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Comprehensive metabolite profiling of *Arum palaestinum* (Araceae) leaves by using liquid chromatography–tandem mass spectrometry

Ibrahim M. Abu-Reidah [a,b,c], Mohammed S. Ali-Shtayeh [a,*], Rana M. Jamous [a], David Arráez-Román [b,c], Antonio Segura-Carretero [b,c]

[a] Biodiversity & Environmental Research Center (BERC), Til, Nablus POB 696, Palestine
[b] Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Avda. Fuentenueva, 18071 Granada, Spain
[c] Functional Food Research and Development Center (CIDAF), Bioregión Building, Health Science Technological Park, PTS Granada, Avda. Del Conocimiento s/n, 18016 Granada, Spain

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ABSTRACT

Arum palaestinum is a wild edible plant used in food and folk medicine within the Mediterranean region including Palestine. The leaves are traditionally consumed as anti-cancerous food. Yet, just few reports are available on its chemical composition. Therefore, in this work, an extensive qualitative identification via liquid chromatography–tandem mass spectrometry (UHPLC–DAD-ESI-MS/MS) of the phytochemical metabolites in *A. palaestinum* leaves has been established. A total of 180 phytochemicals, mainly 53 flavonoids, 33 phenolic acids, 10 terpinoids, 7 iridoids and 6 amino acids have been characterized. Moreover, 11 unknown compounds were also detected, providing the first comprehensive characterization available on the phytochemical composition of the leaves of *A. palaestinum*, highlighting it as an abundant source of antioxidant phenolics and phytochemicals. The obtained results may develop the current knowledge on *A. palaestinum*, boost further research towards bioactive compounds exploring and may encourage more consumption of this important functional food. Further investigations on these characterized bioactive component potential are necessary.

1. Introduction

Cancer is a broad group of various diseases which accounts globally for about 14% of all deaths yearly (WHO, 2014), besides being a major health world-wide problem and the second most common cause of death from disease after the cardiovascular disorders. Because of high death rate and the serious side effects of chemotherapy and radiation therapy associated with cancer, many cancer patients try to find alternative complementary means of treatment (De Martel et al., 2012), such as medicinal plants and functional foods.

Arum palaestinum Boiss (family Araceae), is a species of flowering herbaceous perennial plant native to the Levant (Eastern Mediterranean area). This wild edible plant is traditionally used in the Mediterranean cuisine as well as in folk medicine (El-Desouky, Hawas, & Kim, 2014; Rivera et al., 2006). It is known as Palestine Arum, Solomon's Lily, Black Calla and Priest's Hood. In Palestine, this plant is called "Al-luf", and its leaves are traditionally eaten cooked, especially by persons having or suspecting to have a cancer disease (Ali-Shtayeh, Jamous, & Jamous, 2011; Ali-Shtayeh, Zohara, & Mahajna, 2000; Ali-Shtayeh et al., 2008). The leaves of *A. palaestinum* are consumed to protect from colon cancer, and were reported to be used for internal bacterial infections (Kaileh, Berghe, Boone, Essawi, & Haegeman, 2007; Makhadmeh, Al-Lozi, Duwayri, Shibli, & Migdadi, 2010). Additionally, a decoction prepared from the leaves was reported to be used for the treatment of urinary retention, kidney infections, cancer, poisoning and circulatory system (Abu-Rabia, 2005). It is also far believed that the meals prepared from the plant possess therapeutic properties, which may offer benefits in terms of human health and well-being. Taking in consideration the above-mentioned data, *A. palaestinum* can be regarded as a promising

* Corresponding author. Tel.: +970 92536406.
E-mail address: msshtayeh@yahoo.com (M.S. Ali-Shtayeh).

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functional food for human consumption and as a potential plant for drug discovery research.

In fact, *A. palaestinum* was reported to be the most commonly used plant among cancer patients in Palestine (Ali-Shtayeh et al., 2011). Nevertheless, it is worth noting that *A. palaestinum* is among the few studied plants recommended by the traditional healers for the treatment of cancer (Abu-Dahab & Afifi, 2007). Moreover, the plant has long been used in Traditional Arabic Palestinian Herbal Medicine (TAPHM) for the treatment of various diseases including, coughing with phlegm, hemorrhoids, stomach parasitic worms, constipation, acne, and prostate disorders (Ali-Shtayeh, Al-Assali, & Jamous, 2013a; Ali-Shtayeh et al., 2011). Other traditional uses also involve curing of a number of chronic diseases such as diabetes, hypertension, stomach sourness, atherosclerosis, cancers and toxicity (Ali-Shtayeh, Jamous, & Jamous, 2012; Ali-Shtayeh, Jamous, Jamous, & Salameh, 2013b; Farid et al., 2014; Makhadmeh et al., 2010). Interestingly, Palestinian Arum has been described to be a potent anti-cancerous plant (Ali-Shtayeh et al., 2011).

Lately, a promising anti-cancer effect has been described for *A. palaestinum* water extract, this together with the other published studies on phytochemicals found in different parts of the plant, may support its potential anti-tumor properties (Aboul-Enein, Abu El-Ela, Shalaby, & El-Shemy, 2012; Farid et al., 2014).

Piperazirum, a bioactive alkaloid isolated from *A. palaestinum*, has demonstrated a significant in vitro cytotoxic activity against some tumor cell lines (El-Desouky, Ryub, & Kima, 2007b). Recently, another new diketopiperazine derivative was shown to possess a mild cytotoxic activity against cultured multidrug-resistant human cells (El-Desouky et al., 2014).

Moreover, the flavonoid isoorientin (6-C glucoside of luteolin), isolated from *A. palaestinum* was reported to possess myolytic activity on animals' smooth muscle (Afifi, Khalil, & Abdalla, 1999). However, care should be taken when using *A. palaestinum*, since it may cause negative side effects. The phenolic contents, antioxidant and anti-cancer activities of different organic solvents extracts of *A. palaestinum* have been studied earlier (Aboul-Enein et al., 2012; Diab-Assaf et al., 2012). From the previously obtained results, methanol extract demonstrated the highest total phenolic and flavonoid contents compared to chloroform and ethyl acetate extracts. On the other hand, the reduction in cell proliferation was shown to be dose dependent (Diab-Assaf et al., 2012).

Even though, there are some earlier works done on the chemical composition of *A. palaestinum* (Afifi, Shervington, & Darwish, 1997; Afifi et al., 1999; El-Desouky et al., 2007a; El-Desouky et al., 2007b; El-Desouky et al., 2014; Farid et al., 2014), the need for an extensive identification of the most phytochemical components of this important plant seems imperative. Undoubtedly, the medicinal use of this plant as anti-cancerous food has robustly prompted us to carry out this phytochemical investigation on this promising plant. For that reason, in this work, a comprehensive qualitative characterization through liquid chromatography–tandem mass spectrometry (UHPLC–DAD-ESI-MS/MS) of the phytochemical metabolites in the hydro-methanol extract of *A. palaestinum* leaves has been performed.

2. Materials and methods

2.1. Chemicals

Methanol and acetonitrile of HPLC-grade were purchased from Labscan (Dublin, Ireland). Analytical grade acetic acid (assay >99.5%) was from Fluka (Switzerland). Purified water by using a Milli-Q system (Millipore, Bedford, USA) has been used. Other unmentioned chemicals were of analytical grade.

2.2. Sample preparation

A. palaestinum samples were harvested from the Nablus Mountains in fall of 2012 and were authenticated by Prof. Mohammad S. Ali-Shtayeh from BERC. Collected leaf samples were shade-dried, and then the dehydrated leaves were ground into powder using a household mill and stored at room temperature until they were used for the extraction.

2.3. Extraction of phytochemical compounds

The *A. palaestinum* samples were extracted according to the extraction protocol reported by Abu-Reidah, Arráez-Román, Lozano-Sánchez, Segura-Carretero, and Fernández-Gutiérrez (2013a), with slight changes. The ground leaves of *A. palaestinum* (0.5 g) were extracted with methanol (80%, v/v) and sonicated for 30 min at room temperature. The mixture was then centrifuged for 15 min at 3750 *g* and the supernatant was poured into a round-bottom flask. The extraction procedure was repeated three times. Thereafter, the extract was evaporated in vacuo using a rotary evaporator at 39 °C, then the dry residue was redissolved in aqueous methanol. The extract finally was centrifuged again, and filtered through a 0.22-μm syringe filter and stored at −20 °C until analysis.

2.4. UHPLC–DAD-ESI-QTOF-MS analysis

Separation and detection of the phytochemical compounds from *A. palaestinum* hydro-methanol extract were performed on an Agilent 1200 series LC (Agilent Technologies, CA, Santa Clara, USA) consisting of a vacuum degasser, an autosampler and a binary pump, and diode-array detector (DAD). This instrument was equipped with an Agilent Zorbax C18 column (4.6 × 150 mm, 1.8 μm) from Agilent Technologies. Acetic acid (0.5%, v/v) and acetonitrile were used as mobile phases A and B. The flow rate was 0.80 mL/min and the gradient elution was planed as follows: 0 min, 100% A; 20 min, 80% A; 30 min, 70% A; 40 min, 50% A; 50 min, 25% B; 60 min, 0% A; 62 to 70 min, and 100% A. The column temperature was kept at 25 °C with an injection volume of 10 μL.

The UHPLC system was hyphenated with a micrOTOF-Q II (Bruker Daltonics, Bremen, Germany), supported with an electrospray ionization interface (ESI). The spectra were acquired in negative and positive ionization modes over a mass-to-charge (m/z) ranged between 50 and 1100 Da.

The MS/MS analyses were undergone by full automatic acquisition fragmentation pattern. The most values of the ESI-MS limits were: capillary voltage, ±4.0 kV; drying gas temperature, 210 °C; drying gas flow, 8.0 L/min; nubilizing gas pressure, 2.0 bar; 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; and m/z 1000, 35 eV, and 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.

At some point in the UHPLC analysis, an external calibration has been carried out by using a Cole Palmer syringe pump (Vernon Hills, IL) directly connected to the ESI interface, by passing a solution containing sodium acetate ($C_2H_3NaO_2$). Using this system, an exact calibration curve based on many cluster masses each differing by 82 Da, has been achieved. Due to the compensation of temperature drift in the Q-TOF, this external calibration can give correct 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. Characterization of phenolic and other phytochemical metabolites

A list of all identified compounds from the hydro-methanol extract of *A. palaestinum* by using UHPLC–DAD-ESI-QTOF-MS in the negative and positive ionization modes is given in Table 1. These compounds are summarized along with their retention time (t_R), $[M \pm H]^{\pm}$ (m/z), error (ppm), mSigma value, and first hit of molecular formula for

Table 1
Characterization of metabolites from *Arum palaestinum* leaves extract using UHPLC–DAD-ESI-QTOF-MS in the negative and positive ion modes.

Peak*	t_R (min)	Precursor ion (m/z) $[M-H]^-$	Precursor ion (m/z) $[M+H]^+$	Error (ppm)	mSigma	Molecular formula	MS/MS (m/z) product ion(s)**	Tentative identity
1	2.51	341.1078	–	3.5	2.6	$C_{12}H_{22}O_{11}$	179.0555 (100)	D-Sucrose[a]
2	2.61	133.0135	–	5.7	1.6	$C_4H_6O_5$	115.0036 (100)	Malic acid[b]
3	3.65	278.1245	280.1408	0.2	1.7	$C_{11}H_{21}NO_7$	116.0714 (100)	Fructosyl-valine[b]
4	4.18	337.0771	–	4.7	9.6	$C_{12}H_{18}O_{11}$	338.0799 (12), 277.0577 (37), 174.0167 (30), 113.9973 (6)	Ascorbic acid hexoside[b]
5	4.31	–	136.0613	3.7	3.1	$C_5H_5N_5$	119.0349 (100), 136.0613 (11), 109.0505 (5), 92.0227 (16)	Vitamin B4[b]
6	4.37	191.0195	–	1.4	3.7	$C_6H_8O_7$	111.0083 (100)	(Iso)citric acid[c]
7	4.70	290.0879	–	0.7	2.9	$C_{11}H_{17}NO_8$	200.0560 (38), 170.0447 (7), 128.0346 (100)	Glutimic acid hexose[b]
8	5.71	130.0865	132.1011	4.8	4.4	$C_6H_{13}NO_2$	119.0346 (100)	Isoleucine[c]
9	6.94	180.0668	182.0807	−0.8	4.5	$C_9H_{11}NO_3$	163.0420 (57), 119.0495 (100)	Tyrosine[c]
10	6.95	–	136.0752	3.8	4.5	C_8H_9NO	117.0562 (14), 107.0497 (100), 91.0549 (48)	Phenalgin
11	7.40	–	180.1030	−6.2	13.6	$C_{10}H_{13}NO_2$	115.0536 (100), 91.0528 (39)	Phenylalanine methyl ester[b]
12	8.08	342.1181	344.1351	4	5.8	$C_{15}H_{21}NO_8$	180.0664 (100)	Fructosyl-tyrosine[b]
13	8.20	323.0977	–	2.1	14.0	$C_{12}H_{20}O_{10}$	161.0451 (100)	Difructose anhydride I[b]
14	8.53	292.1398	294.1491	1.2	1.3	$C_{12}H_{22}NO_7$	130.0868 (100)	Fructosyl-leucine[b]
15	8.89	219.0776	221.0912	−0.5	4.2	$C_{11}H_{12}N_2O_3$	157.0767 (100)	5-Hydroxytryptophane[b]
16	9.27	323.0982	–	0.7	3.3	$C_{12}H_{20}O_{10}$	161.0448 (100)	Difructose anhydride II[b]
17	9.42	–	238.1073	0.1	12.0	$C_{12}H_{15}NO_4$	175.0768 (37), 161.0586 (100)	γ-Benzylglutamic acid[b]
18	10.08	329.0868	–	3.1	4.5	$C_{14}H_{18}O_9$	165.0547 (10)	(Iso)vanillic acid hexoside I[a]
19	10.19	–	269.0884	−1.2	42.4	$C_{10}H_{12}N_4O_5$	137.0459 (100)	Oxiamin[b]
20	10.35	282.0840	–	1.4	10.4	$C_{10}H_{13}N_5O_5$	150.0415 (100)	Guanosine[b]
21	10.43	266.0890	268.1044	5	7.3	$C_{10}H_{13}N_5O_4$	134.0464 (100)	Adenosine[c]
22	10.56	358.0765	360.0925	4	15.0	$C_{14}H_{17}NO_{10}$	125.0239 (100), 152.0340 (16)	Triglochinin I[a]
23	10.64	–	237.0872	−1	6.6	$C_{11}H_{12}N_2O_4$	157.0741 (15), 146.0598 (100), 128.0486 (56), 118.0638 (17)	N-formylkynurenine[b]
24	11.02	164.0711	166.0860	3.5	2.6	$C_9H_{11}NO_2$	164.0724 (18), 147.0446 (100), 103.0544 (20)	Phenylalanine[c]
25	11.29	299.0766	–	2.1	9.0	$C_{13}H_{16}O_8$	137.0239 (100), 93.0331 (18)	*p*-Salicylic acid hexoside[b]
26	11.61	358.0764	360.0925	4.3	10.8	$C_{14}H_{17}NO_{10}$	125.0241 (100), 152.0345 (42)	Triglochinin II[a]
27	11.67	326.1235	328.1398	3.2	0.6	$C_{15}H_{21}NO_7$	236.0929 (2), 164.0710 (100)	Fructosyl-phenylalanine I[b]
28	12.16	315.0725	–	4	10.7	$C_{13}H_{16}O_9$	153.0182 (56), 152.0112 (100), 109.0310 (10), 108.0196 (41)	Dihydroxybenzoic acid hexoside[b]
29	12.73	358.0781	360.0780	−0.2	2.6	$C_{14}H_{16}NO_{10}$	314.0888 (3), 152.0352 (16), 125.0242 (100)	Triglochinin III[a]
30	13.42	329.0868	331.1289	3.1	8.6	$C_{14}H_{18}O_9$	167.0344 (100), 123.0452 (32)	(Iso)vanillic acid hexoside II[b]
31	13.55	503.1389	505.1566	3.5	4.3	$C_{21}H_{28}O_{14}$	341.0870 (100), 179.0348 (17), 161.0240 (27)	Caffeoyl-fructofuranosyl-glucopyranoside or 6-*O*-caffeoylsophorose I[b]
32	13.92	–	349.1397	−0.9	8.7	$C_{17}H_{20}N_2O_6$	331.1279 (26), 258.1146 (24), 210.0899 (46), 195.0934 (23), 188.0704 (15), 170.0614 (71), 144.0791 (50), 130.0652 (100)	Geraniol-dinitrobenzoate[b]
33	14.22	204.0304	206.0447	−0.9	3.8	$C_{10}H_7NO_4$	160.0400 (100),132.0447 (11)	Xanthuric acid[b]
34	14.59	–	367.1487	2.5	5.5	$C_{17}H_{22}N_2O_7$	331.1230 (3), 303.1303 (7)	Fructosyl-tryptophan I[b]
35	14.83	355.1023	–	3.3	9.8	$C_{16}H_{20}O_9$	295.0820 (6), 235.0607 (14), 193.0504 (39), 175.0397 (9)	Ferulic acid hexoside I[b]
36	15.03	365.1353	367.1490	0.2	4.2	$C_{17}H_{22}N_2O_7$	203.0827 (100)	Fructosyl-tryptophan II[b]
37	15.14	–	205.0969	1.3	0.6	$C_{11}H_{12}N_2O_2$	170.0591 (6), 155.0590 (5), 143.0720 (52), 118.0644 (100), 91.0525 (9)	Tryptophan[c]
38	15.55	503.1382	–	4.9	16.9	$C_{21}H_{28}O_{14}$	341.0865 (17), 179.0366 (56), 161.0237 (100)	Caffeoyl-fructofuranosyl-glucopyranoside or 6-*O*-Caffeoylsophorose II[b]
39	15.75	341.0868	343.1036	2.8	9.7	$C_{15}H_{18}O_9$	179.0348 (100), 135.0445 (19)	Caffeoyl-hexose I[b]
40	15.79	325.0922	–	2.2	18.1	$C_{15}H_{18}O_8$	163.0393 (73), 119.0501 (100)	Coumaryl-hexose I[b]
41	15.97	259.1289	261.1445	3.9	11.2	$C_{11}H_{20}N_2O_5$	197.1303 (22), 130.0866 (100)	γ-Glutamyl-leucine[b]
42	16.30	–	216.0869	3.2	23.6	$C_{10}H_9N_5O$	142.9529 (100), 132.9575 (52)	Kinetin[c]
43	16.36	341.0886	–	−2.2	3.9	$C_{15}H_{18}O_9$	179.0354 (13), 161.0243 (100)	Caffeoyl-hexose II[b]
44	16.37	517.1555	–	1.5	31.0	$C_{22}H_{30}O_{14}$	355.1019 (37), 193.0530 (100)	Feruloyl-sucrose I[b]
45	16.76	339.0724	–	−0.6	95.0	$C_{15}H_{16}O_9$	177.0190 (100)	Esculetin-*O*-hexoside[b]
46	16.93	503.1396	–	2	15.3	$C_{21}H_{28}O_{14}$	179.0334 (60), 161.0224 (100)	Caffeoyl dihexoside I[b]
47	16.98	659.1834	–	−0.7	17.0	$C_{28}H_{36}O_{18}$	497.1293 (100), 335.0773 (62)	Symcomoside B[b]
48	17.30	627.1561	–	1	12.0	$C_{27}H_{32}O_{17}$	537.1263 (16), 507.1114 (100), 287.0781 (16), 197.0428 (19), 167.0346 (34)	Calodendroside A[b]
49	17.43	497.1300	499.1430	0.1	5.0	$C_{22}H_{26}O_{13}$	335.0778 (100), 291.0877 (1), 179.0352 (23)	Verproside I[b]
50	17.45	519.1104	–	−3.7	19.2	$C_{31}H_{20}O_8$	357.0589 (100), 335.0721 (21), 193.0509 (8), 179.0377 (7)	Bisphenol A diphthalic anhydride[b]
51	17.53	355.1040	–	−1.6	13.2	$C_{16}H_{20}O_9$	193.0506 (100)	Ferulic acid hexoside II[b]
52	17.70	481.1379	483.1483	1.8	36.6	$C_{22}H_{26}O_{12}$	319.0827 (100), 163.0401 (58), 155.0347 (72), 137.0237 (27)	Catalposide I[b]
53	17.78	401.1446	–	1.8	19.7	$C_{18}H_{26}O_{10}$	239.0928 (100), 179.0711 (38)	7-*O*-Ethylsweroside[b]

Table 1 (*continued*)

Peak*	t_R (min)	Precursor ion (m/z) $[M-H]^-$	Precursor ion (m/z) $[M+H]^+$	Error (ppm)	mSigma	Molecular formula	MS/MS (m/z) product ion(s)**	Tentative identity
54	18.15	341.0875	–	0.8	5.9	$C_{15}H_{18}O_9$	179.0352 (100), 135.0453 (13)	Caffeoyl-hexose III[b]
55	18.34	503.1406	–	0.1	37.9	$C_{21}H_{28}O_{14}$	341.0843 (17), 179.0342 (9), 161.0241 (17)	Caffeoyl dihexoside II[b]
56	18.51	517.1553	–	2	5.6	$C_{22}H_{30}O_{14}$	193.0510 (100)	Feruloyl-sucrose II[b]
57	18.71	325.0936	–	−2.1	11.1	$C_{15}H_{18}O_8$	163.0403 (100), 119.0502 (48)	Coumaryl-hexose II[b]
58	18.77	246.0993	248.1135	−4.1	6.1	$C_{10}H_{17}NO_6$	210.0775 (46), 130.0877 (100)	Unidentified
59	19.02	–	627.1551	0.8	13.2	$C_{27}H_{30}O_{17}$	465.1015 (2), 303.0486 (4)	Quercetin di hexoside I[c]
60	19.04	325.0934	–	−1.5	18.0	$C_{15}H_{18}O_8$	163.0413 (9), 145.0295 (100)	Coumaryl-hexose III[b]
61	19.20	–	627.1586	−4.8	6.5	$C_{27}H_{30}O_{17}$	303.0486 (4)	Quercetin dihexoside II[c]
62	19.31	481.1348	483.1483	0.8	23.7	$C_{22}H_{26}O_{12}$	325.0913 (10), 155.0348 (100), 163.0402 (75), 111.0439 (22)	Catalposide II[b]
63	19.53	335.0780	–	−2.3	31.6	$C_{16}H_{16}O_8$	179.0353 (100), 135.0461 (48)	(trans) Caffeoylshikimic acid I[b]
64	19.70	609.1465	611.1599	−0.7	9.5	$C_{27}H_{30}O_{16}$	591.1368 (1), 519.1120 (3), 489.1031 (9), 447.0928 (47), 357.0607 (2), 327.0513 (3)	Lucenin-2[b]
65	19.88	593.1522	595.1653	−2.6	70.4	$C_{27}H_{30}O_{15}$	503.1187 (6), 473.1104 (21)	6,8-Di-C-β-glucosylapigenin (Vicenin 2)[a]
66	19.92	497.1303	499.1430	−0.4	8.6	$C_{22}H_{26}O_{13}$	335.0778 (100), 179.0345 (23)	Verproside II[b]
67	19.96	–	757.2203	−2.3	3.3	$C_{33}H_{40}O_{20}$	637.1794 (7), 415.1006 (39), 397.0932 (54), 379.0752 (32), 367.0796 (30), 337.0701 (54), 313.0725 (100), 283.0604 (39), 271.0609 (4)	Quercetin-rhamnosylrutinoside or Kempferol-rutinoside-glucoside[b]
68	19.98	–	773.2144	−1.2	5.9	$C_{33}H_{40}O_{21}$	431.0991 (42), 353.0636 (52), 329.0648 (100), 287.0583 (2)	Kaempferol-sophoroside-glucoside[b]
69	20.00	595.1642	–	4.4	7.0	$C_{27}H_{32}O_{15}$	505.1336 (3), 475.1249 (22), 415.1047 (5), 385.0909 (15), 355.0828 (14)	Naringenin-6,8-di-*C*-glucoside[b]
70	20.37	355.1033	–	0.3	5.0	$C_{16}H_{20}O_9$	193.0519 (100), 179.0344 (55)	Ferulic acid hexoside III[b]
71	20.39	179.0357	–	−4.2	2.5	$C_9H_8O_4$	135.0450 (100)	Caffeic acid[a]
72	20.45	671.1620	–	−0.5	9.7	$C_{32}H_{32}O_{16}$	515.1169 (28), 427.0873 (84), 359.0751 (10)	6-*O*-vanilloyliridin[b]
73	20.47	–	177.0541	3	11.9	$C_{10}H_8O_3$	135.0414 (49), 117.0308 (100), 107.0491 (26), 89.0366 (55)	Cantabilin[b]
74	20.54	547.1692	549.2450	−4.3	29.7	$C_{23}H_{32}O_{15}$	265.0709 (16), 223.0621 (100), 205.0513 (91)	β-D-Fructofuranosyl-(2 → 1)-α-D-[6-*O*-sinapoyl]-glucopyranoside (Arillanin C)[b]
75	20.55	709.2192	–	0.6	28.0	$C_{29}H_{42}O_{20}$	485.1496 (100), 425.1302 (10), 407.1228 (19), 223.0607 (20)	Arillatose D[b]
76	20.56	623.1618	625.1751	−0.1	25.5	$C_{28}H_{32}O_{16}$	533.1321 (4), 503.1177 (16), 299.0689 (1)	Diosmetin-6,8-di-*C*-hexose[b]
77	20.71	–	595.1656	0.2	17.1	$C_{27}H_{30}O_{15}$	433.1110 (100)	Kaempferol rutinoside[b]
78	20.81	341.0880	–	−0.6	14.1	$C_{15}H_{18}O_9$	179.0366 (100), 135.0446 (16)	Caffeoyl-hexose IV[b]
79	20.92	609.1465	611.1599	0	12.0	$C_{27}H_{30}O_{16}$	519.1136 (5), 489.1037 (18), 447.0933 (100), 357.0624 (5), 327.0509 (11)	Di-*C*-glucosylluteolin I[c]
80	20.96	593.1519	–	−1.2	17.1	$C_{27}H_{30}O_{15}$	473.1039 (7), 431.1906 (1), 210.0782 (13)	Vitexin-*O*-glucoside[c]
81	21.39	497.1305	–	−0.8	27.0	$C_{22}H_{26}O_{13}$	335.0776 (100), 179.0359 (48)	Verproside III[b]
82	21.53	609.1459	611.1597	0.3	1.2	$C_{27}H_{30}O_{16}$	591.1365 (2), 519.1118 (5), 489.1031 (7), 447.0930 (13), 357.0609 (2), 327.0500 (3)	Di-*C*-glucosylluteolin II[c]
83	21.60	335.0774	–	−0.5	0.9	$C_{16}H_{16}O_8$	179.0350 (100), 161.0244 (81), 135.0447 (34)	(trans) Caffeoylshikimic acid II[b]
84	21.73	593.1508	595.1653	0.7	11.2	$C_{27}H_{30}O_{15}$	575.1312 (1), 503.1169 (1), 473.1092 (5), 431.0992 (1), 353.0679 (1)	Apigenin-6, 8-di-*C*-glucoside (Vicenin II)[a]
85	21.81	289.0723	–	−2	12.6	$C_{15}H_{14}O_6$	245.0833 (100), 203.0731 (77), 179.0350 (39), 161.0626 (32), 151.0406 (60), 137.0230 (48), 109.0293 (45)	(Epi)catechin[a]
86	21.91	481.1344	–	0.8	23.7	$C_{22}H_{26}O_{12}$	319.0825 (100), 163.0402 (55), 155.0347 (23)	Catalposide III[b]
87	22.07	579.1349	581.1496	1.1	7.5	$C_{26}H_{28}O_{15}$	561.1264 (2), 519.1111 (4), 489.1009 (13), 459.0925 (3), 399.0731 (1), 369.0560 (2)	Kaempferol 3-*O*-arabinosylgalactoside[c]
88	22.33	335.0779	337.0921	−1.9	1.7	$C_{16}H_{16}O_8$	179.0355 (100), 161.0240 (21), 135.0448 (36)	(trans) Caffeoylshikimic acid III[b]
89	22.54	693.2958	–	2.5	14.8	$C_{31}H_{50}O_{17}$	693.2977 (100), 549.2578 (10), 531.2447 (6), 357.0565 (26), 335.0757 (11), 179.0487 (3)	Blumenol-*C*-9-*O*-β-(6′-*O*-rhamnosyl-2′-*O*-β-glucuronosyl-glucoside)[b]
90	22.60	609.1461	611.1597	0	25.0	$C_{27}H_{30}O_{16}$	447.0926 (100), 285.0443 (2)	Kampferol-3, 7-di hexoside or Eriodictyol-3′, 5-di hexoside[b]
91	23.02	755.2078	757.2201	−5.1	138.0	$C_{33}H_{40}O_{20}$	593.1553 (58), 531.2419 (39)	Kaempferol sophoroside-rhamnoside[c]
92	23.31	497.1293	–	1.5	23.8	$C_{22}H_{26}O_{13}$	335.0762 (100), 179.0362 (24)	Catalposide IV[b]

(*continued on next page*)

Table 1 (*continued*)

Peak*	t_R (min)	Precursor ion (m/z) $[M-H]^-$	Precursor ion (m/z) $[M+H]^+$	Error (ppm)	mSigma	Molecular formula	MS/MS (m/z) product ion(s)**	Tentative identity
93	23.53	563.1400	565.1542	1	6.8	$C_{26}H_{28}O_{14}$	545.1318 (1), 473.1073 (2), 443.0968 (4), 383.0787 (1), 353.0695 (1)	Isoshaftoside[a]
94	23.56	549.2546	–	1.2	5.2	$C_{25}H_{42}O_{13}$	505.2677 (5), 487.2545 (5), 447.2216 (14), 405.2103 (16), 179.0551 (11), 125.0253 (13)	Nicoblumin[b]
95	23.62	–	445.1129	4.3	54.1	$C_{22}H_{20}O_{10}$	287.0544 (5)	Pseudobaptigenin-*O*-hexoside (Rothindin)[b]
96	23.68	447.0929	449.1072	0.9	2.0	$C_{21}H_{20}O_{11}$	429.0812 (21), 387.0708 (3), 357.0613 (100), 327.0511 (95), 285.0403 (4)	Luteolin-6-*C*-glucoside (Isoorientin)[a]
97	23.84	611.2541	–	−7.1	30.3	$C_{33}H_{39}O_{11}$	551.2301 (2), 491.2033 (4), 449.2022 (100), 431.1892 (73), 371.1831 (1)	Euphopubescenol[b]
98	24.48	447.0932	449.1062	0.3	3.4	$C_{21}H_{20}O_{11}$	429.0832 (16), 357.0598 (100), 327.0497 (95), 285.0416 (4)	Luteolin-8-*C*-glucoside (Orientin)[a]
99	24.50	319.0827	–	−1.1	7.7	$C_{16}H_{16}O_7$	163.0386 (32), 145.0303 (100), 117.0325 (14), 111.0432 (14)	(trans)-*p*-Coumaric acid-*O*-shikimate[b]
100	24.62	335.0776	–	−1.9	1.7	$C_{16}H_{16}O_8$	179.0349 (100), 161.0255 (18), 135.0449 (36)	(trans) Caffeoylshikimic acid IV[b]
101	24.70	563.1414	–	−1.4	11.0	$C_{26}H_{28}O_{14}$	473.1045 (3), 443.0972 (4)	Shaftoside[a]
102	25.62	529.2285	531.2419	1.1	12.4	$C_{25}H_{38}O_{12}$	427.1976 (43), 179.0549 (5), 151.0787 (3)	Caffeoyl-feruloylquinic acid[b]
103	25.76	319.0831	–	−2.1	2.3	$C_{16}H_{16}O_7$	163.0386 (100), 145.0303 (100), 137.0244 (25), 119.0504 (45), 155.0357 (13), 145.0300 (18)	(trans)-*p*-Coumaric acid-*O*-shikimate I[b]
104	26.23	431.0975	433.1116	1.7	4.2	$C_{21}H_{20}O_{10}$	341.0667 (44), 311.0564 (100), 283.0597 (2), 269.0484 (1)	Isovitexin[a]
105	26.36	193.0510	–	−1.8	2.7	$C_{10}H_{10}O_4$	178.0255 (23), 179.0316 (4), 134.0366 (100), 135.0404 (9)	(Iso)ferulic acid I[a]
106	26.50	531.2438	–	−3.3	5.1	$C_{25}H_{40}O_{12}$	429.2119 (20), 387.2020 (100), 161.0458 (22), 125.0244 (46)	Zizyvoside I[b]
107	26.62	–	579.1832	−3	24.6	$C_{27}H_{32}O_{15}$	289.0706 (100), 153.0165 (14)	Eriodictyol-*O*-rutinoside[b]
108	26.77	449.1089	451.1221	0.1	5.1	$C_{21}H_{22}O_{11}$	287.0559 (100), 151.0036 (21)	Aromadendrin-*O*-hexoside or Eriodictyol-*O*-hexoside I[b]
109	26.97	593.1512	595.1650	0	7.3	$C_{27}H_{32}O_{15}$	447.0972 (1), 285.0380 (1)	Cyanidin-3-rutinoside[a]
110	26.98	461.1090	463.1220	−0.2	11.1	$C_{22}H_{22}O_{11}$	443.0961 (2), 401.0835 (1), 371.0769 (32), 341.0674 (100), 299.0501 (1), 298.0479 (3)	Isoorientin-methyl ether or Swertiajaponin[b]
111	27.00	413.1430	–	−0.9	27.6	$C_{15}H_{22}N_6O_8$	269.1030 (100), 161.0453 (30), 125.0240 (19)	Unidentified
112	27.12	785.1943	787.2099	−1.1	104.0	$C_{37}H_{38}O_{19}$	623.1393 (93), 447.0950 (10)	Caerulescenoside[b]
113	27.14	447.0929	449.1065	0.9	26.3	$C_{21}H_{20}O_{11}$	285.0407 (54)	Kaempferol-hexoside or Luteolin-hexoside I[b]
114	27.47	431.0972	433.1104	2.6	26.1	$C_{21}H_{20}O_{10}$	341.0672 (41), 311.0546 (100)	Vitexin[a]
115	27.51	529.2274	–	3.2	63.8	$C_{25}H_{38}O_{12}$	323.0986 (61), 221.0656 (21), 179.0564 (33), 161.0456 (44), 147.0453 (100), 125.0246 (21)	Eurycomaoside I[b]
116	27.52	193.0510	–	−1.9	10.0	$C_{10}H_{10}O_4$	178.0255 (7), 134.0366 (100), 135.0404 (17)	(Iso)ferulic acid II[a]
117	27.54	771.1772	773.1937	0.8	48.5	$C_{36}H_{36}O_{19}$	609.1230 (30), 429.0838 (28)	Kaempferol trihexoside
118	27.84	319.0821	–	0.6	5.8	$C_{16}H_{16}O_7$	163.0403 (100), 155.0348 (15), 145.0303 (17), 137.0247 (27), 119.0501 (39), 111.0432 (14)	(trans)-*p*-Coumaric acid-*O*-shikimate II[b]
119	28.00	755.1828	757.1996	−2.8	16.0	$C_{36}H_{38}O_{18}$	595.1465 (100), 449.1030 (33), 287.0536 (17)	Kaempferol-3-*O*-β-(6-*O*-E-*p*-coumaroylglucoside)-7-*O*-β-hexoside[b]
120	28.27	785.1930	787.2106	−3.3	8.6	$C_{37}H_{38}O_{19}$	625.1568 (100), 449.1075 (21), 287.0536 (9)	Kaempferol-3-*O*-[(6-*O*-E-feruloyl)-β-D-glucopyranosyl]-(1 → 2)-β-D-galactopyranoside[b]
121	28.35	529.2291	531.2438	3.3	81.0	$C_{25}H_{38}O_{12}$	529.2254 (78), 323.0986 (61), 221.0656 (21), 179.0564 (33), 161.0456 (44), 147.0453 (100), 125.0246 (21)	Eurycomaoside II[b]
122	28.58	579.2085	–	−1.4	13.5	$C_{28}H_{36}O_{13}$	417.1554 (100)	(+)-Syringaresinol-β-D-glucoside (Eleutheroside E1)[a]
123	29.16	785.1930	787.1989	−1.9	15	$C_{36}H_{36}O_{18}$	595.1474 (100), 433.1191 (32), 271.0611 (17)	Apigenin trihexoside[b]
124	29.20	579.1725	–	−1	12.6	$C_{27}H_{32}O_{14}$	271.0609 (9)	Naringenin-7-neohesperidoside[a]
125	29.47	449.1084	–	1.2	10.6	$C_{21}H_{22}O_{11}$	287.0560 (100), 151.0300 (22)	Aromadendrin-*O*-hexoside or Eriodictyol-*O*-hexoside II[b]
126	29.51	529.2285	531.2420	3.1	38.3	$C_{25}H_{38}O_{12}$	151.0756 (100), 127.0382 (99), 145.0492 (67), 207.1383 (59), 103.0385 (45)	Eurycomaoside III[b]
127	29.62	739.1905	–	−3.4	32.4	$C_{36}H_{36}O_{17}$	607.1661 (100), 513.2341 (30), 413.0900 (18), 287.1548 (7)	Kaempferol-3-*O*-2-(6′-*p*-coumaroyl) glucosyl rhamnoside[b]
128	29.72	607.1669	609.1804	−0.1	6.0	$C_{28}H_{32}O_{15}$	299.0562 (13)	Diosmetin-neohesperidoside[b]
129	29.74	447.0931	449.1064	0.5	19.2	$C_{21}H_{20}O_{11}$	285.0407 (54)	Kaempferol hexoside or Luteolin hexoside II[b]

Table 1 (*continued*)

Peak*	t_R (min)	Precursor ion (m/z) $[M-H]^-$	Precursor ion (m/z) $[M+H]^+$	Error (ppm)	mSigma	Molecular formula	MS/MS (m/z) product ion(s)**	Tentative identity
130	29.89	769.1984	771.2135	0.1	20.6	$C_{37}H_{38}O_{18}$	607.1434 (100), 447.0927 (31), 431.0973 (32), 413.0858 (93)	Feruloylsaponarin[b]
131	29.98	–	625.1797	9.6	39.0	$C_{39}H_{28}O_8$	301.0716 (100)	Chrysoeriol dihexoside[b]
132	30.15	–	611.1401	−1	34.4	$C_{30}H_{26}O_{14}$	301.0707 (100)	Quercetin-3-*O*-β-D-(6-*O*-(E)-*p*-coumaryl) glucopyranoside[b]
133	30.30	–	493.1388	−1.8	7.6	$C_{23}H_{24}O_{12}$	331.0796 (100)	Tricin-7-glucoside or Rhamnazin-3-glucoside[b]
134	30.34	461.1118	463.1221	−6.2	31.8	$C_{22}H_{20}O_{11}$	299.0585 (3)	Chrysoeriol-7-β-D-glucoside[c]
135	30.53	463.1251	–	−1.1	8.8	$C_{22}H_{22}O_{11}$	301.0724 (100)	Hesperetin hexoside[b]
136	30.66	449.1094	–	−1	25.1	$C_{21}H_{22}O_{11}$	287.0568 (100), 151.0030 (27)	Aromadendrin-*O*-hexoside or Eriodictyol-*O*-hexoside III[b]
137	31.13	447.0937	–	−0.9	15.0	$C_{21}H_{20}O_{11}$	285.0413 (100)	Kaempferol-hexoside or Luteolin-hexoside III[b]
138	31.84	513.2321	515.2467	0.7	9.6	$C_{25}H_{38}O_{11}$	323.0987 (16), 263.0784 (16), 221.0661 (20), 179.0548 (79), 161.0453 (79), 125.0246 (100)	Taxchinin J I[b]
139	31.97	677.2978	–	−1.6	38.0	$C_{38}H_{46}O_{11}$	575.2696 (16), 533.2587 (55), 341.1038 (3), 203.0563 (10)	Gibberellin A1 anhydride[b]
140	32.37	513.2332	515.2474	1.9	8.0	$C_{25}H_{38}O_{11}$	323.0963 (21), 263.0790 (24), 221.0652 (25), 179.0565 (38), 161.0454 (100), 125.0250 (100)	Taxchinin J II[b]
141	32.58	515.2498	517.2620	0	1.8	$C_{25}H_{40}O_{11}$	371.2077 (100), 161.0462 (9), 125.0243 (31)	Volvaltrate C I[b]
142	33.05	515.2490	517.2633	1.6	9.1	$C_{25}H_{40}O_{11}$	371.2069 (8), 161.0460 (65), 125.0248 (100)	Volvaltrate C II[b]
143	33.28	593.1301	595.1429	−0.1	41.4	$C_{30}H_{26}O_{13}$	431.0955 (100), 413.0849 (50), 285.0408 (22), 179.0324 (21)	Kaempferol-3-*O*-(6-*O*-*p*-coumaroyl) glucoside (Potengriffioside A)[b]
144	33.42	515.2493	517.2626	0.9	5.9	$C_{25}H_{40}O_{11}$	371.2069 (100), 161.0451 (15), 125.0241 (31)	Volvaltrate C III[b]
145	33.55	407.1905	–	4.3	13.8	$C_{18}H_{32}O_{10}$	263.1505 (100), 125.0227 (6), 99.0461 (7)	Unidentified
146	34.86	523.1805	–	3	22.9	$C_{25}H_{32}O_{12}$	361.1266 (30), 259.0972 (31), 291.0871 (100)	Ligustroside[b]
147	35.43	272.0926	–	0.9	4.4	$C_{15}H_{15}NO_4$	124.0402 (100)	Thyronine[b]
148	35.87	287.0559	289.0720	0.9	4.2	$C_{15}H_{12}O_6$	151.0029 (90), 136.0476 (9), 125.0216 (7)	(+)-Eriodictyol[a]
149	36.53	285.0414	287.0553	−3.3	15.9	$C_{15}H_{10}O_6$	217.0555 (2), 201.0237 (3), 199.0387 (2), 175.0402 (2), 151.0026 (3), 133.0317 (2)	Luteolin[a]
150	38.91	327.2173	–	1.3	16.6	$C_{18}H_{32}O_5$	309.2055 (7), 291.1947 (16), 239.1299 (10), 229.1447 (33), 211.1350 (48), 171.1023 (49), 137.0951 (7)	Unidentified
151	39.85	359.0744	361.0907	7.9	31.9	$C_{18}H_{16}O_8$	344.0550 (98), 329.0358 (100)	Rosemarinic acid[a]
152	40.00	301.0732	–	−4.6	18.0	$C_{16}H_{14}O_6$	217.0036 (72), 151.0023 (100)	Hesperitin[b]
153	40.12	331.2501	–	−3.3	28.9	$C_{18}H_{36}O_5$	283.1923 (56), 265.1788 (10)	Trihydroxystearic acid[b]
154	40.17	299.0544	301.0705	5.8	11.3	$C_{16}H_{12}O_6$	284.0327 (100), 256.0358 (4), 217.0006 (9)	Chrysoriol[c]
155	40.57	329.2328	–	1.6	11.1	$C_{18}H_{34}O_5$	229.1450 (34), 211.1343 (43), 171.1023 (40), 139.1131 (8)	Trihydroxy-10-trans-octadecenoic acid[b]
156	40.91	327.2176	–	0.3	78.3	$C_{18}H_{32}O_5$	197.1185 (100), 171.1041 (20), 111.0804 (11)	Trihydroxy-10,15-octadecadienoate I[b]
157	41.62	287.2233	–	−1.7	15.7	$C_{16}H_{32}O_4$	201.0227 (3)	Diglycol laurate[b]
158	41.95	327.2176	–	0.4	15.3	$C_{16}H_{32}O_4$	197.1182 (100)	Trihydroxy-10,15-octadecadienoate II[b]
159	41.97	–	513.3053	1	21.0	$C_{27}H_{44}O_9$	351.2498 (26), 259.2095 (100), 161.1297 (32)	26-Hydroxypolypodine B I[b]
160	42.84	–	518.3468	1.5	28.1	$C_{30}H_{47}NO_6$	500.3208 (13)	N-Linolenoylethanolami ne[b]
161	43.68	–	282.2780	3.9	6.1	$C_{18}H_{35}NO$	201.0473 (100), 219.0536 (6)	Laurocapram[b]
162	43.98	–	513.3047	−0.4	11.1	$C_{27}H_{44}O_9$	351.2498 (23), 259.2092 (100), 161.1297 (21)	26-Hydroxypolypodine B II[b]
163	44.37	307.1916	–	−0.4	7.2	$C_{18}H_{28}O_4$	235.1329 (89), 211.1346 (49), 185.1182 (100), 137.0942 (11), 121.0662 (51)	Dihydrocapsiate[b]
164	45.55	311.1866	–	−0.7	10.9	$C_{17}H_{28}O_5$	293.1750 (28), 267.1966 (100)	Dihydroartemisinin ethyl ether I[b]
165	45.58	–	277.1804	−2	5.8	$C_{17}H_{24}O_3$	137.0591 (100), 109.0670 (19)	[6]-Shogaol[c]
166	46.28	–	677.3732	1.7	27.5	$C_{33}H_{56}O_{14}$	335.2644 (12), 261.2221 (100), 243.2130 (25)	Gingerglycolipid A I[a]
167	46.43	–	177.0538	4.8	6.2	$C_{10}H_8O_3$	121.0300 (10), 149.0199 (52), 93.0309 (15)	7-Methoxycoumarin[b]
168	46.96	311.2232	–	−1.3	4.0	$C_{18}H_{32}O_4$	293.2114 (11), 275.2011 (9), 253.1814 (2), 235.1706 (8), 223.1699 (100)	Linoleic acid 13-hydroperoxide I[b]
169	46.99	593.2622	–	−3.1	23.1	$C_{30}H_{42}O_{12}$	Nd.	Aceroside-3[b]
170	47.09	-	577.2638	0.9	40.8	$C_{30}H_{40}O_{11}$	351.2519 (28), 259.2064 (100), 241.1959 (22)	7-Acetyllushanrubescen sin A[b]
171	47.17	309.2075	–	−1.3	7.0	$C_{18}H_{30}O_4$	201.1141 (100)	Hydroxy-trans-di-epoxy-octadecenoic acid[c]

(*continued on next page*)

Table 1 (*continued*)

Peak*	t_R (min)	Precursor ion (m/z) $[M-H]^-$	Precursor ion (m/z) $[M+H]^+$	Error (ppm)	mSigma	Molecular formula	MS/MS (m/z) product ion(s)**	Tentative identity
172	47.29	313.2390	–	−1.8	5.9	$C_{18}H_{34}O_4$	293.2137 (7), 241.1414 (10), 183.1389 (28)	9,12-Dihydroxy-10-octadecenoic acid[c]
173	47.37	–	659.3643	−0.8	5.9	$C_{33}H_{54}O_{13}$	335.2603 (100), 261.2214 (30), 145.0493 (26)	Silenoside C[b]
174	47.95	–	353.2679	2	4.1	$C_{21}H_{36}O_4$	261.2174 (32), 135.1164 (76), 121.1008 (87), 107.0872 (100)	Linolenic acid monoglyceride[b]
175	48.01	675.3604	677.3724	−1	3.2	$C_{33}H_{56}O_{14}$	415.1450 (29), 397.1355 (100), 277.2176 (64)	Gingerglycolipid A II[a]
176	48.53	309.2066	–	1.6	14.1	$C_{18}H_{30}O_4$	291.1978 (14), 277.2124 (2), 197.1191 (100), 211.1331 (20)	Linolenic acid 13-hydroperoxide II[b]
177	48.62	–	518.3225	−0.1	16.9	$C_{28}H_{43}N_3O_6$	500.3129 (3), 335.2592 (3), 258.1116 (4), 184.0730 (100), 104.1068 (29)	Unidentified
178	49.02	–	640.3458	−0.7	30.6	$C_{32}H_{45}N_7O_7$	556.3040 (14), 337.2740 (100), 188.0913	Unidentified
179	49.56	–	627.2806	−1	11.9	$C_{34}H_{42}O_{11}$	567.2625 (11)	Swietemahonin F[b]
180	50.23	–	478.2914	−0.5	24.5	$C_{25}H_{39}N_3O_6$	337.2738 (100), 306.2818 (24)	Unidentified
181	50.50	–	520.3388	−0.3	18.5	$C_{28}H_{45}N_3O_6$	502.3292 (3), 337.2746 (4), 258.1121 (3), 184.0732 (100), 104.1077 (30)	Unidentified
182	51.17	–	496.3383	−0.5	10.2	$C_{26}H_{45}N_3O_6$	184.0728 (100)	Unidentified
183	51.52	–	553.4238	2.3	2.5	$C_{36}H_{56}O_4$	535.4125 (13), 445.3278 (8), 341.2455 (13), 145.1015 (17)	Kahweol palmitate[b]
184	51.84	–	496.3383	−0.4	14.9	$C_{26}H_{45}N_3O_6$	313.2728 (6), 184.0728 (100), 104.1069 (30)	Unidentified
185	51.94	293.2126	–	0.3	2.2	$C_{18}H_{30}O_3$	275.2042 (26), 223.1694 (100)	Juvenile hormone I[b]
186	53.76	295.2281	–	−0.7	1.6	$C_{18}H_{33}O_3$	277.2178 (82), 195.1388 (28), 171.1020 (19)	α-Artemisolic acid[b]
187	53.77	–	279.2321	−1	0.7	$C_{18}H_{30}O_2$	131.0842 (22), 121.1000 (22), 109.0975 (33), 95.0839 (100)	α-Linolenic acid[a]
188	53.79	–	557.4545	3.4	7.7	$C_{36}H_{60}O_4$	539.4454 (11), 521.4321 (12), 415.3520 (8), 317.2474 (10)	Unidentified
189	54.58	471.3463	–	3.5	12.6	$C_{30}H_{48}O_4$	293.2036 (1),277.2024 (1), 141.0164 (1)	Masilinic acid or Corsolic acid[b]
190	56.68	205.1604	–	−2.8	5.9	$C_{14}H_{22}O$	189.1298 (3)	2, 6-Tert-butylphenol[b]
191	58.12	–	611.2863	−2	18.4	$C_{34}H_{42}O_{10}$	567.2967 (38), 538.2669 (13)	Humilinolide C[b]

I, II… etc. denote isomers. Nd: not detected.

[a] Already reported in some *Arum* species like: *A. palaestinum*, *A. maculatum*, *A. orientale*, *A. italicum*, and *A. halicum*.

[b] Being reported for the first time in *Arum palaestinum*.

[c] Already reported in other species of the Araceae family.

* Peak numbers were assigned according to the overall elution order.

** The given fragmentation pattern is taken from the negative ion mode, except for compounds only detected in the positive ion mode.

the detected deprotonated/protonated molecule, MS/MS fragments and the suggested assignment. In the present work 180 phytochemical metabolites have been tentatively identified in the plant leaves by using the combination of MS and MS/MS data and the relevant information previously reported in the literature. The base peak chromatograms (BPC) of the *A. palaestinum* extract in negative and positive ionization modes, together with the detected UV_{240}, UV_{280} chromatograms are presented in Fig. 1. It is worth mentioning that the major part of the identified compounds in the present work has been reported in *A. palaestinum* for the first time. The structures of several tentatively identified compounds in the studied extract are illustrated in Fig. 2.

The characterization process for the compounds in this work was based on the MS data, together with the data obtained from the MS/MS spectra in comparison with those found in the literature. Additionally, the before assigned phytochemicals from same botanical family or species have been utilized in the identification when applicable. Besides, during identification, the following public databases have been used: Phenol-Explorer (www.phenol-explorer.eu), ChemSpider (http://www.chemspider.com), SciFinder Scholar (https://scifinder.cas.org) and KNApSAcK Core System (http://kanaya.naist.jp). Authentic standards were not commercially available for all the phenolics and the phytochemical compounds detected in this work.

3.1.1. Amino and amino-sugar derivatives

At the beginning of the analysis shown in the BPC of *A. palaestinum* (Fig. 1), a total of 7 amino-sugar derivatives (Amadori compounds) have been detected. Compounds **12**, **14**, **27**, **34**, **36** and **37** were tentatively identified as fructosyl-valine (Fig. 2a), glutimic acid hexose, fructosyl-tyrosine, fructosyl-leucine (Fig. 2b), and fructosyl-tryptophan I & II, respectively. All the previously mentioned compounds have demonstrated the neutral loss of sugar moiety (fructose or glucose), resulting in the appearance of the product ion (amino acid residue). So, for instance, in the MS/MS spectra, fructosyl-valine has exhibited the product ion at m/z 116.0714 (which corresponds to valine in structure). Similar compounds were described in dried tobacco (Leffingwell, 1999), as well, the fragmentation pattern of these compounds has been reported elsewhere in the bibliography (Wang, Lu, Liu, & He, 2008).

Compound **37** detected at t_R 15.14 min, with the molecular formula $C_{11}H_{12}N_2O_2$, has been assigned as tryptophan; an essential amino acid previously described in the Araceae family (Liang et al., 2013).

As such, the product ions at m/z 128.0346, 180.0664, 130.0868, 164.0710, with 100% relative intensity, were referred to as glutamic acid, tyrosine, leucine, and phenylalanine (Fig. 2c), respectively.

On the other hand, peaks detected at the retention times (5.71, 6.94, 7.40, 8.89, 9.42, 11.02 min) were characterized as isoleucine, tyrosin, phenylalanine methyl ester, 5-hydroxytryptophane, phenylalanine, respectively. Three nucleoside derivatives, namely, oxiamin, guanosine, and adenosine were also detected in *A. palaestinum*.

3.1.2. Phenolic acid derivatives

Thirty three phenolic acid derivatives were characterized by the method utilized in the present study.

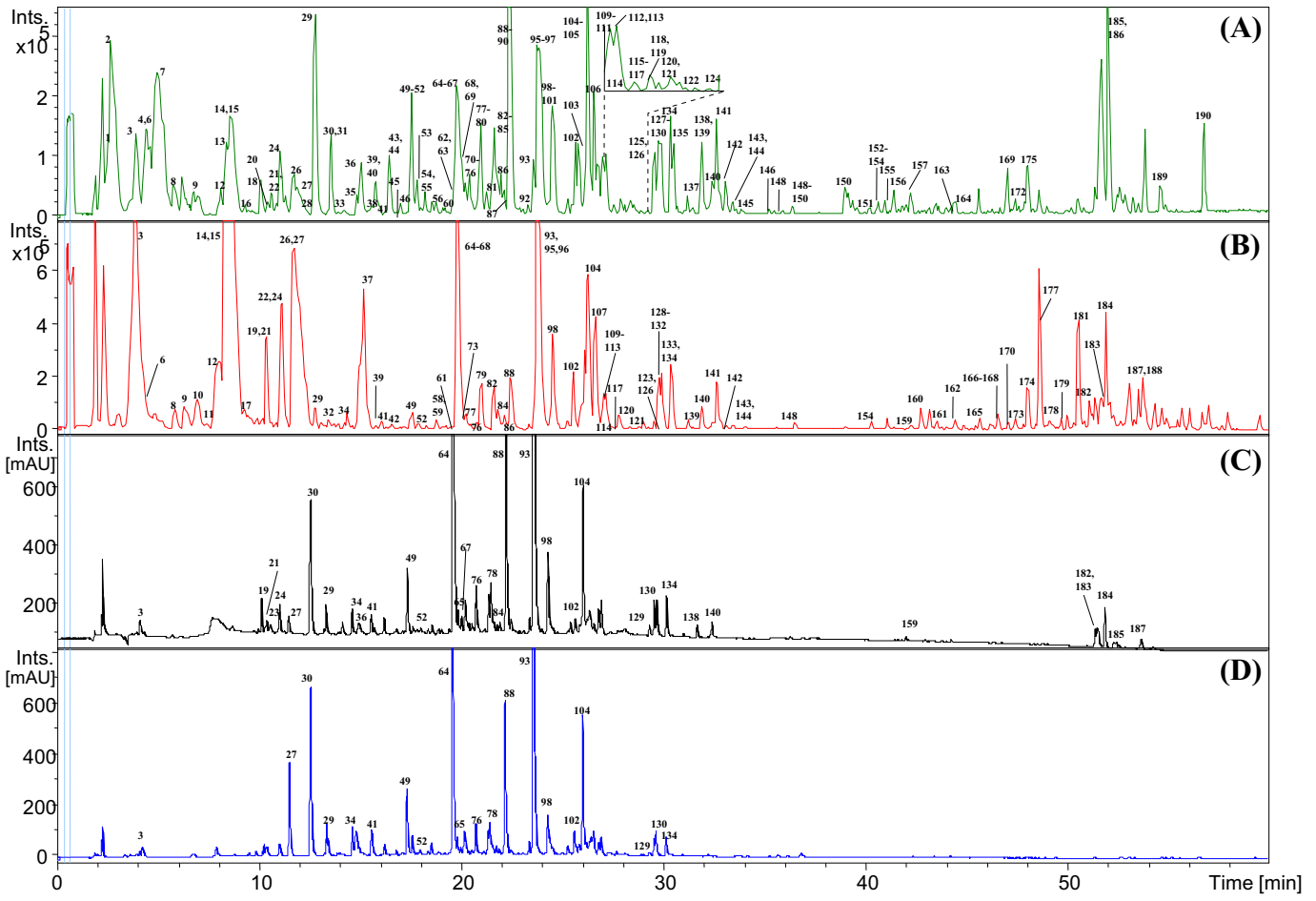

Fig. 1. UHPLC-DAD-ESI-QTOF-MS analysis of the hydro-methanol extract of the dried leaves of *Arum palaestinum*. (**A**) Base peak chromatogram (BPC), negative ion mode, *m/z* 50–1100; (**B**) BPC, positive ion mode, *m/z* 50–1100; (**C**) UV chromatogram: 240 nm; (**D**) UV chromatogram: 280 nm.

Several conjugated and glycosylated forms of caffeic, *p*-coumaric and ferulic acids have been detected in the *A. palaestinum* hydro-methanol extract. Thus, compounds **39**, **43**, **54** and **78** with precursor ions at *m/z* 341.0868/343.1036 in the negative and positive ion modes, were characterized as caffeoyl-hexose, depending on the MS data and fragmentation pattern, that demonstrated the neutral loss of a hexose moiety (162 Da) at *m/z* 179.0348 (indicates caffeic acid in structure).

Similarly, the ion at *m/z* 503.1406, which appeared at the retention times 16.93 and 18.34 min, was identified as caffeoyl dihexoside, due to the loss of a dihexose moiety and from the yielded ions at *m/z* 341.0843 [M−H−162]−, 179.0342 [M−H−162−162]−, 161.0241 [M−H−162−162−18]−, which implies losses of hexose, hexose and H_2O, respectively.

Likewise, peaks **40**, **57**, and **60** with the molecular formula $C_{15}H_{18}O_8$, were detected in the negative ion mode at [M−H]−*m/z* 341.087. In the MS/MS spectra, the fragment ion at *m/z* 163.0413 was referred to the coumaric acid in structure. Therefore, the three compounds were suggested as coumaryl-hexose isomers.

Compounds **31** and **38**, with the identical molecular ion in the MS spectra, and had the molecular formula $C_{21}H_{28}O_{14}$, were assigned as caffeoyl-fructofuranosyl-glucopyranoside or 6-*O*-caffeoylsophorose.

The detected ions [M−H]−at *m/z* 517.1553, which correspond to peaks **44** and **56** showed a loss of dihexose moiety (sucrose) resulting in the fragment ions at *m/z* 355.1019 and 193.0566, which corresponds to feruloyl glucose and ferulic acid, respectively. Therefore, they were suggested as feruloylsucrose isomers. These compounds are being reported for the first time in *A. palaestinum*.

On the other hand, ferulic acid hexoside was proposed for compounds **35**, **51** and **70**. In the QTOF-MS analysis these compounds have displayed the product ion at *m/z* 193.0506 (ferulic acid).

Peaks **63**, **83**, **88** and **100** with the pseudo-molecular ion at *m/z* 335.0780, have been tentatively assigned as (trans)caffeoylshikimic acid isomers. These compounds are reported in this study in *A. palaestinum* for the first time. In the QTOF-MS analysis, MS/MS data have displayed the product ions at *m/z* 179.0353 [M−H−156]−and 135.0461 [M−H−156−44]−, which implies the neutral loss of shikimic acid and CO_2, respectively. The fragmentation pathway is discussed in Fig. 4l.

Compound **151** which had the precursor ion at *m/z* 359.0744/361.0907, with the molecular formula $C_{18}H_{16}O_8$, has been identified as rosmarinic acid, based on the correct data obtained by QTOF-MS. Interestingly; this bioactive compound has also been reported in *Arum dioscoridis* (Uguzlar, Maltas, & Yildiz, 2012). Rosmarinic acid has been reported to possess different biological effects, including anti-carcinogenic, anti-microbial, anti-inflammatory, anti-Alzheimer, and anti-depressant properties (Bhatt, Mishra, & Bansal, 2013).

Peak **102** (t_R 25.62 min) was tentatively assigned as 4-caffeoyl-5-feruloylquinic acid (Fig. 2d, Fig. 3). The fragmentation behavior was previously reported in chrysanthemum flower (*Chrysanthemum morifolium* Ramat) (Lin & Harnly, 2010).

3.1.3. Flavonoid derivatives

A total of 53 flavonoids and derivatives have been tentatively identified in *A. palaestinum* by the technique used.

The compound at *m/z* 339.0724 (t_R 16.46 min) with molecular formula $C_{15}H_{16}O_9$ showed a neutral loss of a hexose moiety [M−H−

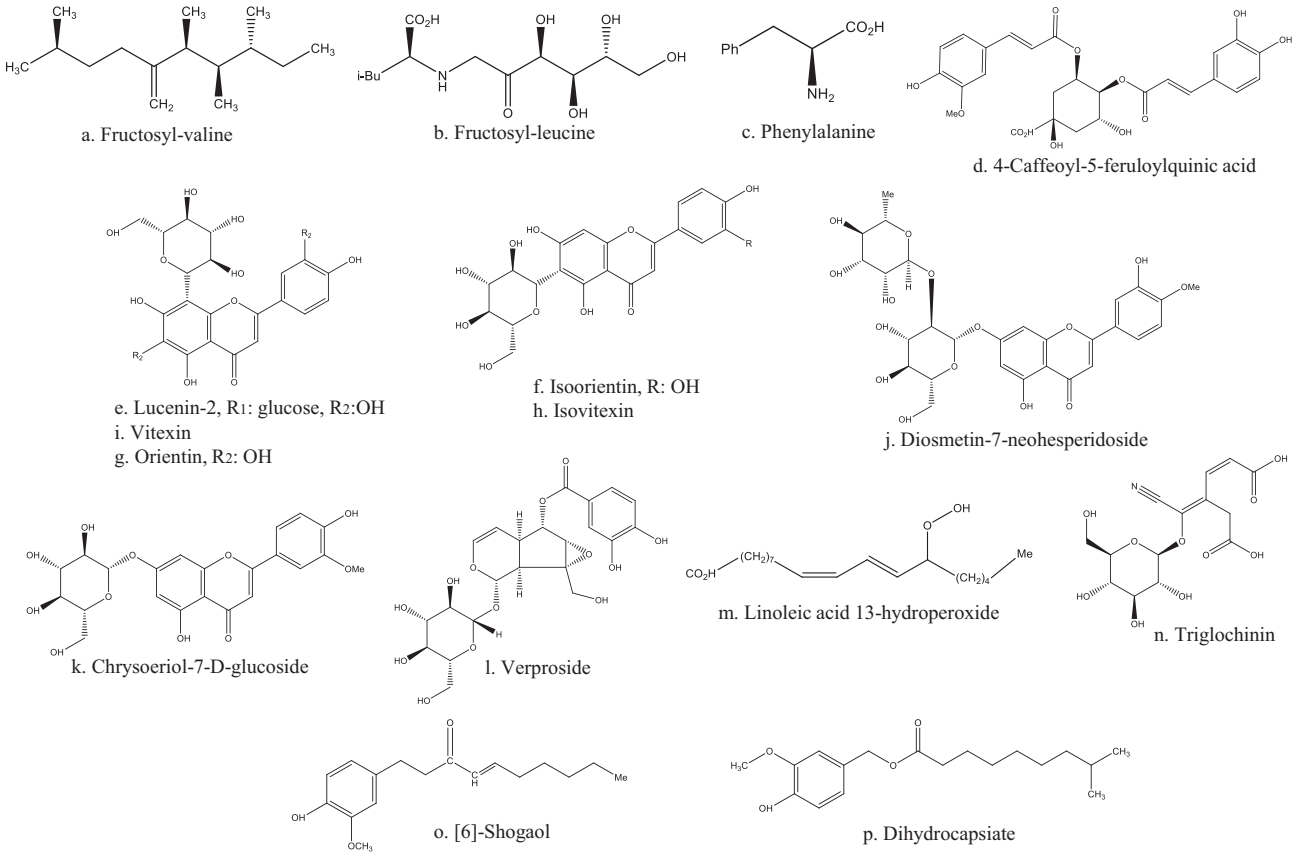

Fig. 2. Structures of phytochemical metabolites detected and characterized in *Arum palaestinum* leaves.

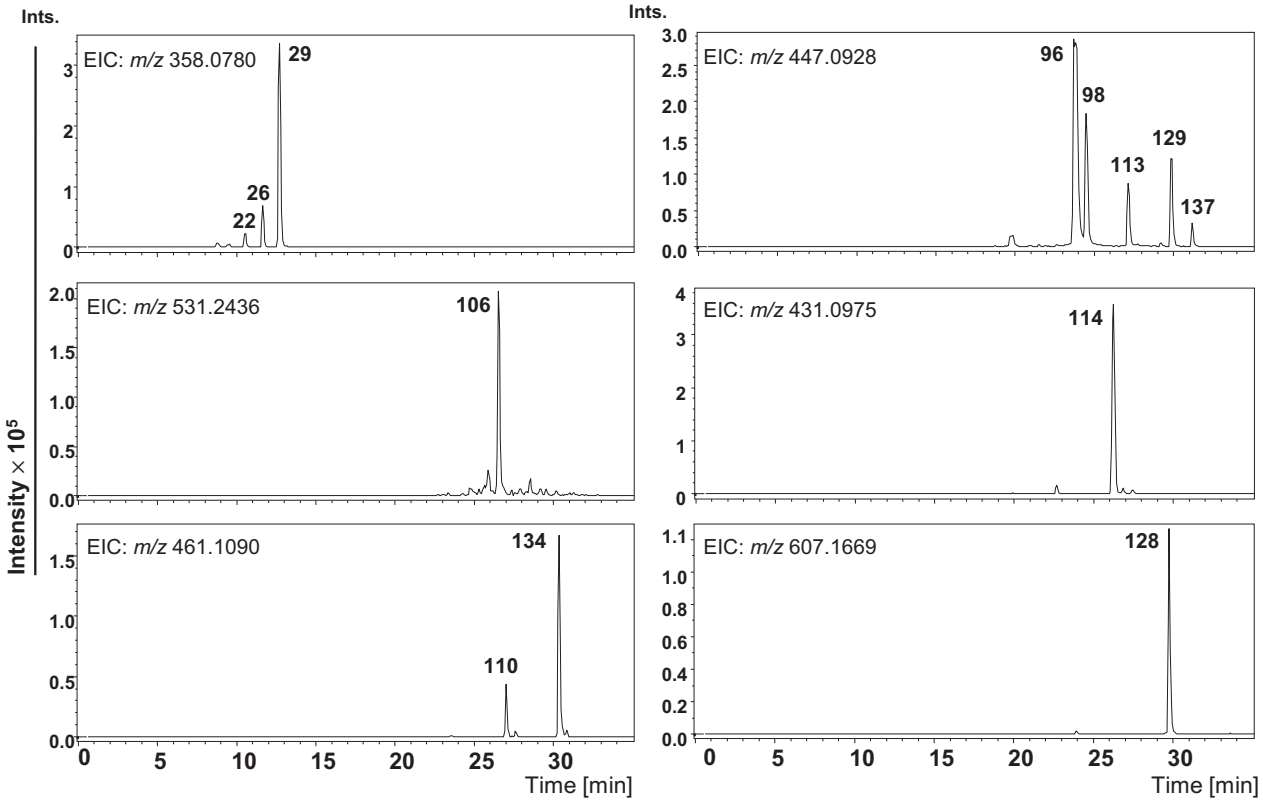

Fig. 3. Extracted Ion Chromatogram (EIC) of some detected phytochemicals from *Arum palaestinum* (0-35 min).

162]−to form the fragment ion at *m/z* 177.0190 which corresponds to esculetin. Thus, compound **45** was proposed as esculetin-*O*-hexoside.

In the positive ion mode, peaks **59** and **61** (19.02 and 19.20 min) with the pseudo-molecular ion at 627.1586, were proposed as quercetin dihexoside. Relying on the correct data of MS and MS/MS spectra, which showed the neutral loss of dihexoside (−324 Da) and the arising of the product ion at *m/z* 303.0486 (quercetin). Likewise, peak **65** was suggested as 6,8-Di-*C*-β-glucosylapigenin (Vicenin 2), an already reported compound in *A. palaestinum* (El-Desouky et al., 2007a).

With the same molecular formula ($C_{27}H_{30}O_{17}$) obtained by the DataAnalysis 4.0™ program, two peaks (**59** and **61**), showed the neutral loss of 324 Da, which is in harmony with the loss of two hexose moieties. The two isomers were characterized as quercetin dihexoside, a similar compound also was identified in *Oronrium trquaticum* (Araceae).

The precursor ions at *m/z* 609.1459/611.1597 exhibited two peaks (*Rt* 21.53 and 24.21 min) which were suggested as di-*C*-glucosylluteolin. In the MS/MS spectra, these compounds showed neutral losses which pertain to the *C*-glycoside fragmentation pattern (Table 1). On the other hand, compound **64** (t_R 19.70 min), which gave the same MS information, but with a different fragmentation pattern, so it was tentatively assigned as lucenin-2 (Fig. 2e).

Compound 80 detected at 20.96 min, has been identified as vitexin-*O*-glucoside, a flavonoid derivative already found in *Dracontium asperum* (Araceae) (Williams, Harborne, & Mayo, 1981).

Peaks **67** and **91** (t_R 19.96 and 23.02 min) with same molecular formula ($C_{33}H_{40}O_{20}$) were tentatively suggested as quercetin-*O*-rhamnosylrutinoside or kempferol-*O*-rutinoside-*O*-glucoside isomers.

Two compounds: isoshaftoside and shaftoside (**93** and **101**) were already detected in the Araceae plants: *Anthurium bellum*, *Philodendron eichlerit*, and *Philodendron smithii* (Williams et al., 1981), and being reported herein for the first time in *A. palaestinum*.

Di-*C*-glucosylluteolin has been assigned for the two detected peaks at (*tR* 20.92 and 21.53 min), in agreement with the previous literature on *Philodendron saxicolum* (Araceae) (Williams et al., 1981).

Compound **117** at *m/z* 771.1772/773.1937 was assigned as kaempferol trihexoside. These compounds showed neutral losses of three hexose moieties (−162 Da × 3). The fragment ions at *m/z* 609.1230 and 429.0838 were observed in the MS/MS spectra. This fragmentation pattern is in agreement with the already reported literature (Llorach, Gil-Izquierdo, Ferreres, & Tomas-Barberan, 2003).

Cyanidin-3-rutinoside has been characterized for peaks **77** and **109**. The MS/MS spectrum in the negative ion mode has demonstrated the product ions at *m/z* 447.0972 and 285.0380, while they showed the product ion at *m/z* 433.1110 in the positive mode. This compound was reported in *Arum maculatum* (Baxter, Harborne, & Moss, 1998).

Peak **76** (t_R 20.56 min) exhibited a deprotonated molecule at *m/z* 623.1618/625.1751 and the MS/MS fragment ions at *m/z* 533.1321 [M−H−90]−, 503.1177 [M−H−120]−, and 299.0689 [M−H−324]−(diosmetin). Consequently, this compound has been suggested as diosmetin-6,8-di-*C*-hexose.

On the other hand, peak **85** was assigned as (epi)catechin, depending on the QTOF-MS acceptable data, and on the literature cited on *A. dioscoridis* (Araceae) (Uguzlar et al., 2012).

The ion at *m/z* 563.1400 exhibited two peaks (t_R 23.53 and 24.70 min), which were suggested as isoshaftoside and shaftoside. Based on MS/MS data, it has been possible to distinguish between the two isomers (Ferreres, Silva, Andrade, Seabra, & Ferreira, 2003). These compounds are reported for the first time in *A. palaestinum*.

Similarly, compounds **96** and **98** with the identical molecular formula ($C_{21}H_{20}O_{11}$) had the molecular ion at *m/z* 447.0929 (Fig. 3). These compounds were identified as isoorientin (Fig. 2f) and orientin (Fig. 2g), respectively, relying on their fragmentation behavior as shown. Moreover, both compounds have been already described in *A. palaestinum* (Afifi et al., 1997; Afifi et al., 1999; El-Desouky et al., 2007a).

Interestingly, the compound at *m/z* 445.1129, detected in the positive ion mode, gave the fragment ion at *m/z* 287.0544 (corresponds to pseudobaptigenin in structure) followed to a neutral loss of

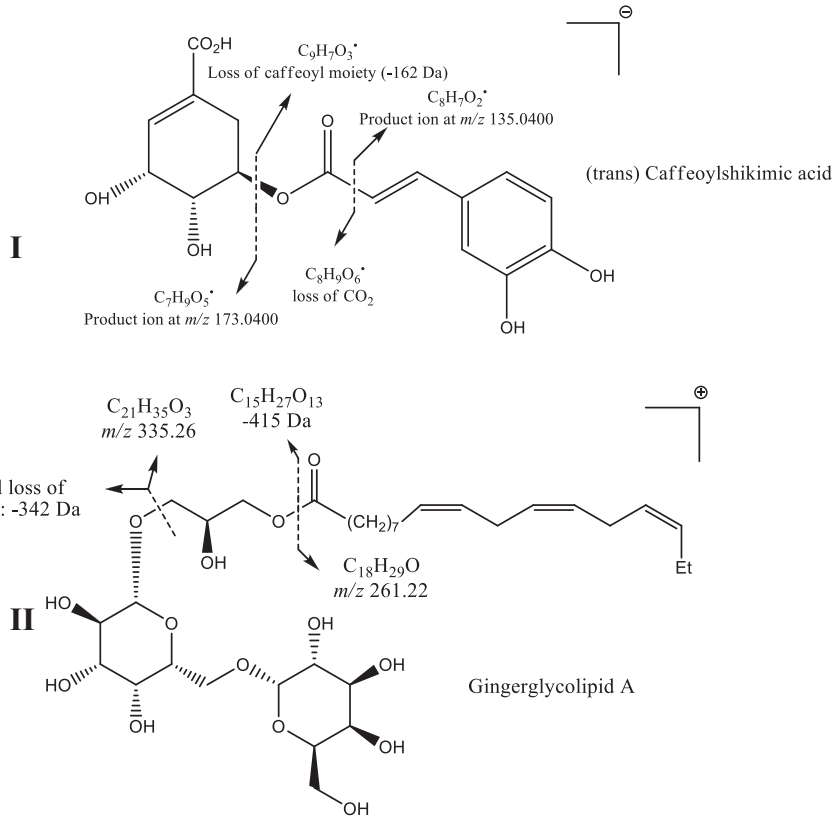

Fig. 4. MS/MS based proposed fragmentation pathway of two newly characterized compounds: **I** (trans) Caffeoylshikimic acid, and **II** Gingerglycolipid A.

a hexose moiety (−162 Da). Therefore, compound **95** was assigned as pseudobaptigenin-*O*-hexoside (Rothindin).

With same molecular formula $C_{21}H_{22}O_{11}$, three peaks (**108**, **125**, and **136**) were detected at *m/z* 449.1084 in the negative ion mode. In the MS/MS spectra, the loss of hexose moiety [M−H−162]−and the appearance of the ion at *m/z* 287.0559 in the MS/MS spectra, which corresponds to the aglycone aromadendrin. Thus, the compounds have been tentatively identified as aromadendrin-*O*-hexoside; a newly identified phenolic compound in the *Arum* genus.

Compounds **113**, **129** and **137** were characterized as kaempferol hexoside or luteolin hexoside. These suggested compounds have shown the same fragment ions at *m/z* 285.0407 which correspond to the neutral losses of [M−H−162]−(hexose moiety), that results in the arising of the product ion at *m/z* 285.0408 (kaempferol or luteolin in structure).

With the precursor ion at *m/z* 431.0975, two isomers (**104** and **114**) have been detected. Compound **104** was identified as isovitexin (Fig. 2h), an already reported flavonoid derivative in *A. palaestinum* (Farid et al., 2014). The fragmentation pattern was the same as reported by Abu-Reidah, Arráez-Román, Segura-Carretero, and Fernández-Gutiérrez (2013b). Otherwise, compound **114** has been identified as vitexin (Fig. 2i, Fig. 3), a previously discussed compound in *A. palaestinum* (Afifi et al., 1997; Afifi et al., 1999).

Naringenin-7-neohesperidoside (**124**), has been assigned for the molecular ion at [M−H]−*m/z* 579.1725 and the product ion at *m/z* 271.0609 (indicates naringenin in structure). Curiously, this compound was already described in *A. dioscoridis* (Uguzlar et al., 2012).

At the retention time 29.72 min, the molecular ion at *m/z* 607.1669/609.1804, has been detected ($C_{28}H_{32}O_{15}$). In the QTOF-MS analysis, it has demonstrated the product ion at *m/z* 299.0562 (diosmetin) which arose subsequent to the neutral loss of a disaccharide moiety. Thus, compound **126** has been tentatively identified as diosmetin-7-neohesperidoside (Fig. 2j, Fig. 3).

In the positive ion mode, peak **131** showed the product ion at *m/z* 301.0716, which indicates chrysoeriol in structure, and the neutral loss of two moieties of hexose $[M+H-324]^+$. Accordingly, this compound was tentatively proposed as chrysoeriol dihexoside.

Chrysoeriol-7-β-D-glucoside (Fig. 2k) has been assigned for compound **134** (*m/z* 461.1118/463.1221), based on the data obtained from MS and MS.MS spectra (Fig. 3), also on the previous bibliography on *A. palaestinum* (Afifi & Abu-Dahab, 2012).

In this work, simple aglycones have been also detected and characterized. Thus, peaks **148** (*m/z* 287.0559), **149** (*m/z* 285.0414), **152** (*m/z* 301.0732), and **154** (*m/z* 299.0544), have been identified as (+)-eriodictyol (Uguzlar et al., 2012), luteolin (El-Desouky et al., 2007a), hesperitin, and chrysoriol, respectively.

In the positive mode, the molecular ion $[M+H]^+$ at *m/z* 493.1388 (*Rt* 30.30 min), has been tentatively characterized as tricin-7-glucoside or rhamnazin-3-glucoside. This compound has demonstrated the product ion at *m/z* 331.0796 which appeared after a glucose moiety loss [M−H−162]−.

3.1.4. Flavonoid–phenolic acid conjugated compound derivatives

Four conjugated flavo-phenolic acid glycosidic compounds were detected and characterized for the first time in *A. palaestinum*.

Thus, the compounds **127**, **130**, **132**, and **143** were tentatively assigned as kaempferol-3-*O*-2″-(6‴-p-coumaroyl) glucosyl rhamnoside, feruloylsaponarin, quercetin-3-*O*-β-D-(6″-*O*-(E)-p-coumaryl) glucopyranoside, and kaempferol-3-*O*-(6″-*O*-*p*-coumaroyl) glucoside (Potengriffioside A), respectively.

3.1.5. Iridoid derivatives

Seven iridoids and derivatives were detected at the retention times, 17.70, 19.31, 19.92, 21.39, 21.91, and 23.31 min. Thus compounds **49**, **66**, and **81** which gave the molecular ion at *m/z* 497.1300/499.1430 were tentatively identified as verproside isomers (Fig. 2l), based on the correct data from QTOF-MS analysis; which is in accordance with the fragmentation pattern already described by Hong et al. (2010). On the other hand, the peaks **52**, **62**, **86**, and **92** with the molecular formula $C_{22}H_{26}O_{12}$, have been tentatively suggested as catalposide isomers.

Three isomers (**141**, **142**, and **144**) exhibited the pseudo-molecular ion at *m/z* 515.2498/517.2620, and the product ions at *m/z* 371.2077, 161.0462, 125.0243 in the QTOF-MS analysis. These compounds were tentatively suggested as volvaltrate C.

The compound with the precursor ion at [M−H]−*m/z* 579.2085, gave the fragment ion at *m/z* 417.1554 (indicates syringaresinol in structure) with 100% relative intensity. Consequently, compound **122** was identified as (+)-syringaresinol β-D-glucoside, an iridoid, already separated from *Arum italicum* (Greca, Molinaro, Monaco, & Previtera, 1993).

3.1.6. Terpenoid derivatives

One sesquiterpenic compound was detected with the precursor ion at *m/z* 693.2958 in the negative ion mode, and has been tentatively proposed to be blumenol-*C*-9-*O*-β-(6′-*O*-rhamnosyl-2′-*O*-β-glucuronosylglucoside). This compound was already found in *Ornithogalum umbellatum* (Schliemann et al., 2006).

The compound **97** (t_R23.84 min) was tentatively assigned as euphopubescenol, based on the acceptable data from MS and MS/MS spectra (Valente et al., 2004); this compound was reported to own anti-cancer activity (Reis et al., 2012).

Three isomers of quassinoid-type glycoside have been detected and characterized for the peaks **115**, **121**, and **126**, to be eurycomaoside.

Taxchinin J has been suggested for the compounds **138** and **140**, which gave the molecular ion at *m/z* 513.2321/515.2467, and the fragment ions at *m/z* 323.0963, 263.0790, 221.0652, 179.0565, 161.0454 and 125.0250.

Based on QTOF-MS data, the molecular ion at *m/z* 471.3463 with the molecular formula $C_{30}H_{48}O_4$ has been tentatively assigned as masilinic acid or corosolic acid.

Compound **191** (t_R 58.12 min) gave precursor ion at *m/z* 611.2863 and was tentatively characterized as humilinolide C.

3.1.7. Coumarin derivatives

Two coumaric compound derivatives have been characterized in *A. palaestinum*. Thus, peaks **73** and **167** (t_R 20.47 and 46.43 min) have been assigned as cantabilin and 7-methoxycoumarin, respectively.

3.1.8. Other compounds

The UHPLC–DAD-ESI-QTOF-MS has shown to be a powerful method for the identification of phenolic and non-phenolic metabolites in *A. palaestinum*.

Nearly at the end of the chromatogram (BPC) of the hydro-methanol extract, the presence of several peaks corresponding to fatty acids has also been revealed: Trihydroxystearic acid (**153**), trihydroxy-10-trans-octadecenoic acid (**155**), trihydroxy-10,15-octadecadienoate I & II (**154** and **158**), linoleic acid 13-hydroperoxide I & II (**168** and **176**) (Fig. 2m), linolenic acid monoglyceride (**174**), kahweol palmitate (**183**), α-artemisolic acid (**186**), and α-linolenic acid (**187**).

Three cyanogenic glucoside derivatives (t_R 10.56, 11.61, and 12.73 min) with the pseudo-molecular ion at *m/z* 358.0765/360.0925, have been detected and assigned as triglochinin isomers (Fig. 2n, Fig. 3). In the MS/MS spectra, these compounds displayed the product ions at *m/z* 125.0239, 152.0340. This compound has been already identified in *A. maculatum* (Nahrstedt, 1975), but for the first time in *A. palaestinum*.

Interestingly, the ginger constituent [6]-shogaol (Fig. 2o) has been detected in the positive ion mode and was assigned for peak **165**. The characterization process was based on QTOF-MS acceptable data, and the data obtained from the literature on Araceae species (Liang et al., 2013). This phyto-component was described to attenuate the inflammation (Moon et al., 2014). Moreover, this compound and its

metabolites were reported to inhibit growth and induces apoptosis cancer cell (Kim et al., 2014; Warin, Chen, Soroka, Zhu, & Sang, 2014).

Two peaks (t_R 26.28 and 28.01 min) gave the precursor ion at m/z 675.3604/677.3724 in the negative and positive ion modes with same molecular formula $C_{33}H_{56}O_{14}$, and were characterized as gingerglycolipid A. A proposed fragmentation behavior for this compound in the positive mode is presented in the Fig. 4II.

Compound **163** (t_R 44.37 min) with the precursor ion $[M-H]$ at m/z 307.1916 has been characterized as dihydrocapsiate (Fig. 2p). It is worth mentioning that this compound has been reported to be an anti-cancer agent (Inada & Miyaura, 2009; Shin, Kwon, Pyun, & Kim, 2009).

Vitamin B4 has been proposed for the molecular ion $[M+H]^+$ at m/z 136.0613 with the molecular formula $C_5H_5N_5$. It is to note that this compound has been already described in the Araceae family (Lu, Luo, Chi, & Wu, 2011).

Finally, the antioxidant compound; 2,6-tert-butylphenol has been tentatively proposed for peak **190** ($C_{14}H_{22}O$).

4. Conclusion

The present study represents the first comprehensive phytochemical analysis of *A. palaestinum*, a wild edible plant of the Mediterranean region. The LC–MS/MS-based method described here proved to be superior with regard to sensitivity, selectivity, and speed of analysis. A total of 180 metabolites were tentatively identified in *A. palaestinum* by using the correct and acceptable data of MS and MS/MS together with the information previously reported in the literature. The obtained results could explain the past and current usage of *A. palaestinum* as food, in folk medicine; also may support its further uses in health and nutrition as a functional food. Thorough research on *A. palaestinum* might put up to the discovery of new bioactive and health-promoting functional components.

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