

**Chemical Profiling of *Farsetia aegyptia* Turra and *Farsetia longisiliqua* Decne. and their Chemosystematic Significance**Mona M. Marzouk<sup>1</sup>, Ahmed Elkhateeb<sup>1</sup>, Mona El-Shabrawy<sup>1</sup>, Mai M. Farid<sup>1\*</sup>, Salwa A. Kawashty<sup>1</sup>, El-Sayed S. Abdel-Hameed<sup>2</sup>, Sameh R. Hussein<sup>1</sup><sup>1</sup>Department of Phytochemistry and Plant Systematics, National Research Centre, 33 El Bohouth St., Dokki, Giza, Egypt<sup>2</sup>Laboratory of Medicinal Chemistry, Theodor Bilharz Research Institute, Giza, Egypt

## ARTICLE INFO

## ABSTRACT

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The genus *Farsetia* Turra belongs to the family Brassicaceae Burnett and has approximately 30 accepted species distributed worldwide. Amongst them, *Farsetia aegyptia* Turra and *Farsetia longisiliqua* Decne. are two common species characteristic to the Egyptian flora. The present study considers the first characterization of the chemical constituents of *F. longisiliqua* aiming to compare with those identified from the medicinal species (*F. aegyptia*). Additionally, the chemosystematic relationships between the two studied species were evaluated and highlight the medicinal importance for *F. longisiliqua*. The chemical profiling of their aqueous methanol extracts were carried out using LC-ESI-MS technique and afforded 54 compounds belonging to different chemical groups. Flavonoids were the major constituents and were represented by 32 compounds (two C-glycosyl flavone, four flavones and 26 flavonols). Their structural variations and common constituents confirmed the chemosystematic significance of the two species. Moreover, the flavonoid profiles showed major common constituents between the two investigated species, which predicted the medicinal importance of *F. longisiliqua*.

**Keywords:** Brassicaceae, *Farsetia*, LC-ESI-MS, Glucosinolates, Flavonoids chemosystematics.

## Introduction

The family Brassicaceae Burnett is one of the largest angiosperm families.<sup>1</sup> It comprises approximately 338 genera and more than 3350 species distributed worldwide.<sup>2</sup> The family is represented in Egypt by 53 genera and 107 species.<sup>3,4</sup> It has multiple biological effects, including anticancer and antioxidant activities due to its high content of flavonoids and phenolic compounds.<sup>5,6</sup> Many members of the family Brassicaceae are also known to be used by the native Bedouins for relieving rheumatic pains and as an antispasmodic, anti-diabetic and taken internally as cooling medicine after pounding.<sup>6</sup> The genus *Farsetia* Turra is represented in Egypt by three species; *Farsetia aegyptia* Turra, *F. longisiliqua* Decne. and *F. stylosa* R. Br.

*F. aegyptia* is a long-lived perennial (shrub), it grows on the gravelly soils, sandy plains, on the stony wadis and slopes. It is distributed in desert areas of North Africa, Sinai, Eastern Mediterranean region, Asia, Arabia to Pakistan and Afghanistan.<sup>3</sup> The plant extract indicated the presence of glucosinolates, coumarins, phenolic acids and flavonoids e.g; kaempferol and apigenin; flavonols and their glycosides are the major components.<sup>7-9</sup> Betulin, friedelin,  $\beta$ -amyrin, scopoletin and coumarin were also isolated from its low polar fraction.<sup>10</sup> *F. aegyptia* was evaluated for antibacterial and antifungal activities which showed maximum inhibition against *Klebsiella pneumoniae* and no activity against *Candida albicans*.<sup>7</sup>

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*F. longisiliqua* is a perennial plant grows on the stony wadis, slopes and sandy plains. It is distributed in the desert areas of tropical Northeast Africa, from Egypt to Somalia, and Arabia.<sup>3</sup>

There is no information in the literature regarding the polar constituents and the biological importance of *F. longisiliqua*. Therefore, the objective of the current study is to compare the phytochemical constituents of *F. longisiliqua* with those of the prominent medicinal *Farsetia* species (*F. aegyptia*) using LC-ESI-MS analysis as well as to evaluate their chemosystematic importance.

## Materials and Methods

## Plant material and extraction

*F. aegyptia* and *F. longisiliqua* were collected along Alexandria-Matrouh desert road in 14 March 2018. The herbarium samples (no. 827 & 828) were deposited in the herbarium of National Research Centre, Dokki, Giza, Egypt (CAIRC). Each plant species (200 g) were dried in shadow, grinded and extracted with MeOH:H<sub>2</sub>O (7:3) using 2 L of the solvent and soaked for three days which afforded aqueous methanol extracts of *F. aegyptia* and *F. longisiliqua* (AME\_FA and AME\_FL). These extracts were evaporated to dryness under reduced pressure (Rotavapor<sup>®</sup>, Heidolph, Germany) then stored until further investigation.

## Acid hydrolysis

Sugars and aglycones were identified depending on the complete acid hydrolysis using 10 mL HCl 2N at 100°C for 2 h with 100 mg of the two prepared extracts (AME\_FA and AME\_FL) according to the methods of Marzouk *et al.*<sup>11</sup> Sugar samples (E. Merck, Darmstadt, Germany) and flavonoid aglycones (Phytochemistry and Plant Systematics Department) were used as authentic samples.<sup>12</sup>

## LC-ESI-MS analysis

AME\_FA and AME\_FL were analyzed by LC-ESI-MS system as stated by Hussein *et al.*<sup>13</sup> Identified peaks were recognized by corresponding the retention time and MS fragments with the authentic

samples (purity 95-98%, HPLC, UV, NMR and ESI) which were isolated and identified previously by our research group (Phytochemical and Plant Systematics Department, NRC).<sup>9,12,14,15</sup> The other peaks were tentatively identified by relating the MS spectra and fragmentation pathways with compounds reported before in the genus *Farsetia* and other genera of Brassicaceae family.

## Results and Discussion

### Acid hydrolysis

Five aglycones were observed through paper chromatography examination of the ethyl acetate fraction, confirming the *O*-glycoside configuration. Two major spots showed similarities with kaempferol and isorhamnetin as well as three minor aglycones matched to quercetin, rhamnocitrin and apigenin. In addition, trace dark spots unchanged through acid hydrolysis process, confirming the *C*-glycoside structure. Arabinose, glucose and rhamnose were detected as major sugar moieties in the aqueous fraction.

### LC-ESI-MS analysis

In total, 54 constituents made up of one amino acid, two organic acids, fifteen glucosinolates, four phenolic acids, and 32 flavonoids were characterized according to their MS fragmentation pathway and comparison with the authentic compounds. The detected flavonoids are represented as two flavone-*C*-glycosides, four flavones/*O*-glycosides and 26 flavonols/*O*-glycosides (Table 1, Figure 1).

### Amino acids

Tryptophan **11** ( $m/z$  203) was the only amino acid detected and found in *F. aegyptia* based on the deprotonated molecular ion peak and the fragmentation pattern reported in a previous study.<sup>16</sup>

### Organic acids

The MS spectrum of compound **2** showed a deprotonated molecular ion peak at  $m/z$  195 and a daughter ion at  $m/z$  129 [M-H-CH<sub>2</sub>O-2H<sub>2</sub>O], suggesting gluconic/galactonic acid,<sup>17</sup> while compound **3** at  $m/z$  191 was identified as quinic acid, based on the daughter ions at  $m/z$  127 [M-H-CO-2H<sub>2</sub>O]<sup>-</sup> and  $m/z$  111 [M-H-CO<sub>2</sub>-2H<sub>2</sub>O]<sup>-</sup>.<sup>18</sup>

### Glucosinolates

Fifteen glucosinolates (GLs) were characterized in AME\_FA and AME\_FL (Table 1, Figure 1); eleven aliphatic GLs (**4**, **6-8**, **12**, **18**, **25**, **45**, **46**, **52** and **53**), three aromatic GLs (**5**, **10** and **21**) and one indole GLs (**50**).

In all negative ion ESI-MS spectra of these compounds, the generation of a fragment ion at  $m/z$  97 ([HSO<sub>4</sub>]<sup>-</sup>) was observed as the major fragmentation pattern. Some additional fragments at  $m/z$  154 ([C<sub>2</sub>H<sub>4</sub>O<sub>5</sub>NS]<sup>-</sup>) and  $m/z$  75 ([C<sub>2</sub>H<sub>3</sub>OS]<sup>-</sup>) were very common (Table 1). Generally, the MS spectra of the detected glucosinolates also contain fragment ion matching to the loss of SO<sub>3</sub> group (80 Da) from the [M-H]<sup>-</sup> ion and at  $m/z$  195 ([C<sub>6</sub>H<sub>11</sub>O<sub>5</sub>S]<sup>-</sup>), corresponding to the D-thioglucose group (Table 1). Other glucosinolates specific fragment ions at  $m/z$  259 [M-(R-N=C=S)-H]<sup>-</sup> and 275 [M-(R-N=C=O)-H]<sup>-</sup> were also observed, where R is a side chain intact GLs. It may be aliphatic, aromatic or indole group. The ion at  $m/z$  241 originates after the loss of H<sub>2</sub>O ion from  $m/z$  259. The characterization of the detected GLs were also based on the existence of ions with neutral losses of the following  $m/z$  values; [M-196-H]<sup>-</sup>, [M-178-H]<sup>-</sup>, or [M-162-H]<sup>-</sup>, which informative for [RC<sub>2</sub>NHO<sub>5</sub>S]<sup>-</sup>, [RCNHO<sub>5</sub>S]<sup>-</sup> or [RCNHO<sub>4</sub>S]<sup>-</sup>, respectively.<sup>19</sup> On the basis of the above fragmentation pattern and the GLs isolated previously from *F. aegyptia*,<sup>20</sup> the genus *Farsetia*,<sup>21</sup> and other genera of the family Brassicaceae,<sup>22</sup> the detected GLs were tentatively identified as shown in Table 1.

### Phenolic acids

Salicylic acid (**9**;  $m/z$  137) was identified by direct comparison with authentic sample, while coumaric acid *O*-glucoside isomers (**13** and **14**;  $m/z$  325) and coumaric acid di-*O*-glucoside (**16**;  $m/z$  487) were tentatively identified on the bases of the existence of product ions at

$m/z$  163 [Coumaric acid-H]<sup>-</sup>, 145 [Coumaric acid-H<sub>2</sub>O-H]<sup>-</sup>, 119 [Coumaric acid-CO<sub>2</sub>-H]<sup>-</sup> (Table 1).

### Flavonoids

Around sixty percent of the detected constituents corresponded to flavonoids (Table 1, Figure 1), mainly flavonol *O*-glycosides (kaempferol, quercetin and isorhamnetin derivatives), established by the data obtained from acid hydrolysis. Most flavonoid peaks showed different losses from molecular ion peaks including 162, 146, and/or 132 amu corresponding to glucose, rhamnose, and/or arabinose (based on the data obtained from acid hydrolysis), indicative of sugar cleavage in *O*-glycoside structures. Some flavonoid peaks also showed the loss of 146 amu, but accompanying with the appearance of two fragments at  $m/z$  163 and 119 indicative of the coumaroyl moiety. Two flavonoid peaks showed different cleavage patterns as [M-60-H]<sup>-</sup>, [M-74-H]<sup>-</sup>, [M-90-H]<sup>-</sup> and [M-104-H]<sup>-</sup>, which is specific for *C*-glycoside structures.

### Luteolin *C*-glycoside derivatives

Compounds **17** ( $m/z$  417) and **19** ( $m/z$  431) showed fragmentation pathways of flavone-*C*-glycoside indicative of the cross-ring cleavages of the sugar moiety; as revealed product ions at  $m/z$  327 [M-90-H]<sup>-</sup> and  $m/z$  357 [M-60-H]<sup>-</sup> for compound **17** and at  $m/z$  327 [M-104-H]<sup>-</sup>, and  $m/z$  357 [M-74-H]<sup>-</sup> for compound **19**. Therefore, compounds **17** and **19** were identified to be luteolin -*C*-pentoside and luteolin -*C*-deoxyhexoside, respectively (Figure 3).<sup>23</sup>

### Kaempferol derivatives

Ten kaempferol glycoside derivatives were detected in the present study, confirmed by the generation of a product ions at  $m/z$  285, 267 and 227.<sup>24</sup> The detected tetraglycoside derivatives (**20**, **23**, **35** and **37**) and the triglycosides (**30** and **32**) have not been reported previously in the investigated species (Figure 3). Additionally, four mono glycoside derivatives of kaempferol were distinguished and represented as compounds **24**, **40**, **42** and **48**. Compound **20** ( $m/z$  917) was found in *F. aegyptia* and showed a major product ion at  $m/z$  431 [M-H-3×162] due to the loss of three glucose units attached to the same hydroxyl group and suggested the presence of kaempferol 3-*O*-rhamnoside. Another minor fragment at  $m/z$  771 is due to the loss of a rhamnoside unit [M-146-H]<sup>-</sup>, suggested the present of 7-*O*-triglucoside of kaempferol.<sup>25</sup> Therefore, compound **20** was tentatively assigned as kaempferol 3-*O*-rhamnoside-7-*O*-triglucoside. Similarly, compound **35** ( $m/z$  903) was characterized as kaempferol 3-*O*-arabinoside-7-*O*-triglucoside, on the basis of the product ions  $m/z$  771 [kaempferol+(3×162)-H]<sup>-</sup> and 417 [kaempferol+(132)-H]<sup>-</sup>.<sup>25</sup> On the other hand compound **23** ( $m/z$  901) was observed in the both *Farsetia* species and it characterized as kaempferol 3,7-*O*-di (rhamnosyl glucoside) from its fragment ions appearing at  $m/z$  609 [M-(2×146)-H]<sup>-</sup>, 593 [M-(162+146)-H]<sup>-</sup> and 447 [M-(162+2×146)-H]<sup>-</sup>. Compound **37** ( $m/z$  887) produced a major fragment at  $m/z$  755 corresponding to the loss of an arabinose moiety (-132 amu), indicating the presence of kaempferol 3-*O*-rhamnosyl-diglucoside structure and confirmed by the appearance of fragment ion at  $m/z$  469 which was assigned to the dehydrated trisaccharides residue (two glucose + rhamnose). Another fragment appeared at  $m/z$  417 [Kaempferol+132 -H] and indicated the presence of kaempferol 7-*O*-arabinoside structures. Thus, compound **37** was tentatively identified as kaempferol 3-*O*-rhamnosyl diglucoside-7-*O*-arabinoside. Compounds **30** ( $m/z$  755) and **32** ( $m/z$  725) are triglycosides of kaempferol and showed a common fragment ions at  $m/z$  593 [kaempferol+(162+146)-H]<sup>-</sup> and 431 [kaempferol+146-H]<sup>-</sup> with minor intensity, indicating the presence of kaempferol 7-*O*-glucosyl rhamnoside. Other two major product ions appeared at  $m/z$  447 [kaempferol+162-H]<sup>-</sup> and 417 [kaempferol+132-H]<sup>-</sup>, signifying the occurrence of kaempferol 3-*O*-glucoside and kaempferol 3-*O*-arabinoside moieties in compounds **30** and **32**, respectively. Accordingly, they were tentatively identified as kaempferol 3-*O*-glucoside-7-*O*-glucosyl rhamnoside and kaempferol 3-*O*-arabinoside-7-*O*-glucosyl rhamnoside, respectively.<sup>38</sup> Two monoglycoside derivative of kaempferol (compound **40** and **42**) were identified as kaempferol 3-*O*-arabinopyranoside and kaempferol 7-*O*-arabinopyranoside by direct comparison with authentic samples, while

the monoacyl glycoside derivatives with a deprotonated molecular ions at  $m/z$  533 (**24**) and 593 (**48**) showed a common fragment ion at  $m/z$  447 [kaempferol+162-H]<sup>-</sup>, after the loss of malonyl moiety (-86 amu) or coumaroyl one (-146 amu), respectively. Therefore, compounds **24** and **48** were tentatively identified as kaempferol 3-*O*-malonyl glucoside and kaempferol 3-*O*-coumaroyl glucoside, respectively.<sup>25</sup>

#### Quercetin derivatives

Six quercetin derivatives (**15**, **27**, **28**, **29**, **31** and **47**) have common fragments at 301, 179 and 151 (Table 1). Compounds **28** ( $m/z$  771) and **29** ( $m/z$  741) are suggested to be the quercetin analog of compounds **30** and **32**, thus they were identified as quercetin 3-*O*-glucoside-7-*O*-glucosyl-rhamnoside and quercetin 3-*O*-arabinose-7-*O*-glucosyl-rhamnoside, respectively. Compounds **27** and **31** are quercetin-di-*O*-glycosides and showed the same quasi-molecular ion at  $m/z$  579. Compound **27** was characterized as quercetin 3-*O*-arabinosyl rhamnoside,<sup>14</sup> while compound **31** was identified as quercetin 3-*O*-rhamnoside-7-*O*-arabinoside by comparing with authentic sample. The monoacyl glycoside derivative with a deprotonated molecular ions at  $m/z$  609 (**47**) showed a product ion at  $m/z$  463 [quercetin +162-H]<sup>-</sup>, after the loss of coumaroyl moiety (-146 amu) and was tentatively identified as quercetin-3-*O*-coumaroyl glucoside.<sup>25</sup> Quercetin-*O*-sulphate (**15**) was detected based on the loss of SO<sub>3</sub> group (80 Da) from the [M-H]<sup>-</sup> ion ( $m/z$  381) (Figure 3).

#### Isorhamnetin derivatives

The isorhamnetin (**51**) and the other eight isorhamnetin-*O*-glycoside derivatives (**22**, **26**, **33**, **34**, **36**, **39**, **41** and **44**) have common fragments at 315, 299, 271 (Table 1). Compound **39** ( $m/z$  917) is the only isorhamnetin tetraglycosides reported in the current study and considered to be the first reported in *F. aegyptia*. It produced a major fragment at  $m/z$  785 corresponding to the loss of an arabinose moiety (-132 amu) and indicating the presence of isorhamnetin 3-*O*-rhamnosyl-diglucoside structure. This evidence is confirmed by the appearance of fragment ion at  $m/z$  469 which was assigned to the dehydrated trisaccharides residue which is composed of two glucose units and one rhamnose molecule. Another fragment appeared at  $m/z$

447 [Isorhamnetin +132 -H]<sup>-</sup> and indicated the presence of isorhamnetin 7-*O*-arabinoside. These evidences allowed the tentative identification of compound **39** as isorhamnetin 3-*O*-rhamnosyl-diglucoside-7-*O*-arabinoside. Compounds **22**, **33** and **34** are triglycoside derivatives of isorhamnetin. Compound **22** ( $m/z$  801) showed fragment ions at  $m/z$  639 [Isorhamnetin+(2×162)-H]<sup>-</sup> and 477 [Isorhamnetin+162-H]<sup>-</sup>, which suggested the tentative identification of isorhamnetin 3-*O*-glucoside-7-*O*-diglucoside. By the same manner compound **33** ( $m/z$  785) was characterized as isorhamnetin 3-*O*-glucoside-7-*O*-glucosyl-rhamnoside, confirmed by the presence of fragment ions at  $m/z$  477 [M-H-308]<sup>-</sup> and  $m/z$  623 [M-H-162]<sup>-</sup>. Whereas compound **34** was identified as isorhamnetin-3-*O*-β-arabinopyranoside-7-*O*-(2'''-β-glucopyranosyl)-α-rhamnopyranoside based on the authentic sample isolated before from *F. aegyptia*.<sup>8,9</sup> Two isorhamnetin diglycoside derivatives were identified; compounds **26** ( $m/z$  639) was characterized as isorhamnetin 3-*O*-sophroside,<sup>25</sup> and compound **36** ( $m/z$  593) was identified as isorhamnetin 3-*O*-rhamnopyranoside-7-*O*-arabinopyranoside on the basis of authentic sample. The mono glycoside derivatives of isorhamnetin (compound **41** and **44**) were identified as isorhamnetin 7-*O*-glucopyranoside and isorhamnetin 3-*O*-arabinopyranoside by direct comparison with authentic samples (Figure 3).

#### Rhamnocitrin derivatives

Rhamnocitrin-3-*O*-coumaroyl glucoside ( $m/z$  607) (**43**) was detected only in AME\_FL and characterized by the loss of coumaroyl moiety (-146 amu) to give rhamnocitrin-*O*-glucoside molecule ( $m/z$  461), confirmed by the additional product ions at  $m/z$  299, 163 and 119.<sup>26</sup>

#### Apigenin derivatives

The flavone structures were characterized as apigenin (**49**) and apigenin 7-*O*-glucoside (**38**), confirmed by the retention time and mass fragments of the authentic samples. Additionally, two isomers of apigenin-*O*-coumaroyl glucoside ( $m/z$  577) (**54** and **55**) were also detected and characterized by the loss of coumaroyl moiety (-146 amu) to give apigenin-*O* glucoside molecule ( $m/z$  431) and two other fragments at  $m/z$  163 and 119 (Table 1).

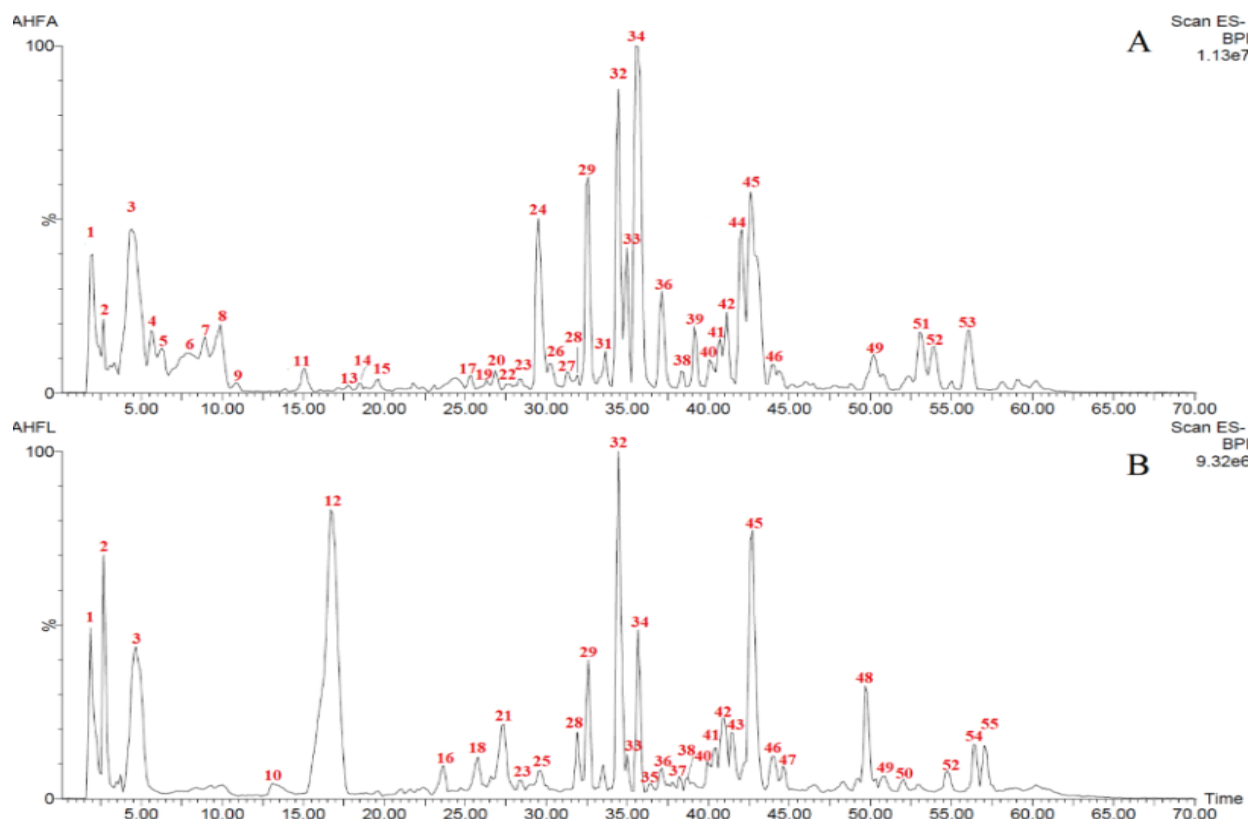
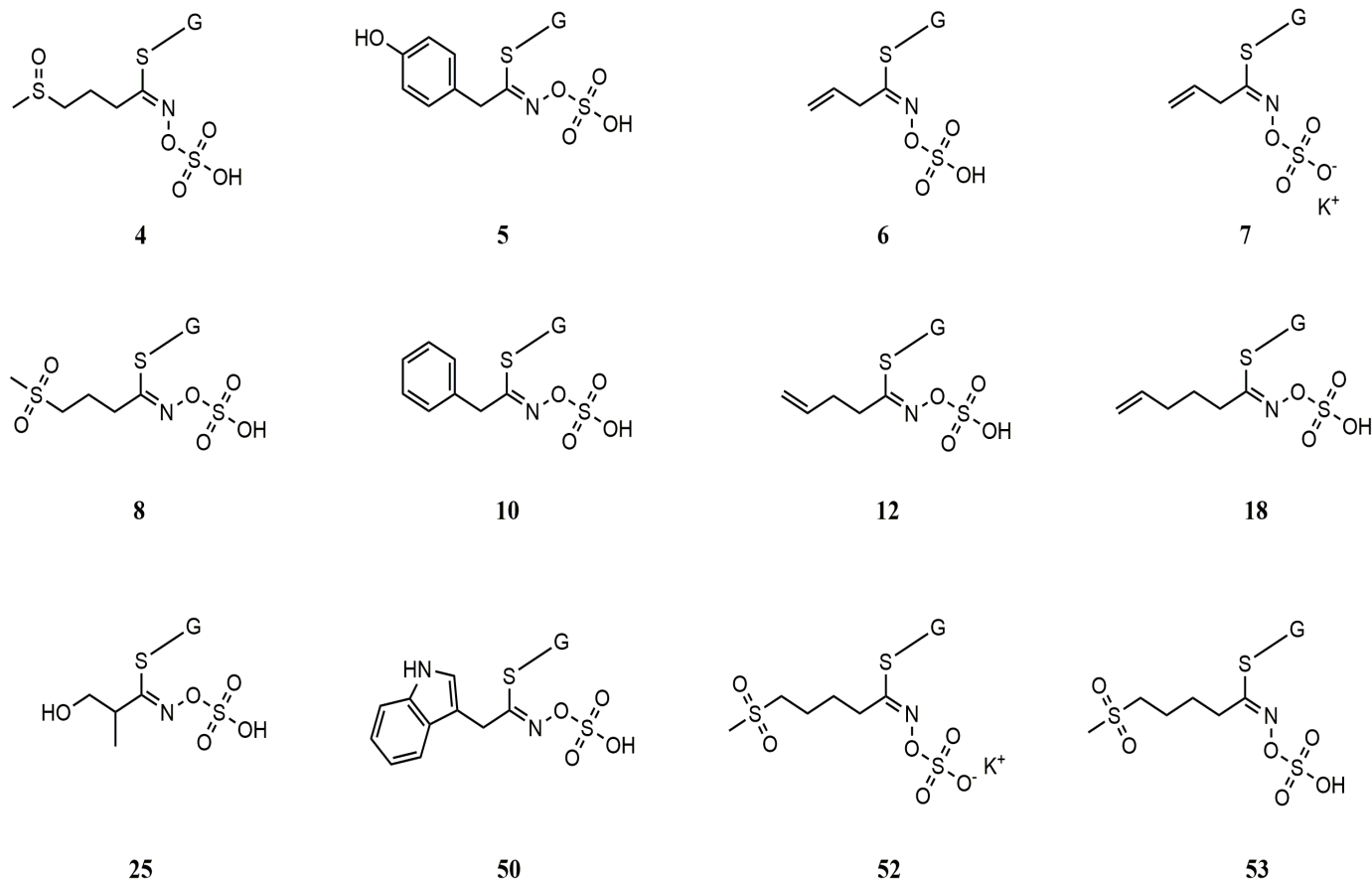


Figure 1: LC-ESI-MS chromatogram of (A) *Farsetia aegyptia* and (B) *Farsetia longisiliqua*



**Figure 2:** Some glucosinolates detected in the present study, G = Glucose

**Table 1:** Tentative identification of chemical compounds in aqueous methanol extracts of *Farsetia aegyptia* (AME\_FA) and *Farsetia longisiliqua* (AME\_FL)

No.	Rt (min)	[M-H]	m/z fragments	Tentative identification			References
				Compounds	AME_FA	AME_FL	
1	2.01	549	533,517,419,403,289, 273, 131	Unknown	+	+	-
2	2.67	195	129	Gluconic/galactonic acid	+	+	[17]
3	4.41	191	127, 111	Quinic acid <sup>a</sup>	+	+	[18]
4	5.61	422	407, 358, 275, 259, 196, 180,145, 97, 75	Methylsulfinylpropyl glucosinolates (Glucoiberin) <sup>b</sup>	+	-	[27]
5	6.27	424	344, 275, 259, 228, 197, 97, 75	Hydroxybenzyl glucosinolate (Sinalbin)	+	-	[27]
6	7.75	358	275, 259, 196,154, 116, 97, 75	Allyl glucosinolates (Sinigrin) <sup>b</sup>	+	-	[28]
7	8.81	396	358, 275, 259, 195, 97, 75	Sinigrin potassium salt	+	-	[27]
8	9.88	438	275, 241, 197, 161,131, 97,75	Methylsulfonylpropyl glucosinolate (Glucocheirolin) <sup>b</sup>	+	-	[29]
9	10.81	137	93	Salicylic acid <sup>a</sup>	+	-	[30]
10	13.21	408	390,348, 257, 241, 212,153,97, 75	Benzylglucosinolate (Glucotropaeolin) <sup>b</sup>	-	+	[27]
11	15.09	203	116,72	Tryptophan	+	-	[16]
12	16.82	372	292,275,259,241,139,129,97,75	Butenylglucosinolate (Gluconapin) <sup>b</sup>	-	+	[27]
13	17.75	325	163, 145, 119	Coumaric acid- <i>O</i> -glucoside	+	-	[31]
14	18.43	325	163, 145, 119	Coumaric acid- <i>O</i> -glucoside isomer	+	-	[31]
15	19.63	381	301,241,151,97, 75	Quercetin- <i>O</i> -sulphate	+	-	

16	23.63	487	163, 145, 119	Coumaric acid- <i>O</i> -di glucoside	-	+	[24]
17	25.37	417	357, 327	Luteolin- <i>C</i> -pentoside	+	-	[23]
18	25.77	386	306, 241, 259, 195, 135, 97, 75	Pentenyl glucosinolate (Glucobrassicinapin)	-	+	[27]
19	26.30	431	357, 327	Luteolin- <i>C</i> -deoxyhexoside	+	-	[23]
20	26.84	917	771, 609, 431, 285, 267, 227	Kaempferol 3- <i>O</i> -rhamnoside-7- <i>O</i> -triglucoside	+	-	
21	27.37	488	408, 275, 259, 241, 212, 96, 75	Glucotropaeolin - <i>O</i> -sulphate	-	+	[32]
22	27.51	801	639, 477, 315, 299	Isorhamnetin 3- <i>O</i> -glucoside 7- <i>O</i> -diglucoside	+	-	[33]
23	28.44	901	609, 593, 447, 285, 267, 227	Kaempferol 3,7- <i>O</i> -di (rhamnosyl-glucoside)	+	+	[34]
24	29.51	533	491, 447, 285, 267, 239, 227	Kaempferol 3- <i>O</i> -malonylglucoside	+	-	[35]
25	29.64	377	259, 241, 153, 97, 75	Methyl-hydroxyethyl glucosinolate (Glucosisybrin)	-	+	[36]
26	30.31	639	315, 299	Isorhamnetin 3- <i>O</i> -sophroside <sup>b</sup>	+	-	[25]
27	31.38	579	447, 301, 179, 151	Quercetin- <i>O</i> -arabinosyl rhamnoside	+	-	[37]
28	31.91	771	609, 463, 301, 179, 151	Quercetin 3- <i>O</i> -glucoside-7- <i>O</i> -glucosyl- rhamnoside	+	+	[38]
29	32.58	741	609, 433, 301, 179, 151	Quercetin 3- <i>O</i> -arabinose-7- <i>O</i> -glucosyl- rhamnoside	+	+	
30	33.51	755	593, 447, 431, 285, 268, 239, 227	Kaempferol 3- <i>O</i> -glucoside-7- <i>O</i> -glucosyl rhamnoside	-	+	[38]
31	33.65	579	447, 433, 301, 179, 151	Quercetin 3- <i>O</i> - $\alpha$ -rhamnopyranoside -7- <i>O</i> - $\beta$ - arabinopyranoside <sup>a</sup>	+	-	[14]
32	34.45	725	593, 431, 417, 285, 268, 239, 227	Kaempferol 3- <i>O</i> -arabinoside-7- <i>O</i> -glucosyl rhamnoside	+	+	
33	34.98	785	623, 477, 315, 299, 151	Isorhamnetin 3- <i>O</i> -glucoside-7- <i>O</i> -glucosyl- rhamnoside	+	+	
34	35.65	755	623, 447, 431, 315, 299, 271, 151	Isorhamnetin 3- <i>O</i> - $\beta$ -arabinopyranoside-7- <i>O</i> -(2'''- $\beta$ -glucopyranosyl)- $\alpha$ -rhamnopyranoside <sup>a,b</sup>	+	+	[9]
35	36.45	903	771, 447, 417, 285, 255, 227	Kaempferol 3- <i>O</i> -arabinoside-7- <i>O</i> -tri glucoside	-	+	
36	37.12	593	461, 447, 315, 299, 151	Isorhamnetin 3- <i>O</i> -rhamnopyranoside-7- <i>O</i> - $\beta$ - arabinopyranoside <sup>a</sup>	+	+	[12]
37	38.18	887	755, 609, 469, 417, 285, 268, 239, 227	Kaempferol 3- <i>O</i> -rhamnosyl diglucoside-7- <i>O</i> - arabinoside	-	+	
38	38.45	431	269, 151, 117	Apigenin 7- <i>O</i> - $\beta$ -glucopyranoside <sup>a,b</sup>	+	+	[39]
39	39.12	917	785, 469, 447, 315, 300, 151	Isorhamnetin 3- <i>O</i> -rhamnosyl diglucoside-7- <i>O</i> - arabinoside	+	-	[40]
40	40.1	417	285, 255, 117	Kaempferol 3- <i>O</i> - $\beta$ -arabinopyranoside <sup>a</sup>	+	+	[41]
41	40.7	477	315, 299, 271, 151	Isorhamnetin 7- <i>O</i> - $\beta$ -glucopyranoside <sup>a</sup>	+	+	[42]
42	41.12	417	285, 255, 117	Kaempferol 7- <i>O</i> - $\beta$ -arabinopyranoside <sup>a</sup>	+	+	
43	41.52	607	299, 461, 163, 119	Rhannocitrin 3- <i>O</i> -coumaroyl glucoside	-	+	[26]
44	42.06	447	315, 299, 271, 151	Isorhamnetin 3- <i>O</i> - $\beta$ -arabinopyranoside <sup>a</sup>	+	-	
45	42.72	467	259, 241, 165, 97	Glucosinolate derivative	+	+	[19]
46	43.93	466	386, 306, 259, 195, 135, 116, 97, 75	Glucobrassicinapin- <i>O</i> -sulfate	+	+	[43]
47	44.59	609	463, 301, 179, 163, 151, 145, 119	Quercetin 3- <i>O</i> -coumaroyl glucoside	-	+	[44]
48	49.8	593	447, 285, 163, 145, 119	Kaempferol 3- <i>O</i> -coumaroyl glucoside	-	+	[31]
49	50.2	269	151, 149, 117	Apigenin <sup>a,b</sup>	+	+	[39]
50	52.07	447	275, 259, 205, 97, 75	Indolylmethylglucosinolate (Glucobrassicin)	-	+	[28]
51	53.01	315	299, 271, 151, 107	Isorhamnetin <sup>a,b</sup>	+	-	[9]
52	53.9	452	417, 327, 275, 210, 241, 195, 165, 97, 75	Methylsulfonylbutyl glucosinolates (Glucoerysolin)	+	+	[45]
53	56.08	490	452, 417, 327, 275, 210, 241, 195, 165, 97, 75	Glucoerysolin potassium salt	+	-	[45]
54	56.48	577	431, 269, 163, 151, 145, 119	Apigenin 7- <i>O</i> -coumaroyl-glucoside	-	+	[46]
55	57.15	577	431, 269, 163, 151, 145, 119	Apigenin 7- <i>O</i> -coumaroyl-glucoside isomer	-	+	[46]

<sup>a</sup> Compounds identified by comparing their retention times and mass spectrum with the authentic.

<sup>b</sup> Compounds previously reported from *F. aegypti*

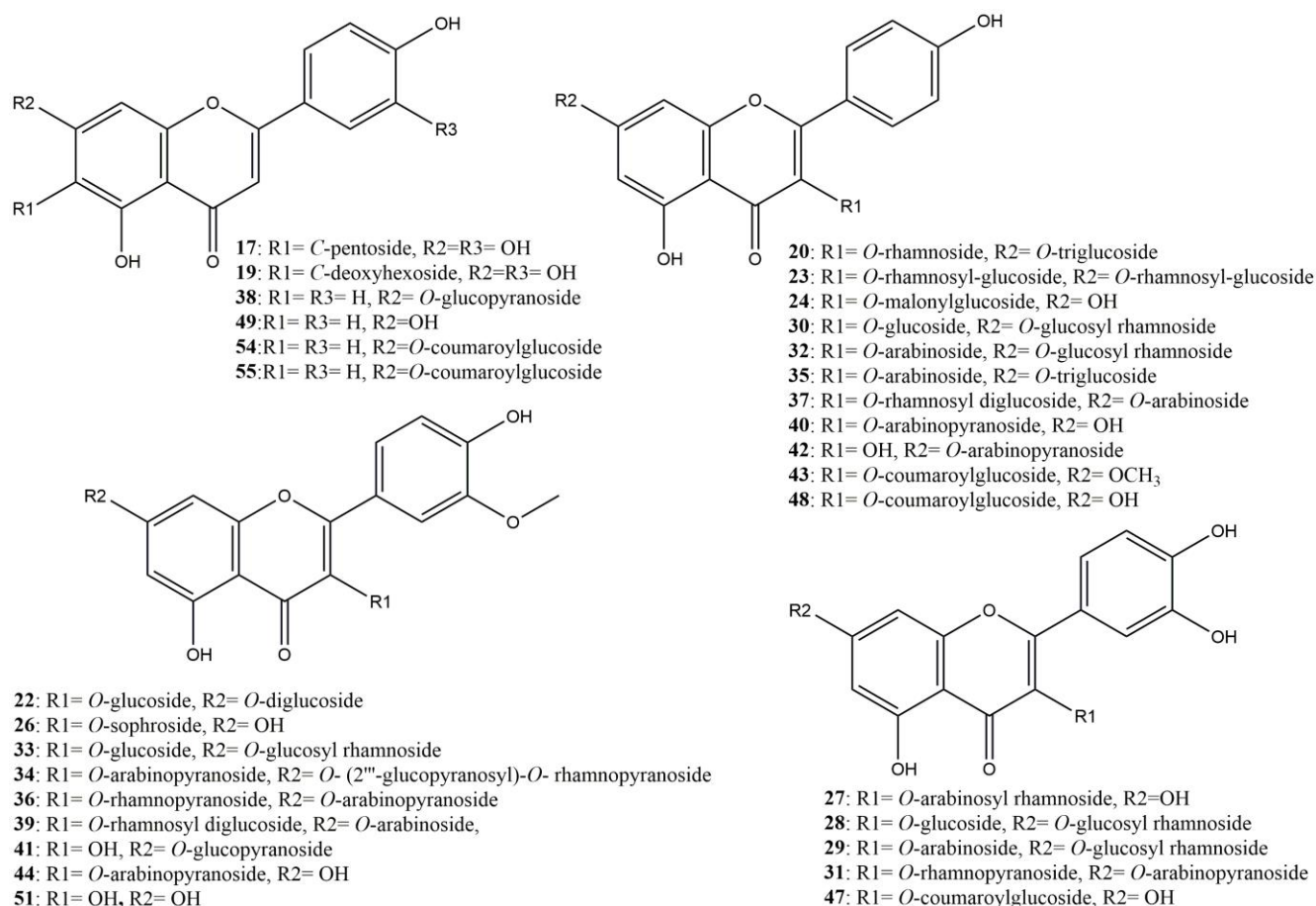


Figure 3: Flavonoids detected in the present study

#### Chemosystematic significance

The genus *Farsetia* belongs to the family Brassicaceae, it contains 30 accepted species and subspecies besides 9 unresolved names.<sup>47</sup> In the Egyptian flora, *Farsetia* is represented by three species viz. *F. aegyptia*, *F. longisiliqua* and *Farsetia stylosa* R. Br.<sup>3</sup> Except for *F. aegyptia*, there is no enough data concerning the isolation of flavonoid compounds from other *Farsetia* species. The present study is the first report of the chemical constituents of *F. longisiliqua*. For the best of our knowledge, the chemosystematic relationship of the genus *Farsetia* has not been discussed before.

From the flavonoids point of view; *F. aegyptia* and *F. longisiliqua* are comparable in forming flavone, methylated flavone and flavonol nuclei, while quercetin was the only flavonoid reported in previous study from *F. stylosa*.<sup>48</sup>

The acylation is common in *F. longisiliqua* and rare in *F. aegyptia*, from which we can distinguished between the two species, it is represented by one malonyl (aliphatic acid) flavonol derivative in *F. aegyptia* (compound 24) and five coumaroyl (aromatic acid) substituents in *F. longisiliqua*; three of which are flavonol derivatives (compounds 43, 47 and 48) while the other two substituents are flavone (compounds 54 and 55) (Figure 3).

Also, the chemical profile of both species can be distinguished by the presence of C-glycosyl flavonoids in *F. aegyptia* (compounds 17 and 19) and absence of such compounds in *F. longisiliqua*. These distinctive differences are supported by different fruit morphological characters. They are characterized as silicula (1-2.5 x 0.6-0.9 cm), broadly oblong for *F. aegyptia*, while siliqua (2.5-5 x 0.25-0.5 cm), narrowly oblong for *F. longisiliqua*.<sup>3</sup> Overall, the majority of the chemical constituents of *F. longisiliqua* seem to be related to those of

*F. aegyptia*, which can forecast its medicinal significance. To have a complete picture of the relationship between the *Farsetia* species, more investigations of the other species is needed. Furthermore, biological investigations are needed to discover the medicinal importance of *F. longisiliqua*.

#### Conclusion

The present study considers the first report of the chemical constituents of *F. longisiliqua* and the first evaluation carried out on the chemosystematic relationships of the *Farsetia* species. Fifty-four compounds were characterized for *F. aegyptia* and *F. longisiliqua* by LC-ESI-MS analysis. Flavonoids (32 compounds) were the commonly detected compounds and have been used successfully as chemosystematic markers for differentiation between the studied species. Generally, the chemical profile of *F. longisiliqua* seems to be comparative with those of *F. aegyptia*, which can be predictive for its medicinal importance.

#### Conflict of interest

The authors declare no conflict of interest.

#### Authors' Declaration

The authors hereby declare that the work presented in this article is original and that any liability for claims relating to the content of this article will be borne by them.

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