



## Comparative Study of *Oxalis* L. Species Growing Wild in Egypt: GC-MS Analysis and Chemosystematic Significance

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### Abstract

Five *Oxalis* L. plants belonging to three different sections were collected and subjected to GC-MS analysis to evaluate and understand the relationship between them from the chemosystematic point of view. The GC-MS analysis revealed the identification and characterization of thirty seven compounds belonging to different non-polar chemical classes of which nine compounds (two aliphatic hydrocarbons, one diterpene, one fatty acid, four fatty acid esters and one fatty alcohol) were identified before from the genus while, the rest compounds were identified for the first time. The GC-MS results were chemosystematically significant among *Oxalis* species and were found to be a good parameter in finding a tangible demarcation between *O. corniculata* and *O. corniculata* var. *repens*, on the other hand it is difficult to differentiate between *Oxalis* sections by the obtained data.

Keywords: Non-polar constituents; Oxalidaceae; Chemotaxonomy; Corniculatae; Cernuae; Ionoxalis.

### 1. Introduction

Genus *Oxalis* L. belongs to family Oxalidaceae R.Br. and comprising about 504 accepted species distributed worldwide specially in the area extending from South America to the southern part of North America and at the South-Western Cape region of South Africa [1-4]. The genus is represented in Egypt by five species and one variety viz; *Oxalis anthelmintica* A. Rich., *O. corniculata* L., *O. corniculata* var. *repens* (Thunb.) Zucc., *O. corymbosa* DC., *O. latifolia* Kunth and *O. pes-caprae* L. [2, 5, 6]. The data concerning isolation and identification of non-polar and volatile constituents from *Oxalis* species are limited. Only Karimzadeh *et al.* [7], Aruna *et al.* [8], Durgawale *et al.* [9] and Unni *et al.* [10] reported the chemical profile of *O. corniculata* using GC-MS technique and there were not any previous investigations for detecting the non-polar constituents from the other species of the present study.

Some members of genus *Oxalis* has multiple therapeutic effects and used traditionally for treating various diseases such as *O. corniculata* which used as

anti-diabetic, anti-microbial, antioxidant and hepatoprotective [7-10].

Täckholm [5] and Kabuye [11] reported *repens* as a variety of *O. corniculata*. While, some other authors considered *O. corniculata* as a multiform species showing high variability of morphological expressions as a result of ecological variations [12] and they considered *O. corniculata* var. *repens* as a synonym of *O. corniculata* [2, 4]. The present study aims to evaluate the non-polar constituents of the five different *Oxalis* plants using GC/MS and studying the intraspecific relationships among the studied species.

### 2. Experimental

#### 2.1. Plant material

In the present investigation, five plants (Four species & one variety) of genus *Oxalis* were identified by Dr. Eman M. Shams in the Herbarium of Microbiology and Botany Dept., Faculty of Science, Cairo University. Samples were collected from different localities in Egypt and were deposited in the herbarium of Cairo University (CAI). *O. corniculata* L. (voucher No. A301), *O. corniculata*

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var. *repens* (voucher No. A302) and *O. corymbosa* DC. (voucher No. A303) were collected from National Research Centre gardens, Dokki, Giza in March, 2019, while *O. pes-caprae* L. (voucher No. A304) was collected from Bramly's grotto, Burg El-Arab in February, 2019 as well as *O. latifolia* Kunth (voucher No. A305) was collected from Faculty of Science gardens, Cairo University, Giza in April, 2019.

## 2.2. GC-MS analysis

The whole plants under investigation were dried and grounded to powder then 15 grams of each plant was soaked in 100 ml diethyl ether for 24 hrs. The extract was filtered using Whatman filter paper No.1 and the resulted filtrates were reduced under pressure using rotary evaporator then subjected to GC-MS analysis to identify their non-polar constituents. GC/MS analysis was carried out according to the methods of Hussein et al. [13] and Farid et al. [14] using Gas Chromatography (Thermo Scientific TRACE GC Ultra) directly coupled to ISQ Single Quadruple Mass spectrometer. GC/MS results are represented in (Table 1, Figure 1).

## 3. Results and discussion

### 3.1. GC-MS analysis

The GC-MS analysis revealed the identification and characterization of thirty seven compounds belonging to different non-polar chemical classes of which nine compounds were identified before from the genus while, the rest of compounds were identified for the first time (Table 1). It is apparent that almost all extracts have relatively the same concentration from aliphatic hydrocarbon compounds except for *O. latifolia* which has the lowest percent (17.86%) of alkene compounds and 6.63% of alkanes. Heptadecane is detected in *O. corniculata* and *O. pes-caprae* while triacontane is only present in *O. corniculata* var. *repens* and was isolated before from *Leptadenia reticulata* (Retz.) Wight & Arn. (Asclepiadaceae) [15]. In addition hentriacontane is absent from *O. pes-caprae* and *O. corniculata*. 1-dodecene is lacking from *O. corniculata* var. *repens* and *O. pes-caprae* but present in the rest of species while in contrast, 1-tetradecene is found in *O. corniculata* var. *repens* and *O. pes-caprae* extracts not in all of the other plants.

*O. corymbosa* is the only species which has the ability of synthesizing cyclic aliphatic hydrocarbon compounds (cyclotetradecane, 13.18%) and those compounds were isolated before from *Pelargonium graveolens* L'Hér. (Geraniaceae Juss.) [16]. *O. corniculata* and *O. pes-caprae* are distinguished from the rest of species by being specialized in the formation of naphthalene derivatives which are bicyclic aromatic compounds and those compounds

were previously isolated from *Euphorbia prostrata* Aiton (Euphorbiaceae Juss.), *Geranium robertianum* L. (Geraniaceae) and *Elettaria cardamomum* (L.) Maton (Zingiberaceae Martinov.) [16-18]. Three terpenes were reported in this study; (E)-phytol is not detected this time in *O. corniculata* but was previously isolated by Aruna et al. [8] and Karimzadeh et al. [7], limonene and linalylanthranilate were identified for the first time in *Oxalis* species; the former was previously separated from *Averrhoa bilimbi* L. (oxalidaceae) [19] while the latter was reported before from family lamiaceae Martinov [20, 21]. All carboxylic acid esters in the present study were not isolated before from genus *Oxalis* or even from the family but were identified from other families such as Acanthaceae Juss., Rosaceae Juss., Apiaceae Lindl. and Myrtaceae Schauer [22-26]. The carboxylic acid ester contents in *O. corniculata* var. *repens* is rare (0.37%) with comparison to *O. corniculata* (5.41%). Palmitic acid is the only fatty acid being present in all of *O. species* except for *O. latifolia*. In addition, all investigated species have the ability to produce fatty acid methyl esters except *O. corymbosa* which characterized by lacking of such compounds.

### 3.2. Chemosystematic evaluation

According to the systems proposed by Lourteig [27, 28] and Salter [29], *Oxalis* was divided into three sections; *Corniculatae* DC. to which *O. corniculata* belongs, section *Cernuae* R. Knuth includes *O. pes-caprae* and finally, section *Ionoxalis* (small) R. Knuth which comprises *O. corymbosa* and *O. latifolia*.

*O. repens* was firstly described by Thunberg and later, Zuccarini lowered it to be a variety (*Oxalis corniculata* var. *repens*) [30, 31] and this was accepted by Täckholm [5] and Kabuye [11] while Lourteig [32] synonymized it with *O. corniculata* which was accepted by Boulos [2] and The plant list [4].

By comparing the non-polar chemical constituents of *O. corniculata* var. *repens* and *O. corniculata* that were collected from the same habitat, we found that each plant has a different chemical pattern not only in the type of identified compounds but also in their percentage. *O. corniculata* var. *repens* was characterized by presence of nine different compounds in its extract that were not detected in *O. corniculata* (Table 1) and *O. corniculata* contain eight compounds not recognized in the var. *repens* (Table 1). In addition, the fatty acid methyl ester content in *O. corniculata* var. *repens* (12.14%) is much more than that of *O. corniculata* (1.97%), the fatty alcohols and aldehydes represents (8.96%, 14.08%) of *O. corniculata* var. *repens* total extract and (2.19%, 27.93%) of *O. corniculata* extract respectively and due to these variations we agree with

Täckholm [5] and Kabuye [11] in treating *O. corniculata* var. *repens* as a variety of *O. corniculata* not as a synonym or even as a multiform species as proposed by Malik *et al.* [12].

From the GC/MS data we can distinguish between each of the studied species, where *O. pes-caprae* can be recognized by the absence of dodecane and E-14-hexadecenal compounds in its extract, *O. corymbosa* characterized by presence of cyclic aliphatic hydrocarbon compounds (cyclotetradecane) and absence of fatty acid methyl ester compounds; *O.*

*latifolia* can be separated from the other species by lacking of fatty acids (Palmitic acid) in its extract.

Although the present study helps in understanding the chemical relationship among *Oxalis* species particularly in the differentiation between *O. corniculata* var. *repens* and *O. corniculata* but when studying the relationship on the section level the non-polar constituent is difficult to distinguish them and more chemical investigations are needed for providing a complete image for understanding the variations among *Oxalis* sections.

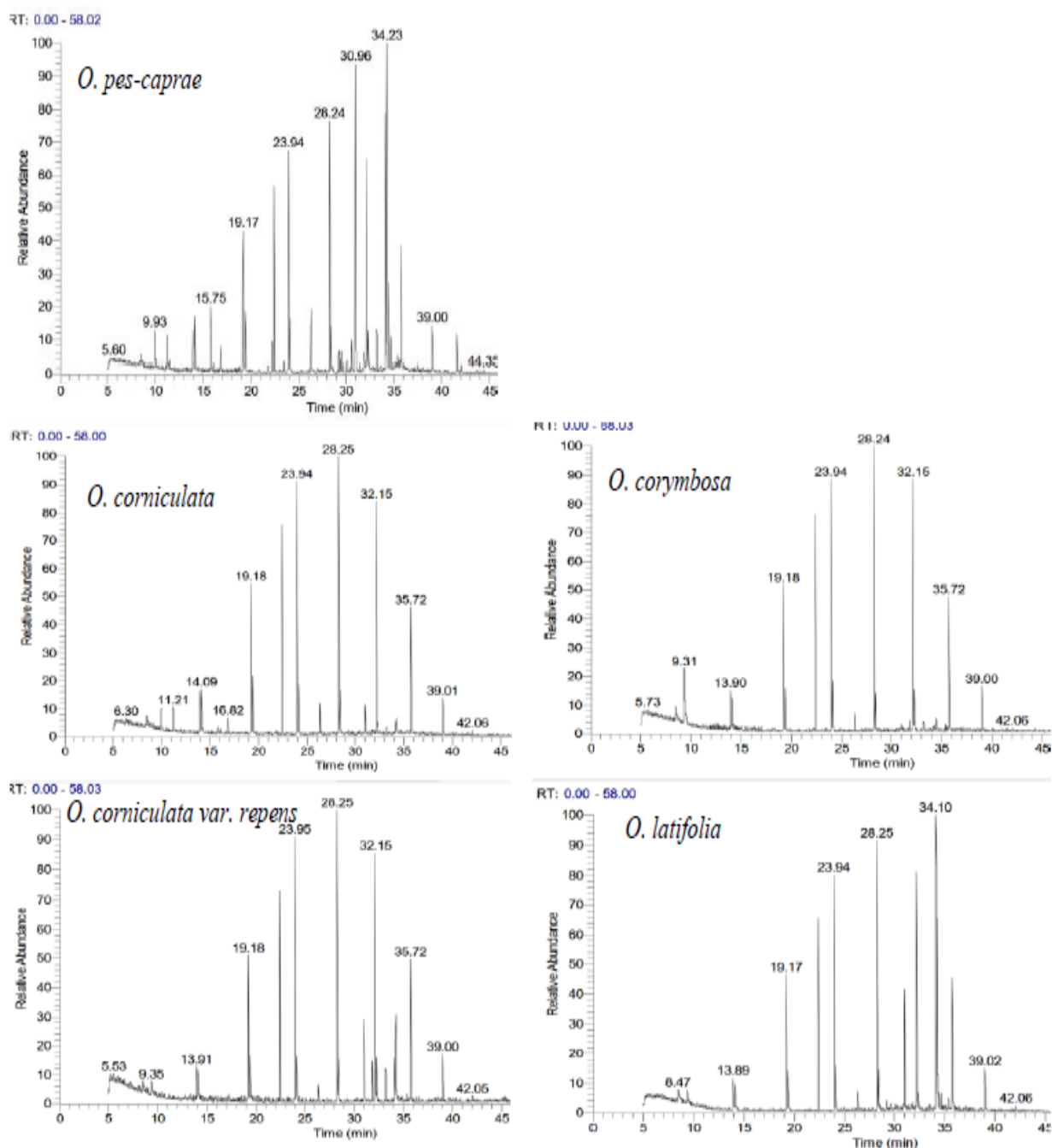


Figure 1. GC/MS analysis of non-polar fractions of *Oxalis*

Table (1): GC-MS analysis of four species and one variety of *Oxalis* L.

Section				Cernuae	Corniculatae		Ionoxalis	
<i>Oxalis</i>				<i>pes-caprae</i>	<i>corniculata</i>	<i>corniculata</i> <i>var. repens</i>	<i>corymbosa</i>	<i>latifolia</i>
Compound name	Rt/ min.	M.wt	M. formula	Area %				
<b>1-Aliphatic hydrocarbons:</b>								
<b>(A)- Acyclic aliphatic hydrocarbons:</b>								
<b>- Alkanes:</b>								
Dodecane	14.09	170	C <sub>12</sub> H <sub>26</sub>	1.77	-	-	-	-
Tridecane	14.1	184	C <sub>13</sub> H <sub>28</sub>	-	1.05	-	-	-
Tetradecane	19.38	198	C <sub>14</sub> H <sub>30</sub>	1.75	3.21	2.33	2.28	1.85
Hexadecane	24.11	226	C <sub>16</sub> H <sub>34</sub>	1.6	2.58	2.1	2.53	1.78
Heptadecane*	26.3	240	C <sub>17</sub> H <sub>36</sub>	1.99	1.83	-	-	-
Henriacontane	26.31	436	C <sub>31</sub> H <sub>64</sub>	-	-	0.9	1.14	1.07
Pentatriacontane	28.38	492	C <sub>35</sub> H <sub>72</sub>	1.41	2.37	2.17	2.39	1.93
Triacontane	32.26	422	C <sub>30</sub> H <sub>62</sub>	-	-	2.09	-	-
<b>-Alkenes:</b>								
1-Octene	8.47	112	C <sub>8</sub> H <sub>16</sub>	-	1.28	1.18	1.04	0.89
1-Dodecene	13.89	168	C <sub>12</sub> H <sub>24</sub>	-	2.81	-	2.42	1.73
1-Tetradecene	13.91	196	C <sub>14</sub> H <sub>28</sub>	1.52	-	2.23	-	-
4-Tetradecene	19.19	196	C <sub>14</sub> H <sub>28</sub>	4.51	7.4	6.99	7.58	5.45
1-Hexadecene	23.94	224	C <sub>16</sub> H <sub>32</sub>	6.92	-	11.73	-	-
1-Nonadecene*	32.15	266	C <sub>19</sub> H <sub>38</sub>	6.7	12.52	11.75	12.95	9.79
1-Docosene	35.72	308	C <sub>22</sub> H <sub>44</sub>	4.18	6.6	-	7.34	-
Subtotal				32.35	41.65	43.47	39.67	24.49
<b>(B)- Cyclic aliphatic hydrocarbons:</b>								
Cyclotetradecane	23.95	196	C <sub>14</sub> H <sub>28</sub>	-	-	-	13.18	-
<b>2-Aromatic compounds:</b>								
<b>(A)- Monocyclic:</b>								
2-tert-Butyl-4-isopropyl-5-methylphenol	22.39	206	C <sub>14</sub> H <sub>22</sub> O	5.86	11.11	9.87	10.69	7.99
Subtotal				5.86	11.11	9.87	10.69	7.99
<b>(B)- Bicyclic:</b>								
Naphthalene, decahydro, cis	9.94	138	C <sub>10</sub> H <sub>18</sub>	1.94	1.9	-	-	-
Subtotal				1.94	1.9	-	-	-
<b>3-Terpenes:</b>								
<b>(A)- Acyclic diterpenes:</b>								
(E) Phytol *	34.44	296	C <sub>20</sub> H <sub>40</sub> O	3.09	-	-	0.74	1.12
<b>(B)- Monocyclic terpenes:</b>								
Limonene	9.34	136	C <sub>10</sub> H <sub>16</sub>	-	-	1.38	4.69	0.86
Linalyl anthranilate	15.75	273	C <sub>17</sub> H <sub>23</sub> NO <sub>2</sub>	2.03	0.55	-	-	-
Subtotal				5.12	0.55	1.38	5.43	1.98
<b>4-Carboxylic acid esters:</b>								
Carbazic acid, 3-(1-propylbutylidene)-ethyl ester	7.24	200	C <sub>10</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	-	0.61	0.37	-	-
Oxalic acid, allyl nonyl ester	14.1	256	C <sub>14</sub> H <sub>24</sub> O <sub>4</sub>	-	2.64	-	-	-
Oxalic acid, allyl decyl ester	14.12	270	C <sub>15</sub> H <sub>26</sub> O <sub>4</sub>	-	-	-	2.03	1.25
Oxalic acid, allyl nonyl ester (isomer)	32.25	256	C <sub>14</sub> H <sub>24</sub> O <sub>4</sub>	1.22	2.16	-	-	-
Oxalic acid, allyl decyl ester (isomer)	32.26	270	C <sub>15</sub> H <sub>26</sub> O <sub>4</sub>	-	-	-	2.13	1.53
Subtotal				1.22	5.41	0.37	4.16	2.78
<b>5-Fatty acids:</b>								
Palmitic acid*	33.2	256	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	1.39	0.5	1.47	0.67	-
Subtotal				1.39	0.5	1.47	0.67	-
<b>6- Fatty acid methyl esters:</b>								
Hexadecanoic acid, methyl ester*	30.97	270	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	10.7	1.97	4.37	-	5.27
Linolelaidic acid, methyl ester*	34.11	294	C <sub>19</sub> H <sub>34</sub> O <sub>2</sub>	8.8	-	1.77	-	12.15
Methyl linolenate *	34.24	292	C <sub>19</sub> H <sub>32</sub> O <sub>2</sub>	13.59	-	6	-	11.26
Octadecanoic acid, methyl ester*	34.68	298	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	1.09	-	-	-	1.08
Subtotal				34.18	1.97	12.14	-	29.76
<b>7-Esters:</b>								
Butyl phthalate	31.8	278	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	-	-	2.14	-	-
Diisooctyl phthalate	41.55	390	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	1.57	-	-	-	-
Subtotal				1.57	-	2.14	-	-
<b>8-Fatty alcohols</b>								
1-Docosanol*	35.73	326	C <sub>22</sub> H <sub>46</sub> O	-	-	6.55	-	5.82
1-Hexacosanol	39.01	382	C <sub>26</sub> H <sub>54</sub> O	1.6	2.19	2.41	2.81	1.88
Subtotal				1.6	2.19	8.96	2.81	7.7
<b>9-Fatty aldehydes</b>								
E-14-Hexadecenal	23.95	238	C <sub>16</sub> H <sub>30</sub> O	-	12.93	-	-	9.39
E-15-Heptadecenal	28.25	252	C <sub>17</sub> H <sub>32</sub> O	8.04	15	14.08	15.67	11.43
Subtotal				8.04	27.93	14.08	15.67	20.82
Total				93.27	93.21	93.88	92.28	95.52

\*Compounds identified before from genus *Oxalis* and detected in the present study.

#### 4. Conclusion

Thirty seven non-polar compounds were recognized from five *Oxalis* species, twenty eight of them were reported for first time in the genus. The GC-MS profiling of *O. corniculata* var. *repens* and *O. corniculata* supported the treatment of *repens* as a variety of *corniculata*. The non-polar constituents of the studied plants are chemosystematically significant on the species level and difficult to be used on the section level of taxonomy.

#### 5. Conflicts of interest

Authors declare that there are no conflicts of interest.

#### 6. Acknowledgments

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