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Comparative study of *Mentha* species growing wild in Egypt: LC-ESI-MS analysis and chemosystematic significance

Mona M. Marzouk[1], Sameh R. Hussein[1*], Ahmed Elkhateeb[1], Mona El-shabrawy[1], El-Sayed S. Abdel-Hameed[2,3], Salwa A. Kawashty[1]

[1]Phytochemistry and Plant Systematics Department, National Research Centre, 33 El Bohouth St., Dokki, Giza, P. O. 12622, Egypt.
[2]Laboratory of Medicinal Chemistry, Theodor Bilharz Institute, Giza, Egypt.
[3]Chemistry Department, Faculty of Science, Taif University, Saudi Arabia.

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ABSTRACT

Mentha longifolia (L.) Huds. and *Mentha pulegium* L. are growing wild in Egyptian flora, they have many biological activities and commonly used as traditional herbal medicines. The aqueous methanolic extracts of the two Egyptian species were subjected to a comparative study for the first time using the LC-ESI-MS fingerprint. 43 compounds belonging to different chemical classes (flavone, flavonol, flavanone, *C*-glycosylflavone, phenolic acids and their glycosides) have been identified. The identified compounds can be used as chemosystematic markers and further our knowledge of the infraspecific relationship between the studied species. Further isolation and *in vitro* testing of metabolites will provide more evidence for the possible uses of *Mentha* sp.

INTRODUCTION

Lamiaceae, previously called Labiatae, is the mint family of flowering plants consisting of 236 genera and more than 7,000 species. It is one of the largest plant families (Hajlaoui *et al.*, 2009). Due to the ease of cultivation, many members of Lamiaceae are widely cultivated for their aromatic qualities. Mint plants are used in medicine, food, and perfume industry. They are used in folk medicine as anti-inflammatory, antiemetic, antispasmodic, carminative, choleretic, emmenagogue, diaphoretic, and have antimicrobial activities (Naghibi *et al.*, 2005). *Mentha* is a genus of about 25 species of flowering plants which distributed across Africa, Asia, Europe, North America, and Australia (Mustafa *et al.*, 2005). These species are commercially grown for its essential oil content. In the Egyptian flora, the genus *Mentha* is represented by two species; *Mentha longifolia* (L.) Huds. and *Mentha pulegium* L. (Mustafa *et al.*, 2006).

The phytochemical constituents reported from *M. longifolia* and *M. pulegium* are flavonoids (Sharaf *et al.*, 1999; Guvenalp *et al.*, 2015; Taamalli *et al.*, 2015), phenolic acids (Guvenalp *et al.*, 2015; Taamalli *et al.*, 2015), essential oils (El-Ghorab, 2006), dihydrochalcone glycosides (Guvenalp *et al.*, 2015) and β-sitosterol glycosides (Ali *et al.*, 2002). Flavonoids are the major reported metabolites, they occurred mostly as flavones and their glycosides (Baris *et al.*, 2011; Orhan *et al.*, 2012; Gulluce *et al.*, 2013; Guvenalp *et al.*, 2015; Taamalli *et al.*, 2015), while *C*-glycosyl flavones (Sharaf *et al.*, 1999), methoxyflavone aglycones (Zaidi *et al.*, 1997; Taamalli *et al.*, 2015), flavanones and their glycosides (Krzyzanowska *et al.*, 2011; Taamalli *et al.*, 2015), and flavonol glycosides (Akroum *et al.*, 2009) were also reported.

M. longifolia and *M. pulegium* are previously reported for their antioxidant (El-Ghorab, 2006; Hajlaoui *et al.*, 2009), cytotoxic (Shirazi *et al*., 2009; Orhan *et al.*, 2012; Al-Ali *et al.*,

*Corresponding Author
Sameh R. Hussein, Phytochemistry and Plant Systematics Department, National Research Centre, 33 El Bohouth St., Dokki, Giza, P. O. 12622, Egypt. E-mail: sameh_reda @ hotmail.com

2013; Gulluce *et al.*, 2015), and antimicrobial (Akroum *et al.*, 2009, Baris *et al.*, 2011) activities.

There are no studies have been reported on phenolic constituents of the two wild *Mentha* species from Egypt. The previous phytochemical study on *M. pulegium* was carried out on a cultivated species (Shalaby *et al.*, 2000). Therefore, the aim of the current study was to perform a full characterization of the phytochemicals existing in the aqueous methanolic extracts of *M. longifolia* and *M. pulegium,* growing in Egypt, using LC-ESI-MS analysis, in an attempt to tentatively identify the polar compounds present in their extracts. In addition, the chemosystematic significance of the detected phenolics was also discussed.

EXPERIMENTAL

Plant material

M. longifolia was collected from west El Fayoum canal bank, Egypt in April 2016 while *M. pulegium* was collected from irrigated canal from Baharryia Oasis, Egypt in March 2016 and authenticated by Dr. Mona M. Marzouk and Dr. Sameh R. Hussein, Department of Phytochemical and Plant Systematics, NRC. A voucher specimen (sn. 3402 and 3256, respectively) were deposited in the Herbarium of NRC (CAIRC, Cairo, Egypt).

Extraction

50 g of each species were air dried and extracted with 70% methanol-water at room temperature twice each for two days. The crude filtered extracts were concentrated under reduced pressure in a rotary evaporator till dryness and preserved in −80°C freezer until LC-MS analysis.

LC-ESI-MS analysis

The LC-ESI-MS analysis of the studied species was carried out on HPLC (Waters Alliance 2695) and mass spectrometry (Waters 3100) and followed the same method of Hussein *et al.* (2018).

RESULTS AND DISCUSSION

LC-ESI-MS analysis

43 compounds were characterized and identified from *M. longifolia* and *M. pulegium* extracts (Table 1; Figure 1(a, b)). Peaks **2** and **3** revealed the same fragments; *m/z* 179, 135, indicating the presence of caffeoyl hexoide derivatives. Compound 3 gave molecular ion peak at *m/z* 665 and fragments at *m/z* 503 [M-hexose]$^-$, 341 [M-2hexose]$^-$, 179 [M-3hexose]$^-$, confirmed that the three hexose moieties were connected to different phenolic hydroxyl groups.

Peak **4** (m/z 191) was characterized as citric acid. Its spectrum showed a fragment ion at *m/z* 111 which corresponds to the loss of H_2O and CO_2 molecules [M-H-CO_2-2H_2O]$^-$ (Taamalli *et al.*, 2015).

Quinic acid was presented as peak **6** (*m/z* 191) in both extracts, confirmed by the presence of the fragment ion at *m/z* 127 [M-H-CO-2H_2O]$^-$ (Taamalli *et al.*, 2015). This compound was identified in various *Mentha* spp. (Taamalli *et al.*, 2015; Xu *et al.*, 2017).

Peaks **8**, **11** & **12** produce the same molecular ion peak at *m/z* 353 and identified as chlorogenic acid derivatives. The product ion at *m/z* 191 [quinic acid-H]$^-$, corresponding to quinic acid and another fragment ion at *m/z* 179 [caffeic acid-H]$^-$, corresponding to caffeic acid. Additional fragment ion was observed in compound **12** at *m/z* 173 [quinic acid-H_2O-H]$^-$, which is characteristic to 4-*O*-caffeoylquinic acid (Ncube *et al.*, 2014). It was identified in both extracts under study. Also, compounds **8** and **11** were identified as *cis*- and *trans*-3-*O*-caffeoylquinic acid, respectively. They were identified in *M. longfolia* only. Other chlorogenic acids were shown for peaks **10**, **15**, **39** and **40**. Compounds **10** and **15** have the same molecular ions at *m/z* 337 and fragmentation ions at *m/z* 191 and 119 [M-H-Coumaroyl]$^-$, 173 [quinic acid-H_2O-H]$^-$, 163 [Coumaric acid-H]$^-$ and 119 [M-H-CO_2]$^-$. They have been identified as coumaroyl quinic acids (Ncube *et al.*, 2014). Compound **39** with a molecular ion at *m/z* 487 and fragments 308 [M-H-caffeoyl] and 179 [M-H-deoxyhexose-hexose]$^-$, confirmed the presence of caffeoyl hexose–deoxyhexose (Chen *et al.* 2011). While compound **40** was identified as 3,4-di-*O*-caffeoylquinic acid, confirmed the presence of fragment ions 353 [M-H-caffeoyl]$^-$, 191 [quinic acid-H]$^-$, 179 [caffeic acid-H]$^-$, 173 [quinic acid-H_2O-H]$^-$ (Ncube *et al.*, 2014).

Peak **9** with a molecular ion *m/z* 609 showed a fragment ion at *m/z* 447 after the loss of hexose moiety [M-H-162]$^-$. The fragment ions at *m/z* 327 [M-H-162-120]$^-$, and at *m/z* 357 [M-H-162-90]$^-$, confirmed the characteristic of luteolin 8-*C*-hexoside (Farag *et al.*, 2016). Therefore, compound **9** was assigned as luteolin 6-*C*-hexoside-*O*-hexoside. Another luteolin diglycosides was detected at peak **36** (*m/z* 593), which exhibited a fragment ion at *m/z* 285 [M-H-(rhamnose+hexose)]$^-$. No fragments were observed at *m/z* 431 and/or 447, indicated that both glycosyl moieties were connected to the same phenolic hydroxyl group (Marzouk *et al.*, 2016). Thus, compound **36** identified as luteolin-*O*-rhamnose-hexose.

Compound **13** produced a molecular ion peak at *m/z* 179 and is identified as caffeic acid, confirmed by the mass fragments and *Rt* of the authentic standard.

Tuberonic acid hexoside (peak **14**) with *m/ z* 387 gave fragments at *m/z* 207, which corresponds to the aglycone after a loss of hexose [M-H-162]$^-$. Tuberonic acid glucoside was previously observed in the extract of *M. pulegium* (Taamalli *et al.*, 2015).

Peak **16** at *m/z* 593 was characterized as vicenin-2 (apigenin 6,8-di-*C*-glucoside), confirmed by the appearance of fragment ions at *m/z* 503 [M-H-90]$^-$ and *m/z* 473 [M-H-90-120]$^-$ as well as by comparing with authentic.

Peak **17**, at *m/z* 305 revealed a main fragment ion at *m/z* 225 [M-H-80]$^-$, after a loss of sulphate moiety, which was assigned to be 12-hydroxyjasmonate sulphate, confirmed by its fragmentation patterns in the literature (Kapp *et al.*, 2013; Taamalli *et al.*, 2015; Xu *et al.*, 2017).

Peaks 18, 19, 24, 26 and 37, showing molecular ion peaks at *m/z* 595, 593, 579, 577 and 591, yielded fragment ions at *m/z* 287, 285, 271, 269 and 283, respectively, after loss of a disaccharide moiety (rhamnose+hexose) [M-H-308]$^-$. These peaks were observed in both chromatograms of the two studied species, except peak 18, which present in *M. pulegium* only. These compounds were proposed to be 7-O-rutinoside of eriodictyol, luteolin, naringenin, apigenin, and acacetin, respectively,

compared with the mass fragments of standards and in the literature (Taamalli *et al.*, 2015). The five compounds have been previously reported in *M. pulegium* extract (Taamalli *et al.*, 2015) as well as in the genus *Mentha* and other Lamiaceae species (Areias *et al.*, 2001; Aksit *et al.*, 2014; Xu *et al.*, 2017), while compounds 19 and 26 were previously reported in *M. longifolia* with highly antimutagenic properties (Orhan *et al.*, 2012; Gullece *et al.*, 2013).

Table 1: Tentative identification of phenolic compounds in *M. longifolia* and *M. pulegium*.

No.	*Rt* (min)	M	$[M–H]^-$	*m/z* fragments	Tentative identification		
					Compounds	*M. longifolia*	*M. pulegium*
1	2.17	518	517	503, 403, 387, 289, 273, 175, 159, 131	Unkown	-	+
2	2.67	990	989	665, 503, 341, 179, 135	Caffeoyl hexosides derivatives	+	-
3	2.7	666	665	503, 341, 179, 135	Caffeoyl trihexoside	+	+
4	3.25	192	191	111	Citric acid[$]	+	+
5	4.08	317	316	194, 128	Unknown	+	+
6	4.49	192	191	173, 128, 85	Quinic acid[$]	+	+
7	15.61	409	408	241	Unknown	+	+
8	17.03	354	353	191, 179, 173, 135	*cis* 3-Caffeoyl quinic acid[$]	+	-
9	17.62	610	609	447, 357, 327	Luteolin 6-*C*-hexoside-*O*-hexoside	-	+
10	20.71	338	337	173, 163, 119	4-*p*-Coumaroyl quinic acid[$]	+	+
11	22.21	354	353	191, 179, 161, 108	*trans* 3-Caffeoyl quinic acid[$]	+	-
12	23.30	354	353	191, 179, 173, 135	4-Caffeoyl quinic acid[$]	+	+
13	24.13	180	179	135, 134, 89, 78	Caffeic acid*	+	+
14	25.38	388	387	207, 163, 101	Tuberonic acid glucoside[$]	+	+
15	26.84	338	337	191, 173, 163	5-*p*-Coumaroyl quinic acid[$]	+	-
16	27.22	594	593	473, 503	Apigenin 6,8-di-*C*-glucoside (Vicenin)*	+	+
17	29.98	306	305	225, 97	12-Hydroxyjasmonate sulfate[$]	+	+
18	31.98	596	595	287, 151, 135, 103	Eriocitrin (Eriodictyol-7-*O*-rutinoside) [$]	-	+
19	33.90	594	593	285	Luteolin 7-*O*-rutinoside*	+	+
20	34.4	610	609	301	Quercetin-*O*-rhamno-hexoside	+	-
21	34.65	448	447	285, 179, 151	Luteolin 7-*O*-glucoside*	+	+
22	35.1	567	566	463, 301	Quercetin *O*-benzoylhexoside	+	-
23	35.18	464	463	301	Quercetin 3-*O*-glucoside*	+	+
24	35.49	580	579	271	Narirutin (Naringenin 7-rutinoside) [$]	+	+
25	36.4	462	461	285	Luteolin 7-*O*-glucuronide*	+	+
26	37.16	578	577	269	Apigenin 7-*O*-rutinoside*	+	+
27	37.9	610	609	301	Quercetin 3-rutinoside*	+	+
28	38.24	448	447	301	Quercetin 3-*O*-rhamnoside*	+	-
29	38.5	432	431	269	Apigenin 7-*O*-glucoside*	+	+
30	39.08	538	537	493, 359, 295, 197, 161	Lithospermic acid[$]	+	+
31	40.08	550	549	387, 207	Medioresinol-*O*-hexoside	+	-
32	40.58	806	805	739, 717, 659, 637, 357, 193, 175	Unknown	-	+
33	41.9	718	717	519, 393, 321, 295	Salvianolic acid B[$]	+	+

34	42.7	462	461	285	Luteolin-*O*-glucuronide	+	-
35	44.42	564	563	387, 207	Medioresinol-*O*-glucoronide	+	-
36	45.09	594	593	285	Luteolin-*O*-rhamnose-hexose	+	+
37	45.67	592	591	283	Acacetin 7-*O*-rutinoside[$]	+	+
38	46.26	286	285	151, 133	Luteolin*	+	+
39	46.67	488	487	308, 179, 135	Caffeoyl hexose-deoxyhexoside	+	-
40	47.67	516	515	353, 191, 179, 173, 135	3,4-Dicaffeoyl quinic acid[$]	+	-
41	49.85	330	329	314, 299, 271, 243, 179	5,7,4'-trihydroxy-6,3'-dimethoxyflavone (Jaceosidin)[$]	+	-
42	50.68	360	359	329, 315, 299	Trihydroxy-trimethoxyflavone isomer	+	-
43	51.02	270	269	225, 151, 119	Apigenin*	-	+
44	52.10	360	359	314, 299, 284	Trihydroxy-trimethoxyflavone isomer	+	+
45	54.02	374	373	359, 344, 329, 314, 285	Dihydroxy-tetramethoxyflavone isomer	+	+
46	55.44	360	359	344, 329, 269	5,6,4'-trihydroxy-7,8,3'-tri-methoxyflavone (Thymonin)[$]	+	+
47	55.61	360	359	329, 315, 285	Trihydroxy-trimethoxyflavone isomer	+	-

*Compounds identified by comparing their retention times and mass spectrum with the authentic.
[$]Compounds identified based on the mass spectral data cited in the literature.

Peaks **20** and **27** presented the same molecular ion peak at *m/z* 609 and the same fragment ion at *m/z* 301, after the loss of disaccharide moiety (rhamnose+hexose). No fragments were observed at *m/z* 447 or 463, indicated that both glycosyl moieties were connected to the same phenolic hydroxyl group (Marzouk *et al.*, 2016). Compound **20** was identified as quercetin-*O*-rhamnose-hexose, while compound **27** was identified as quercetin 3-*O*-rutinoside, confirmed by direct comparison with the standard.

Peak **21** was detected at *m/z* 447 in both extracts and produced fragment at *m/z* 285 [M-H-hexose]$^-$. This compound is assigned to be luteolin 7-*O*-glucoside, by comparing the mass fragmentation and *Rt* of standard, which previously isolated from *M. pulegium* (Taamalli *et al.*, 2015) and *M. longifolia* (Orhan *et al.*, 2012; Guvenalp *et al.*, 2015).

Compound **22** at *m/z* 567 revealed a fragment ion at *m/z* 463 [M-H-104]$^-$ which corresponds to quercetin hexoside, after the loss of benzoyl moiety. Another fragment at *m/z* 301 [M-H-104-162]$^-$ was corresponding to quercetin aglycone by the loss of a hexose moiety. Thus, compound **22** could be identified as quercetin *O*-benzoylhexoside.

Peaks **23** and **28** at *m/z* 463 and 447 revealed the same fragment ion at *m/z* 301 and were identified as quercetin 3-*O*-glucoside and quercetin 3-*O*-rhamnoside, respectively. Their mass fragmentation and *Rt* are matching with the authentic standard.

Peaks **25** and **34** (*m/z* 461) was identified as luteolin-*O*-glucuronide, confirmed by losing of glucuronic acid [M-H-176]$^-$ and a fragment ion at *m/z* 285, which corresponding to luteolin aglycone. Both compounds were detected in the two *Mentha* species. Compound **25** was further identified as luteolin 7-*O*-glucuronide by comparing the mass fragmentation and *Rt* with standards. This compound has been previously reported in *M. pulegium* (Taamalli *et al.*, 2015) and *M. longifolia* (Guvenalp *et al.*, 2015).

Peak **29**, at *m/z* 431 revealed the main fragment ion at 269 which corresponds to apigenin aglycone by the loss of a hexose moiety [M-H-162]$^-$. This compound was confirmed to be apigenin 7-*O*-glucoside by comparison with standard and was previously reported for *M. pulegium* (Taamalli *et al.*, 2015) and *M. longifolia* (Gullece *et al.*, 2015).

Lithospermic acid (peak **30**) was observed in the two extracts at *Rt* 39.08 and showed a molecular ion peak [M-H]$^-$ at *m/z* 537, confirmed by fragments 493, 359, 295, 197 and 161 (Taamalli *et al.*, 2015). It has been previously reported in *M. pulegium*, some *Mentha* species and other species of Lamiaceae (Taamalli *et al.*, 2015). This compound exhibited a strong cytotoxicity against both MCF-7/wt and MCF-7/Adr human breast cancer cells (Berdowska *et al.*, 2013).

Medioresinol-*O*-hexoside and medioresinol-*O*-glucoronide were observed at peaks **31** and **35** with molecular ions at *m/z* 549 and 563, respectively. Both peaks yielded fragment at *m/z* 387, corresponding to a medioresinol moiety, after the loss of a hexose moiety for compound **31** and the loss of a glucoronide moiety for compound **35**. Medioresinol was previously reported in some *Mentha* species and other of family Lamiaceae (Kapp, 2015).

Compound **33** (*m/z* 717) was identified as salvianolic acid B, confirmed by the fragmentation patterns (*m/z* 519, 393, 295, 321) with the literature (Kapp *et al.*, 2013; Kapp, 2015). It was previously detected in *M. longifolia* (Krzyzanowska *et al.*, 2011) and found to possess a potent anti-oxidative competence (Zhao *et al.*, 2008).

Peak **38** at *m/z* 285 was suggested to be luteolin, confirmed by the comparison with the authentic standard and the presence of fragment ions at 151 and 133 after a cleavage of A and B-rings, respectively. In the same manner, compound **44** at 51.02 (*m/z* 269) was identified as apigenin on the basis of the authentic standard.

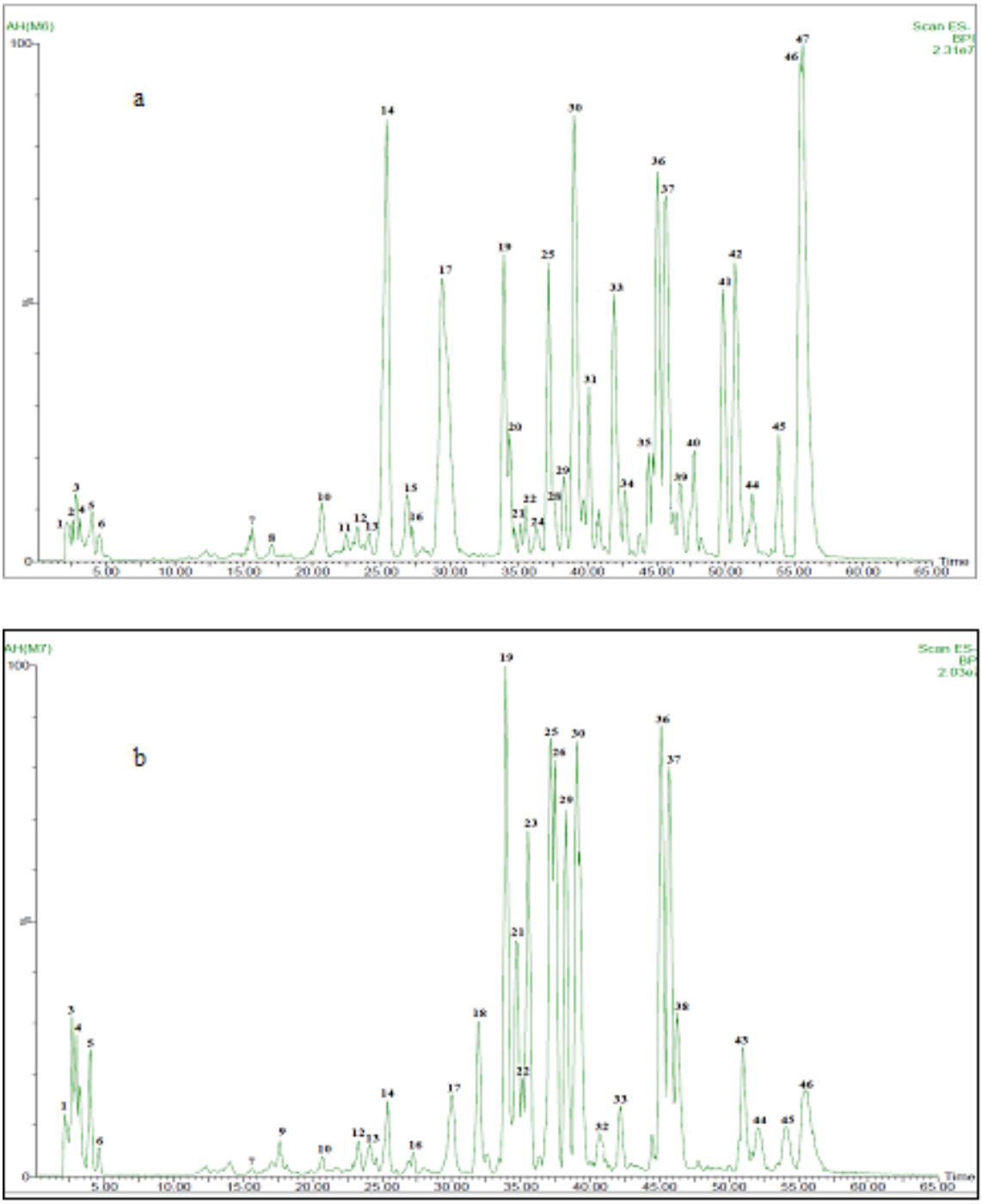

Fig. 1: LC-ESI-MS chromatogram of *M. longifolia* (a) and *M. pulegium* (b).

Several methylated flavones were observed at peaks **41**, **42** and **44**-**47**, exhibiting the loss of CH_3 (15 amu) from the methoxy groups, which is previously detected in the two investigated species (Zaidi *et al.*, 1998), other *Mentha* species (Voirin *et al.*, 1999; Xu *et al.*, 2017) and various species of family Lamiaceae (Tomás-Barberán *et al.*, 1988). On the bases of the mass fragments; peak **41** (*m/z* 329) was identified as a trihydroxy-dimethoxyflavone isomer, peak **45** (*m/z* 373) was identified as a dihydroxy-tetramethoxyflavone isomer, while peaks **42**, **44**, **46** and **47** (*m/z* 359) were characterized as trihydroxy-trimethoxyflavone isomers. Compound **41** was suggested to be 5,7,4’-trihydroxy-6,3’-dimethoxyflavone (Jaceosidin) which previously recorded for *M. pulegium* (Zaidi *et al.*, 1998; Taamalli *et al.*, 2015), while compound **46** was assigned to be 5,6,4’-trihydroxy-7,8,3’-trimethoxyflavone (Thymonin) which previously reported in both species (Zaidi *et al.*, 1998).

Chemosystematics

The members of genus *Mentha* vary from 25-30 (Hajlaoui *et al.*, 2009). According to The plant list (2013), the genus consists of 15 hybrids, 27 basic species, with 14 varieties and subspecies; recently, it's members were grouped in four sections (Kapp, 2015) instead of five (Harley and Brighton, 1977), section *Mentha* contains five basic species and 11 hybrids where *M. longifolia* is one of its basic species moreover, the section could be characterized into three lines according to the inflorescence characters (Lawrence, 2007; Brahmi *et al.*, 2017). *M. pulegium* belongs to section *Pulegium;* members of the section are characterized by the absence of stolons (Kapp, 2015).

Due to the variation in the levels of ploidy and hybridization of the genus, its infraspecific relationship is complicated and many markers (morphological, cytological and chemical) have been used in studying the systematic relationship of *Mentha* species (Mint, 2007; Kapp, 2015; Brahmi *et al.*, 2017).

From the flavonoids point of view; the LC-ESI-MS fingerprint of the studied species elucidated that; *M. pulegium* is characterized by presence of rare contents of flavanols (quercetin 3-*O*-glucoside and rutin) and flavanones (eriocitrin and natirutin) in comparison with flavone compounds which considered the major constituents of *M. pulegium* extract while in *M. longifolia* the flavones are predominant followed by flavanols then by only one flavanone compound (natirutin), eriocitrin was isolated before from *M. longifolia* by Stocker and Pohl (1976) and not detected in the present study. The medioresinol nucleus which distinguished *M. longifolia* from *M. pulegium* was detected previously in *M.* × *piperita* L. (Kapp *et al.* 2013). The presence of caffeic acid and its derivatives in addition to luteolin, apigenin, and their glycosides as a main phenolic constituent in the present study is in agreement with Kapp (2015). The similarity between the two species in synthesis the same phenolic and flavonoidal nucleus moreover the substitution occurs at the same positions make the differentiation between them is too difficult which suggests that *M. pulegium* and *M. longifolia* could be grouped in the same section.

CONCLUSION

The present study is a first record on the chemical fingerprint of wild *Mentha* species grown in Egypt (*M. pulegium* and *M. longifolia*) using LC-ESI-MS analysis. 43 compounds were identified from the methanolic extracts of the studied species and could be used as taxonomic markers in studying the infraspecific relationship among the genus. Further isolation of metabolites will help in providing more evidence for the possible grouping both species in one section.

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REFERENCES

Akroum S, Bendjeddou D, Satta D, Lalaoui K. Antibacterial activity and acute toxicity effect of flavonoids extracted from *Mentha longifolia*. AEJSR, 2009; 4:93-96.

Al-Ali KH, El-Beshbishy HA, El-Badry AA, Alkhalaf M. Cytotoxic activity of methanolic extract of *Mentha longifolia* and *Ocimum basilicum* against human breast cancer. PJBS, 2013; 16:1744-50.

Ali MS, Saleem M, Ahmad W, Parvez M, Yamdagni R. A chlorinated monoterpene ketone, acylated β-sitosterol glycosides and a flavanone glycoside from *Mentha longifolia* (Lamiaceae). Phytochemistry, 2002; 59:889-95.

Areias FM, Valentao P, Andrade PB, Ferreres F, Seabra RM. Phenolic fingerprint of peppermint leaves. Food Chemistry, 2001; 73(3):307-311.

Baris O, Karadayi M, Yanmis D, Guvenalp Z, Bal T, Gulluce M. Isolation of 3 flavonoids from *Mentha longifolia* (L.) Hudson subsp. longifolia and determination of their genotoxic potentials by using the E. coli WP2 test system. J. Food Sci, 2011; 76:9.

Brahmi F, Khodir M, Mohamed C, Pierre D. Chemical Composition and Biological Activities of *Mentha* Species. In Aromatic and Medicinal Plants-Back to Nature. InTech, 2017; 47-80.

Aksit H, Çelik SM, Sen Ö, Erenler R, Demirtas I, Telci I, Elmastas M. Complete isolation and characterization of polar portion of *Mentha dumetorum* water extract. Rec Nat Prod, 2014; 8:277.

Areias FM, Valentao P, Andrade PB, Ferreres F, Seabra RM. Phenolic fingerprint of peppermint leaves. Food Chem, 2001; 73:307-311.

Berdowska I, Zieliński B, Fecka I, Kulbacka J, Saczko J, Gamian A. Cytotoxic impact of phenolics from Lamiaceae species on human breast cancer cells. Food Chem, 2013; 141:1313-1321.

Chen HJ, Inbaraj BS, Chen BH. Determination of phenolic acids and flavonoids in Taraxacum formosanum Kitam by liquid chromatography-tandem mass spectrometry coupled with a post-column derivatization technique. Int J Mol Sci, 2011; 13:260-285.

El-Ghorab AH. The chemical composition of the *Mentha pulegium* L. essential oil from Egypt and its antioxidant activity. J Essent Oil Bear Pl, 2006; 9:183-95.

Farag MA, Otify A, Porzel A, Michel CG, Elsayed A, Wessjohann LA. Comparative metabolite profiling and fingerprinting of genus Passiflora leaves using a multiplex approach of UPLC-MS and NMR analyzed by chemometric tools. Anal Bioanal Chem, 2016; 408:3125-3143.

Gulluce M, Orhan F, Adiguzel A, Bal T, Guvenalp Z, Dermirezer LO. Determination of antimutagenic properties of apigenin-7-*O*-rutinoside, a flavonoid isolated from *Mentha longifolia* (L.) Huds. ssp. *longifolia* with yeast DEL assay. Toxicol Ind Health, 2013; 29:534-40.

Gulluce M, Orhan F, Yanmis D, Arasoglu T, Guvenalp Z, Demirezer LO. Isolation of a flavonoid, apigenin 7-*O*-glucoside, from *Mentha longifolia* (L.) Hudson subspecies *longifolia* and its genotoxic potency. Toxicol Ind Health. 2015; 31:831-40.

Guvenalp Z, Ozbek H, Karadayi M, Gulluce M, Kuruuzum-Uz A, Salih B, Demirezer O. Two antigenotoxic chalcone glycosides from *Mentha longifolia* subsp. *longifolia*. Pharm Biol, 2015; 53:888-96.

Hajlaoui H, Trabelsi N, Noumi E, Snoussi M, Fallah H, Ksouri R, Bakhrouf A. Biological activities of the essential oils and methanol extract of tow cultivated mint species (*Mentha longifolia* and *Mentha pulegium*) used in the Tunisian folkloric medicine. World J Microbiol Biotechnol, 2009; 25:2227-2238.

Harley RM, Brighton CA. Chromosome numbers in the genus *Mentha* L. Bot J Linn Soc, 1977; 74:71-96.

Hussein SR, Abdel Latif RR, Marzouk MM, Elkhateeb A, Mohammed RS, Soliman AAF, Abdel-Hameed ES. Spectrometric analysis, phenolics isolation and cytotoxic activity of Stipagrostis plumosa (Family Poaceae). Chem Pap, 2018; 72:29-37.

Mint JF. In, Biotechnology in Agriculture and Forestry, Transgenic Crops IV. Pua EC, Davey MR (Eds.), Springer-Verlag Berlin Heidelberg, 2007. Vol. 59.

Kapp K, Hakala E, Orav A, Pohjala L, Vuorela P, Püssa T, Vuorela H, Raal A. Commercial peppermint (Mentha× piperita L.) teas: Antichlamydial effect and polyphenolic composition. Food Res Int, 2013; 53:758-66.

Kapp K. Polyphenolic and essential oil composition of *Mentha* and their antimicrobial effect. Faculty of Pharmacy of the University of Helsinki, 2015; 1-73.

Krzyzanowska J, Janda B, Pecio L, Stochmal A, Oleszek W,

Czubacka A, Przybys M, Doroszewska T. Determination of polyphenols in *Mentha longifolia* and *M. piperita* field-grown and *in vitro* plant samples using UPLC-TQ-MS. Journal of AOAC International, 2011; 94:43-50.

Lawrence BM. Mint: the genus *Mentha*. Medicinal and aromatic plants-industrial profiles. CRC Press/Taylor & Francis, Boca Raton, FL. 2007.

Marzouk MM, Hussein SR, Elkhateeb A, Farid MM, Ibrahim LF, Abdel-Hameed ES. Phenolic profiling of *Rorippa palustris* (L.) Besser (Brassicaceae) by LC-ESI-MS: Chemosystematic significance and cytotoxic activity. Asian Pac J Trop Dis, 2016; 6:633-637.

Mustafa AZ, Badr A, El-Galaly MA, Mobarak AA, Hassan MG. Genetic diversity among Mentha populations in Egypt as reflected by isozyme polymorphism. Int J Bot, 2005; 1:188-195.

Mustafa AM, Badr A, El-Galaly MA, Mobarak AA, Hassan MG. Genetic diversity among *Ocimum* populations in Egypt as reflected by morphological, seed proteins and isozyme polymorphism. Int J Bot, 2006; 2:261.

Naghibi F, Mosaddegh M, Mohammadi Motamed M, Ghorbani A. Labiatae family in folk medicine in Iran: from ethnobotany to pharmacology. Iran J Pharm Res, 2010; 4:63-79.

Ncube EN, Mhlongo MI, Piater LA, Steenkamp PA, Dubery IA, Madala NE. Analyses of chlorogenic acids and related cinnamic acid derivatives from *Nicotiana tabacum* tissues with the aid of UPLC-QTOF-MS/MS based on the in-source collision-induced dissociation method. Chem Cent J, 2014; 8:66.

Orhan F, Barış Ö, Yanmış D, Bal T, Güvenalp Z, Güllüce M. Isolation of some luteolin derivatives from *Mentha longifolia* (L.) Hudson subsp. *longifolia* and determination of their genotoxic potencies. Food Chem, 2012; 135:764-769.

Püssa T, Raudsepp P, Toomik P, Pällin R, Mäeorg U, Kuusik S, Soidla R, Rei M. A study of oxidation products of free polyunsaturated fatty acids in mechanically deboned meat. J. Food Comp. Anal, 2009; 22:307-314.

Shalaby NMM, Moharram FA, El-Toumy SAA, Marzouk MSA, Ahmed AAE. Phytochemical and pharmacological studies of *Mentha pulegium* L. Bulletin of Faculty of Pharmacy, Cairo University, Department of Natural Products, National Research Centre, Cairo, Egypt, 2000; 38: 143–151.

Sharaf M, El-Ansari MA, Saleh NA. Flavone glycosides from *Mentha longifolia*. Fitoterapia, 1999; 70:478-483.

Shirazi FH, Ahmadi N, Kamalinejad M. Evaluation of northern Iran *Mentha pulegium* L. cytotoxicity. DARU J Pharm. Sci, 2004; 12:106-110.

Stocker M, Pohl R. Postmortale bildung von 5, 7-dihydroxychromon-7-rutinosid in *Mentha longifolia*. Phytochemistry, 1976; 15:571-572.

Taamalli A, Arráez-Román D, Abaza L, Iswaldi I, Fernández-Gutiérrez A, Zarrouk M, Segura-Carretero A. LC-MS-based metabolite profiling of methanolic extracts from the medicinal and aromatic species *Mentha pulegium* and *Origanum majorana*. Phytochem Anal, 2015; 26:320-330.

Tomás-Barberán FA, Husain SZ, Gil MI. The distribution of methylated flavones in the Lamiaceae. Biochem Syst Ecol, 1988; 16:43-46.

Voirin B, Bayet C, Faure O, Jullien F. Free flavonoid aglycones as markers of parentage in *Mentha aquatica*, *M. citrata*, *M. spicata* and *M. x piperita*. Phytochemistry, 1999; 50:1189-1193.

Xu LL, Xu JJ, Zhong KR, Shang ZP, Wang F, Wang RF, Zhang L, Zhang JY, Liu B. Analysis of non-volatile chemical constituents of menthae haplocalycis herba by ultra-high performance liquid chromatography-high resolution mass spectrometry. Molecules, 2017; 22:1756.

Zaidi F, Voirin B, Jay M, Viricel MR. Free flavonoid aglycones from leaves of *Mentha pulegium* and *Mentha suaveolens* (Labiatae). Phytochemistry, 1998; 48:991-994.

Zhao GR, Zhang HM, Ye TX, Xiang ZJ, Yuan YJ, Guo ZX, Zhao LB. Characterization of the radical scavenging and antioxidant activities of danshensu and salvianolic acid B. Food Chem Toxicol, 2008; 46:73-81.

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