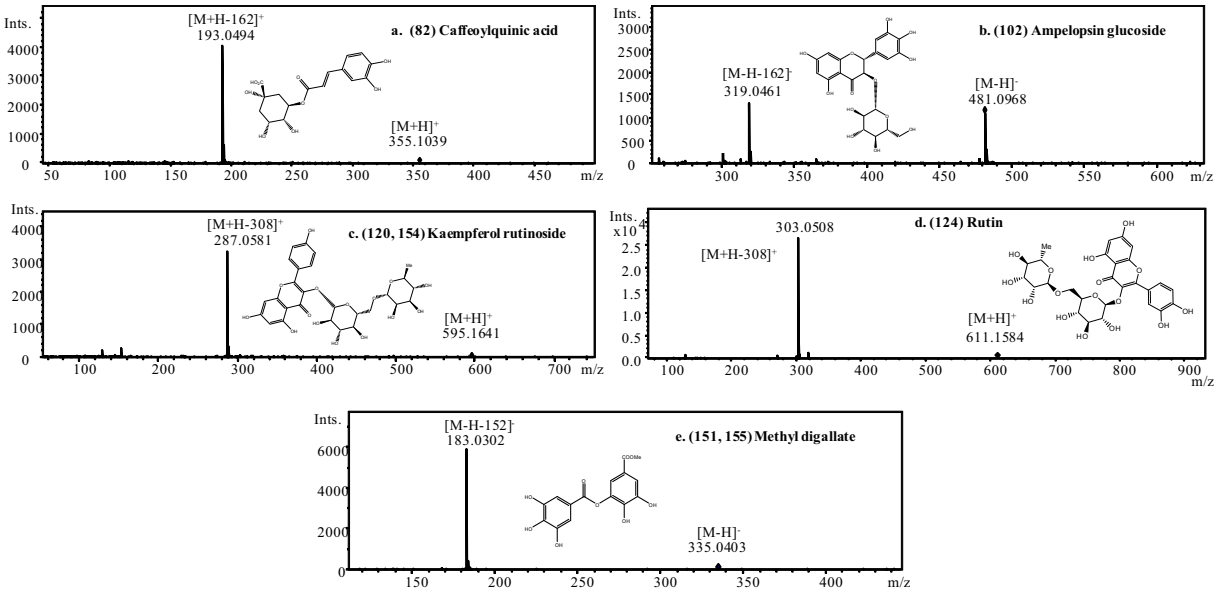

Fig. 2. MS^2 spectra and structure of new phenolics detected in *R. coriaria* by QTOF-MS in NIM and PIM.

isomers. QTOF-MS analysis showed a product ion at *m/z* 331.0666, $[M-H-116]^-$, implying the loss of malic acid ($C_4H_4O_4$) to give a galloylhexose moiety, and a product ion at *m/z* 169.0153 representing gallic acid. Four digalloyl-hexose malic acid isomers (t_R 13.55, 14.26, 15.35, and 16.68 min) were detected in ESI- mode. Loss of malic acid $[M-H-116]^-$ from the precursor ion at *m/z* 483.0794 occurred giving a product ion at *m/z* 169.0142 (gallic acid).

The QTOF-MS analysis revealed the presence of five isomers of kaempferol hexose-malic acid in the ESI- and ESI + modes with ions at *m/z* 563.1010 and 565.1210, respectively. The appearance of fragment ions at *m/z* 447.0904, $[M-H-116]^-$ and a product ion at *m/z* 285.0426 corresponded to kaempferol (Perestrelo et al., 2012). Four isomers of myricetin-hexose malic acid ($C_{25}H_{24}O_{17}$) were observed, as shown by the appearance of product ions at *m/z* 319.0466/317.0687, and corresponded to myricetin in structure after the neutral loss of 287 Da (hexose-malic acid moiety loss).

At 26.56, 27.05, 31.62 and 32.20 min pseudomolecular ions at *m/z* 581.1151/579.0982 were observed. In the MS/MS spectra, product ions at *m/z* 301.0360/303.0520 (quercetin) were observed. These isomers were assigned as quercetin-hexose malic acid. The product ion at *m/z* 463.0879 was proposed as quercetin hexose, in keeping with a previous report on sumac (Regazzoni et al.,

2013). Isorhamnetin hexose-malic acid was tentatively identified as compound **178,** which showed a product ion at *m/z* 317.0700, which corresponds to neutral loss of hexose-malic acid moiety $[M+H-278]^+$, giving the isorhamnetin aglycone. Compound **179** was suggested as kaempferol rhamnose-malic acid.

3.1.5. Flavonoids derivatives

A total of 61 flavonoid derivatives were detected and characterised in sumac.

Five isomers showed a molecular ion at *m/z* 479.1167/477.1030, with a product ion at 317.0671/315.0506 (corresponding to isorhamnetin in structure) in the MS/MS spectra. Based on the MS and MS/MS spectra, compounds **64**, **67**, **98**, **183**, and **188** are suggested as isorhamnetin hexosides. These compound are being suggested as components of sumac for the first time.

Apigenin-7-*O*-(6″-*O*-galloyl)-β-D-glucopyranoside is proposed for compound **77 (***m/z* 585.1241, $[M+H]^+$). In the MS/MS spectra, the loss of hexose and galloyl (−314 Da) moieties gave a fragment ion at *m/z* 271.0618, which corresponds to apigenin in structure. This compound was reported as an active compound in *Euphorbia humifusa* (Tian et al., 2010). In the same manner, compound **89** was tentatively proposed as dihydrotamarixetin galloyl-hexoside.

Compound **102** ([M - H]- at *m/z* 481.0995) has been tentatively assigned as ampelopsin glucoside (Yeom et al., 2003). MS/MS spectrum of this compound has shown the characteristic product ion at *m/z* 319.0460 (Fig. 2b).

Two compounds (**118** and **123)** had pseudomolecular ions at *m/z* 565.1577/563.1385. Based on QTOF-MS data and the previous literature (Abu-Reidah et al., 2013a), these compounds have been characterised as apiin isomers, apigenin glycoside derivatives. These isomers were not observed previously in sumac. Compound **126** is suggested as isovitexin, identified for the first time in sumac; the $[M+H]^+$ ion at *m/z* 433.1116 produced fragment ions at *m/z* 415.1022, 343.0762, 313.0719, corresponding to the *C*-glycoside fragmentation pattern (Abu-Reidah et al., 2013).

The glucuronated form of quercetin at 26.88 min, has molecular ions at *m/z* 479.0825/477.067 and had an MS/MS fragment ion at *m/z* 301.0358, which is due to the loss of glucoronic acid $[M-H-176]^-$ and the presence of quercetin; it is reported for the first time in sumac. A main ion at *m/z* 505.1331 was detected by ESI-. Furthermore, MS/MS revealed a product ion at *m/z* 301, corresponding to chrysoeriol in structure. Thus, compound **131** was characterised as chrysoeriol-6-*O*-acetyl-4′-β-D-glucoside (Chandrashekar, Arun, & Satyanarayana, 2005). Compounds **87** and **134** with the same MS and MS/MS data were tentatively assigned as eriodictyol hexoside or dihydrokaempferol hexoside isomers. Two compounds (t_R 27.54 and 28.31 min) with $[M+H]^+$ at *m/z* 595.1640, ($C_{27}H_{31}O_{15}$), gave a fragment ion at *m/z* 287.0581, corresponding to kaempferol aglycone in structure. Thus, **141** and **150** were identified as kaempferol rutinosides (Fig. 2c). These compounds were previously identified in leaves of *R. sylvestris* (Ding, Nguyen, Choi, Bae, & Kim, 2009).

A precursor ion of *m/z* 579.1717/577.1534 at retention times of 25.82 and 28.43 min, gave fragment ions at *m/z* 269.0452 (apigenin). Compounds **120** and **154** have been proposed as isomers of apigenin neohesperidoside, a compound already found in leaves of other species of *Rhus* (Matsuda, 1966). Rutin was suggested for the precursor ion at *m/z* 611.1627/609.1441. The MS and MS/MS spectra showed a product ion $[M+H]^+$ at *m/z* 303.0512 (quercetin) (Fig. 2d). This compound has been already described in *R. typhina* leaves (Olchowik et al., 2012). Compound **163** was proposed as apigenin glucuronide. In the same manner, apigenin glucoside has been suggested for compounds **65** and **164**. In the MS/MS spectra, both compounds had the fragment ion at *m/z* 271.0613, indicating the existence of apigenin in the structure.

An $[M-H]^-$ ion at *m/z* 599.1008 gave a product ion at *m/z* 301.0358 with 100% relative intensity. This compound was assigned as quercitrin 2″-*O*-gallate (Fig. 3). Similarly, compounds **189** and **174** were proposed as afzelin *O*-gallate and myricitrin *O*-gallate, respectively. These three compounds were described in *Calliandra haematocephala* (Moharram, Marzouk, Ibrahim, & Mabry, 2006). As far as we know, these compounds are reported herein in sumac for the first time. Two isomers (**199** and **201)** with the precursor ion at *m/z* 317.0675/315.0511 have been assigned as rhamnetin (Wollenweber, 1974).

3.1.6. Hydrolysable tannins derivatives

In this work, it was found that hydrolysable tannins derivatives are the most abundant compounds in sumac. Thus, 74 compounds have been characterised in this class.

Five isomers had a pseudomolecular ion at *m/z* 331.0647 in the ESI- mode. Compounds **13**, **14**, **16**, **18**, and **28,** have been characterised as galloylhexose, based on the data obtained by MS and MS/MS data, and literature already cited (Fröhlich, Niemetz, & Gross, 2002). To the best of our knowledge, this is the first characterisation of these compounds in *R. coriaria*. Compound **112** had a molecular ion at *m/z* 393.0449, and was proposed as benzoic acid, 3,4, 5-trihydroxy-, 2-oxo-1,3-propanediyl ester. Five isomers (**19**, **22**, **41**, **45**, and **56**) were tentatively characterised as *O*-galloylnorbergenin isomers.

Five compounds (t_R11.40, 11.92, 16.10, 16.49, and 17.50 min) with the precursor ion at *m/z* 485.0949/483.0793 have been assigned to digalloyl-hexoside relying on the MS and MS/MS spectra that showed product ions at *m/z* 331.067$[M-H-162]^-$, and 169.0143$[M-H-162-152]^-$ corresponding to the neutral losses of hexose and galloyl moieties, respectively. These compounds have been noted in *R. typhina* leaves (Fröhlich et al., 2002), but for the first time in *R. coriaria*.

QTOF-MS revealed two isomers at *m/z* 325.0567 having the same molecular formula $C_{14}H_{13}O_9$. MS/MS spectral data showed a product ion at *m/z* 169.0145, which is due to the neutral loss of shikimate moiety $[M-H-156]^-$, and the appearance of gallic acid. Based on these data, compounds (**32** and **37**) were proposed for the first time in sumac, as galloylshikimic acid. Two compounds (**151** and **155**) had a precursor ion at *m/z* 337.0578/335.0412 and a fragment ion at *m/z* 183.0303 (Shabana, El Sayed, Yousif, El Sayed, & Sleem, 2011). These isomers have been suggested to be methyl digallate isomers (Fig. 2e).

Two compounds at 14.71 and 16.62 min exhibited molecular ions at *m/z* 343.0691 and were assigned to galloylquinic acid. The product ion in the MS/MS spectrum was at *m/z* 191.0570 corresponding to quinic acid in structure, a fragment ion at *m/z* 169.0139 suggested gallic acid. Compounds **(48**, **58**, **62**, **71**, **83**, **97**, **111**, **116**, and **119)** are proposed to be isomers of trigalloyllevoglucosan. Two hydrolysable tannin isomers (**53** and **60)** showed a molecular ion at *m/z* 323.0403/321.0260. Based on the MS and MS/MS data and previous literature (El Sissi, Ishak, & Abd El Wahid, 1972), these compounds were assigned to digallic acid.

The compound (t_R 22.72 min) with the molecular formula $C_{29}H_{27}O_{16}$ and having the precursor ion at *m/z* 631.1306 in the ESI- mode, was been tentatively proposed as myricetin galloylhexoside. In the MS/MS spectrum, this compound produced a fragment ion at *m/z* 317.0675 $[M-H-314]^-$; (314 Da) is referred to gallic acid + hexose moiety loss. Fragment ions at *m/z* 321.0262 and 169.0147 resulted after the successive loss of gallic acid moieties from a main ion at *m/z* 473.0362 in the QTOF-MS analysis. This compound was assigned as trigallic acid, not previously reported in *R. coriaria*. Notably, this compound was discussed in *Toona sinensis* (Wang, Yang, & Zhang, 2007).

A compound (**78**) with molecular ion $[M+H]^+$ at *m/z* 425.1066 was proposed to be *O*-galloyl arbutin. The fragment ion at *m/z*

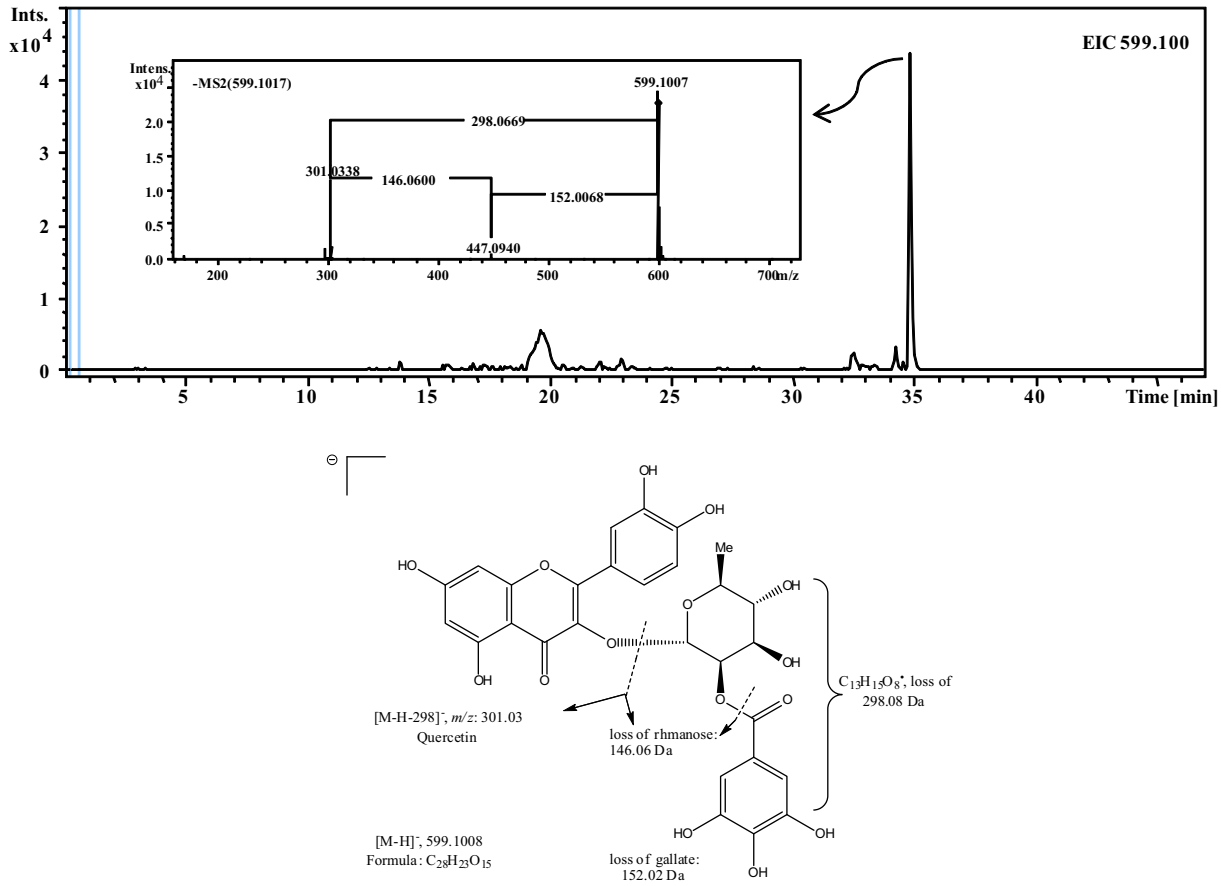

Fig. 3. Extracted ion chromatogram (EIC) together with the fragmentation pathway for the ion separated by HPLC/QTOF-MS at t_R 34.77 min, *m*/*z* 599.1008.

273.0707 was characteristic of arbutin. This compound has been described in the Anacardiaceae family (Shi, & Zuo, 1992). Compound **129** was tentatively suggested as digalloyl-hexoyl-ellagic acid (Wu, McCallum, Wang, Liu, Zhu, & Tsao, 2013). The precursor ion found at *m*/*z* 941.1328/939.1081 was assigned to pentagalloyl-hexoside for five isomers **115**, **125**, **140**, **145**, and **149**. Similarly, compound **160** (t_R 29.42 min) was suggested as hexagalloyl-hexoside. The characterisation was based on the acceptable MS and MS/MS data, in addition to the literature cited on sumac leaves (Regazzoni, Arlandini, Garzon, Santagati, Beretta, & Facino, 2013).

Four isomers with a molecular ion at *m*/*z* 545.0556 in ESI- mode were tentatively identified as dihydroxybenzoic acetate-digallate (Hahn and Fekete, 1954). Compound **167** gave a precursor ion at *m*/*z* 623.1887/621.0596 in the MS spectrum. However, in MS/MS spectrum, we observed a neutral loss of galloyl moiety [M−H−152]$^-$ which yielded the product ion at *m*/*z* 469.5507, indicating valoneic acid bilactone in structure (Sanz et al., 2010). Therefore, the compound has been assigned to galloyl-valoneic acid bilactone.

Compounds **193**, **198**, and **202** showed a precursor ion at *m*/*z* 539.0996/537.0818 in ESI+ and ESI− modes. These compounds have been already noticed in *R. coriaria* leaves and they are being reported herein in the fruits for the first time. By the method used, it was possible to characterise the compounds by their acceptable data from MS and MS/MS together with the literature cited (Van Loo et al., 1988) as isomers of hinokiflavone or amenthoflavone or agathisflavone.

3.1.7. Anthocyanins and derivatives

A total of six anthocyanin derivatives have been detected in *R. coriaria* fruits. Thus, compound **70** (t_R 19.65 min) with product ions at *m*/*z* 601.1186/599.1039, had a fragment ion at *m*/*z* 287.0557/285.0405, indicating cyanidin in structure. So, this compound was proposed as cyanidin-3-*O*-(2''galloyl)-galactoside (Kirby, Wu, Tsao, & McCallum, 2013). Two isomers (**73** and **75**) with the precursor ion at *m*/*z* 631.1301 had the molecular formula $C_{29}H_{27}O_{16}$. These compounds were assigned to 7-*O*-methyl-delphinidin-3-*O*-(2″galloyl)-galactoside (Kirby et al., 2013), the product ion at *m*/*z* 317.0650 indicates methyl-delphinidin aglycone yielded after the neutral loss of galloyl-galactoside moiety.

The compounds **81** and **90** possessed a fragment ion at *m*/*z* 299.0568 and were characterised as 7-*O*-methyl-cyanidin-3-*O*-galactoside and 7-*O*-methyl-cyanidin-3-*O*-(2″-galloyl)-galactoside, respectively; both of them were described in *R. typhina* (Kirby et al., 2013).

3.1.8. Isoflavonoid derivatives

Two isoflavonid derivatives have been detected in the sumac sample analysed. Compound **100** was proposed as glycitein-*O*-glucoside on the basis of its MS spectra, which showed the main ion [M+H]$^+$ at *m*/*z* 447.1282 and an MS/MS fragment ion at *m*/*z* 285.0768 (glycitein), this latter ion was obtained after a neutral loss of glucose moiety. This compound has never been reported previously in sumac. At 33.80 min, one molecular ion [M−H]$^-$ at *m*/*z* 547.1060 was detected and characterised as oxoglycyrrhetinic acid.

3.1.9. Terpenoid derivatives

A couple of isomers (t_R 55.12 and 57.97 min) showed a precursor ion [M+H]$^+$ at *m*/*z* 455.3518. These compounds were assigned to betunolic acid, an already identified compound in sumac leaves (Shabana et al., 2011). This compound was discussed in other

sumac species to have antiviral activity (anti-HIV) (Wang et al., 2008).

One diterpene derivative showed a molecular ion $[M+H]^+$ at m/z 369.2284. This compound was postulated as deacetylforskolin (Zhang, Luo, Wang, Lu, & Kong, 2009). Oxoglycyrrhetinic acid was tentatively identified as the compound detected at 59.70 min with $[M+H]^+$ at m/z 469.3320.

3.1.10. Other compounds

Other compounds were also characterised in sumac, like butein (compound **190**), a bioactive chalcone which was found in other species of *Rhus* (Lee et al., 2008), but we report it in this work for the first time in *R. coriaria*. Iridoid and coumarin derivatives (**52** and **96**) were detected and tentatively characterised as penstemide and umbelliferone, respectively.

4. Conclusion

It has been established in this work that HPLC–DAD/QTOF-MS is a powerful analytical technique for the separation and detection of phenolics and other phytochemicals in *R. coriaria* L. Consequently, by using this method, a total of 211 compounds were tentatively identified in sumac, based on accurate mass determination of the deprotonated/protonated ions which were obtained from the MS data and MS/MS fragmentation pattern, besides other relevant bibliographic information. To our knowledge, this work marks the first extensive study of the phenolic and other phytochemical components from sumac fruit (epicarps) extract. In this context, the obtained data indicate qualitatively that sumac is an abundant source of bioactive phytochemicals. The obtained results could explain the past and current usage of *R. coriaria* L. as a food spice, as well as support the widespread uses of sumac in health, nutrition and pharmacology and as a source of functional ingredients.

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