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Short Communication

Constituents of Peel and Leaf Essential Oils of *Citrus Medica* L

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Abstract

The chemical constituents of leaf and peel essential oil of *Citrus medica* L. were analysed by gas chromatography mass spectroscopy (GC-MS). Nineteen components accounting for 99.9% of the oil were identified in leaf oil. The major constituents are erucylamide (28.43%), limonene (18.36%) and citral (12.95%). The peel oil contains forty three components accounting for 99.8% of the total oil and the major components are isolimonene (39.37%), citral (23.12%) and limonene (21.78%).

Keywords: *Citrus medica*; Essential oils; GC-MS; Erucylamide; Isolimonene.

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1. Introduction

Citrus medica L., commonly known as citron, is a small tree, having large fruit (20-22.5 cm. long) resembling pineapple in shape. The citron was the first citrus fruit cultivated in the Mediterranean region and especially in Crete according to Protopapadakis [1] and Isaac [2]. The citron rind is popular as a dessert, essence in perfumery [3, 4]. The most important part of the citron is the peel which is a fairly important article in international trade. In Bangladesh, India, Indonesia, citron peel is eaten raw with rice. The entire fruit of the 'Fingered citron' is usually eaten [5]. In Guatemala, it is used as flavoring for carbonated soft-drinks. In Malaya, citron juice is used as a substitute for the juice of imported, expensive lemons [6]. In Spain, syrup made from the peel is used to flavor unpalatable medical preparations [7]. Chinese and Japanese people prize the citron for its fragrance and it is a common practice in central and northern China to carry a ripe fruit in the hand or place the fruit in a dish on a table to perfume the air of a room [6]. The dried fruits are put with stored clothing to repel moths [5]. In India, the peel is a remedy for dysentery and is eaten to overcome halitosis [2]. Emmanuel *et al.* [8] reported that *C. medica* essential oil showed fungitoxicity against some fungi. *C. medica* is relevant to treatment of diabetes and alzheimer's disease [9]. The candied peel is sold in China as

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stomachic, stimulant, expectorant and a tonic. In West Tropical Africa, the citron is used only as a medicine, particularly against rheumatism. The flowers are used medicinally by the Chinese. The essential oil of the peel is regarded as an antibiotic. The peel contains citroflavonoids consisting of a mixture of hesperidoside (rhamnoglucoside of hesperetol), naringoside and ecryodietyoside (flavanones). Essential oils and vitamin C are also found, in addition to glucosides hesperidin (vitamin P) and rutin [3-5]. The citroflavonoids also have an anti-inflammatory, antihistamine and diuretic action and can cause dilatation of the coronaries [6].The essential oil of the whole fruit of *C. medica* var. *sarcodactylis* contained limonene, γ-terpinene, (Z)-citral and (E)-citral. The peel oils of *C. medica* contained limonene and α-terpineol [10]. Gurdip *et al*. [11] reported that the major constituents in leaf oil are citronellal, citronellol, limonene, citronellyl acetate, isopulegol, linalool. The peel oil contained limonene, citronellal, citronellol, r-cymene, geranial, γ-terpinene, citronellic acid, α-terineol, linalool. Twenty-seven and twenty nine components were identified in the leaf and peel oils, respectively. Limonene was the major constituent in the oil of leaf and peel, while the content of the other constituents varied. The oxygenated monoterpene geranial, neral, geranyl acetate, neryl acetate and the monoterpenic hydrocarbon myrcene followed [12]. *C. medica* contains a considerable amount of β-pinene, γ-terpinene, α-terpinolene and trans-α-bergamotene [13]. Marie *et al.* [14] reported that limonene, γ-terpinene, geranial, neral were observed for peel oils while leaf oils exhibited the limonene, geranial, neral composition. In addition *C. medica* essential oil contains d-limonene, other terpenes found in the flavedo oil fraction are linalool, geraniol, citronellol, α-terpineol, valencene, mircene, α-pinene, etc. [15]. No report is available regarding *C. medica* growing in Bangladesh. So, the present study represents the first approach for the characterization of the chemical composition of citron peel and leaf essential oils from Bangladesh.

2. Materials and Method

Plant materials: The leaves and peels of *Citrus medica* were collected from the experimental field of Citrus Research Station, BARI, Jaintapur, Sylhet, Bangladesh, during September 2008. One-voucher specimen (N-8) was deposited in the Herbarium of BCSIR Laboratory, Chittagong.

Essential oil isolation: Leaves and the peels of the fresh fruits of *Citrus medica* were harvested from healthy, well-grown plants. Freshly harvested leaves (400 g) and peels (300 g) were chopped in a blender seperately. The fresh leaves and chopped peels were subjected to hydrodistillation using a modified clevenger-type glass apparatus for 4 h for isolation of oils separately [16]. The oil samples were stored at 0°C in air-tight containers after drying them over anhydrous sodium sulfate and filtered before going to GC-MS analysis.

Essential oil analysis: The leaves and peels essential oils of *Citrus medica* were analyzed by electron impact ionization (EI) method on GC-17A gas chromatograph (Shimadzu) coupled to a GC-MS QP 5050A mass spectrometer (Shimadzu); fused silica

capillary column (30m x 0.25mm,i.d.; 0.25 μm film thickness), coated with DB-5 ms (J and W); column temperature 40°C (2 min) to 170°C at the rate of 3°C/min; carrier gas, helium at constant pressure of 90 kPa. Acquisition parameters full scan; scan range 40-350 amu. Samples were injected by splitting and the split ratio 1:20.

Identification of the compounds: Compounds identification were done by comparing the NIST library data of the peaks with those reported in literature , mass spectra of the peaks with literature data . Percentage composition was computed from GC peak areas on DB-5 ms column without applying correction factors.

3. Result and Discussions

Tables 1 and 2 report the constituents of the leaves and peels essential oils of *Citrus medica*. Nineteen constituents have been identified in leaf essential oil which are dominated by erucylamide (28.43%), limonene (18.36%), citral (12.95%), mehp (8.96%), 2,6-octadien-1-ol, 3,7-dimethyl-, acetate, (Z)- (5.23%), 6-octenal, 3,7-dimethyl- (4.39%), 1,2-cyclohexanediol, 1-methyl-4-(1-methylethenyl)- (3.98%) and methoprene (3.51%). On the other hand, forty three components have been identified in peels oil, which were characterized by the presence of isolimonene (39.37%), citral (23.12%), limonene (21.78%), β-myrcene (2.70%), neryl acetate (2.51%) and neryl alcohol (2.25%). Results showed that the leaves and peels oils were a complex mixture of numerous compounds; many of which were present in trace amounts. It is worth mentioning here that there is a great variation in the chemical composition of the leaf and peel essential oil of *C. medica*. Erucylamide and isolimonene are the most important and main components in leaf and

Table 1. Constituents of leaf essential oil from *Citrus medica* L.

Sl.	Name of components	%
1.	Limonene	18.36
2.	7-Oxabicyclo[4.1.0]heptane, 1-methyl-4-(1-methylethenyl)-	1.18
3.	6-Octenal, 3,7-dimethyl-	4.39
4.	Cyclohexanone, 2-methyl-5-(1-methylethenyl)-	2.24
5.	1-Monolinoleoylglycerol trimethylsilyl ether	0.86
6.	6-Octen-1-ol, 3,7-dimethyl-	1.72
7.	n-pentyl(1-propenyl)dimethylsilane	0.82
8.	citral	12.95
9.	2-Octen-1-ol, 3,7-dimethyl-, isobutyrate, (Z)-	1.10
10.	2-Oxocycloheptyl acetate	0.87
11.	2,4-Dodecadienoic acid, 11-methoxy-3,7,11-trimethyl-, methyl ester, (E,E)-	1.22
12.	Methoprene	3.51
13.	Geranyl methyl ether	1.42
14.	13-Heptadecyn-1-ol	1.05
15.	1,2-Cyclohexanediol, 1-methyl-4-(1-methylethenyl)-	3.98
16.	2,6-Octadien-1-ol, 3,7-dimethyl-, acetate, (Z)-	5.23
17.	Mehp	8.96
18.	3,7-Nonadien-2-ol, 4,8-dimethyl-	1.16
19.	Erucylamide	28.43

Table 2. Constituents of peel essential oil from *Citrus medica* L.

Sl.	Name of constituents	%
1.	(1R)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene	0.14
2.	α-Pinene	0.41
3.	3-Octyn-2-ol	0.10
4.	β-Myrcene	2.70
5.	2-Acetyl-5-methylfuran	0.05
6.	Cyclooctyl alcohol	0.17
7.	Limonene	21.78
8.	Isolimonene	39.37
9.	1,3,6-Octatriene, 3,7-dimethyl-, (Z)-	0.43
10.	1-Heptanol, 3-methyl-	0.04
11.	Linalool	0.94
12.	Nonanal	0.25
13.	trans-p-Mentha-2,8-dienol	0.04
14.	7-Oxabicyclo[4.1.0]heptane, 1-methyl-4-(1-methylethenyl)-	0.41
15.	citral	23.12
16.	6-Octenal, 3,7-dimethyl-	0.29
17.	cis-Verbenol	0.09
18.	Carane, 4,5-epoxy-, trans	0.30
19.	1,2-Cyclohexanediol, 1-methyl-4-(1-methylethyl)-	0.03
20.	4-Terpineol	0.08
21.	Terpinyl acetate	0.16
22.	β-Terpinyl acetate	0.52
23.	Decanal	0.33
24.	Neryl acetate	2.51
25.	Neryl Alcohol	2.25
26.	Undecanal	0.10
27.	Neryl acetate	0.60
28.	Dodecanal	0.08
29.	(Z,E)-α-Farnesene	0.05
30.	Caryophyllene	0.59
31.	α-Bergamotene	0.48
32.	1,6,10-Dodecatriene, 7,11-dimethyl-3-methylene-, (Z)-	0.04
33.	Tetrakis(trimethylsiloxy)silane	0.04
34.	α-Caryophyllene	0.08
35.	Germacrene D	0.05
36.	cis-.α-Bisabolene	0.07
37.	γ-Elemene	0.05
38.	β-Bisabolene	0.71
39.	δ-Cadinene	0.05
40.	Tetradecanal	0.10
41.	Neoisolongifolane, hydroxy-	0.07
42.	β-Bisabolol	0.12
43.	n-Hexadecanoic acid	0.12

peel oil of Bangladesh but it is totally absent in all other reported oils. So, we can conclude that erucylamide and isolimonene are the first reported component in *C. medica* leaf and peel oils. Linalool, γ-terpinene, (Z)-citral ,(E)-citral, citronellal, citronellol, citronellyl acetate, isopulegol, r-cymene, geranial, citronellic acid, α-terineol, which have

been reported as major constituents in the leaves and peels oil of others countries, were totally absent in our sample [10, 11]. This confirms that the variations in the cultivar reported is not due to geographic divergence and ecological conditions, it may be due to different chemotype. On the basis of above fact it may be concluded that *C. medica*, growing widely in Bangladesh, may be utilized as a source for the isolation of natural erucylamide and isolimonene respectively. The high concentration of erucylamide and isolimonene in leaf and peel oil make it potentially useful in the medicines because they exhibit fungitoxicity [8]. It is worth mentioning that the oil of *C. medica* has been reported to be used in folk medicine in the treatment of dysentery, rheumatism, diabetes and alzheimer's disease [9]. Dung *et al.* [17] studied two chemotypes of citron peel essential oils (*C. medica*, L. var. *sarcodactylis*) and found that the major oil constituents of the one chemotype were limonene and p-cymene, while the oil of the other chemotype contained predominantly limonene and γ-terpinene. The oil of both leaves and peel was also studied by Fleisher and Alexander [4] who found that limonene was the main constituent in peel oil followed by γ-teqjinene, geranial, α-teqrineol, terpinen-4-ol, p-cymene and neral, while in the leaf oil the most abundant constituent was geranial and then limonene and neral. In the study of citron peel oil by Poiana *et al.* [18] limonene was also found as the main constituent followed by γ-terpinene, γ- and β-pinene. The high content of oxygenated compounds in the studied cultivar may explain the powerful and characteristic odor of these plants as is referred to by Lund *et al.* [19]. The increased content of linalool supports the idea that it can be a predominant substance in biogenesis of many constituents of citrus, as is reported by Attaway *et al.* [20]. Gramshaw and Sharpe [21] considered that citral was the key aroma component of citrus odor and flavor and they accepted its content as indicative of the essential oils quality. It would indicate that our oils are of good quality due to the presence of citral.

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