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Mini Review

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A Mini-Review on the Biomarkers in Essential Oils from Peels of *Citrus Reticulata* Blanco and their Antioxidant Activities

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ABSTRACT

Citrus reticulata Blanco belonging to Citrus of Rutaceare is an important economical fruit plants planted all over the world. Usually, its peels were discarded as waste while they are rich in bioactive compounds like essential oils (EOs). Up to now, more than 1000 compounds have been identified in EOs from peels, flowers, leaves of Citrus species. Among these compounds, fourteen biomarkers like Limonene, γ-Terpinene, p-Cymene, Linalool, Decanal, Thymol, α-Farnesene, Methyl methanthranilate, Tricosane, α-Terpineol, Terpinene-4-ol, Spathulenol, α-Sinensal, and n-Hexadecanoic acid were selected from hundreds of compounds identified in essential oils from peels of Citrus reticulata Blanco by us. The antioxidant activities is an important biological activities of these EOs, and more and more attention were focused on them these years. At the same time, the antioxidant activities of these EOs and those biomarkers were summarized in this paper.

Keywords: *Citrus reticulata* Blanco; Peel; Essential oils; Biomarkers; Antioxidant activities

INTRODUCTION

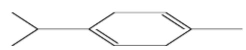
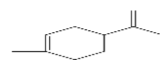
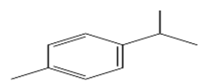
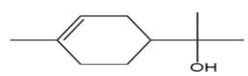
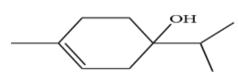
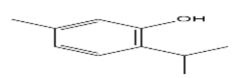
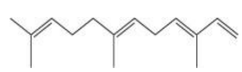
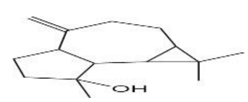
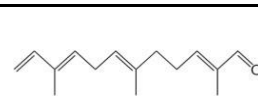
After years of cultivation and selection, *Citrus* has become a common fruit in people's life with great economic and market value. There are many species of *Citrus* all over the world. *Citrus reticulata* Blanco (mandarin) belonging to *Citrus* of *Rutaceae* were planted all over the world, which have many varieties. In China, the peels from some varieties like C. *chachiensis Hort*, *C. kinokuni* Tanaka, C. *reticulata* ‘Dahongpao’, etc., can be used as two kinds of Chinese materia medica (CMM) like *Citri Reticulatae Pericarpium* (CRP) and *Citri Reticulatae Pericarpium Viride* (CRPV), which has been consumed daily as food and dietary supplement for centuries [1-2]. These peels are rich in biological compounds like Essential Oils (EOs), flavonoids, limonoids, etc. Essential oils (EOs) are the main ingredients in these peels, which are valuable in the perfume, food, and beverage industries, and have also enjoyed use as aromatherapy and medicinal agents [3]. As a result, the researchers all over the world have done a lot of researches on it. Up to now, more than 1000 compounds have been identified in EOs from peel, leaves, and flowers of *Citrus* species [4], but only a few of them can be selected as biomarkers of these EOs. In this paper, 14 biomarkers were picked from these compounds. At the same time, these EOs and those biomarkers have many biological activities like anti-proliferative, chemoprotective, antioxidant, antibacterial, antifungal [3]. These years, more and more attention were focused on the antioxidative activities of these EOs and the biomarkers, in which some compounds showed strong anti-oxidant activities, especially the phenol such as thymol, which was reported to have the abilities to stop or restart the negative effects of free radicals [5,6]. In this paper, the antioxidant activities of these EOs and those biomarkers were also summarzied in brief.

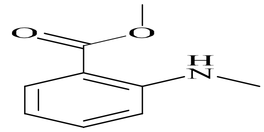
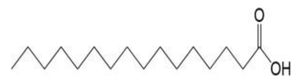
Biomarkers

49 volatile compounds have been described as the common compounds in 10 most studied *Citrus* species, in which C. *reticulata* Blanco is one of them. In some way, they could be considered as those defining the characteristic *Citrus* volatile profile and most of them are monoterpenoids. On the other hand, 410 compounds of ample chemical diversity have been described up to date in only one of these species, most often in only one study. When unambiguously identified, they could be considered as biomarkers for each particular species [4]. The major fractions in the C. *reticulata* Blanco peel oils were monoterpenes, with limonene occupying a dominant percentage (60.0-95.0%) [4,7]. The representative sesquiterpenes in the EOs extracted from C. *reticulata* Blanco included tr-caryophyllene, α-selinene, tr, tr-α-farnesene (the most distinguished one with content as trace-0.2%, trace means the content is less than 0.05%), α-copaene, β-cubebene, ô-cadinene, germacrene D [8].

Fourteen biomarkers were summarized by us based on past researches [1-6, 8,9], which could be seen in Table 1.

Table 1: The fourteen biomarkers identified in EOs from peels of C. *reticulata* Blanco

No.	Classification	Chemicals	CAS	Structure	Ref.
1	Hydrocarbon monoterpene	Limonene	138-86-3		[1-7, 10]
2		γ-Terpinene	99-85-4		[1-7]
3		p-Cymene	99-87-6		[1-7]
4	Alcohol monoterpene	Linalool	78-70-6		[1-6, 11-12]
5		α-Terpineol	98-55-5		[1, 3-4, 6]
6		Terpinene-4-ol	562-74-3		[3-6]
7	Phenol monoterpene	Thymol	89-83-8		[3-6]
8	Hydrocarbon sesquiterpene	tr, tr-α-Farnesene	502-61-4		[3-4]
9	Alcohol sesquiterpene	Spathulenol	6750-60-3		[1-2, 4]
10	Aldehyde sesquiterpene	*α*-Sinensal	17909-77-2		[1-2, 4-5]
11	Aldehyde	Decanal	112-31-2		[3-4, 6]

12	N included	Methyl-N-methylanthranilate	85-91-6		[2, 4, 8-9]
13	Acid	n-Hexadecanoic acid	57-10-3		[1, 4]
14	Alkane	Tricosane	638-67-5		[1]

γ-Terpinene and p-Cymene usually were the high content compounds besides limonene in these EOs. Linalool is a representative compuond in peel EOs of *C. reticulata* 'Dahongpao' [1]. α-Terpineol and tr, tr-α-Farnesene are two important characterisitc compounds in peel EOs of C. *kinokuni Tanaka* [1]. Decanal is a representative unterpenoid aldehyde in peel EOs of C. *reticulata* Blanco and can be used as a biomarker [4]. Methyl-N-methylanthranilate is an important aroma compound from mandarin peel oil, which only in a few cases has been reported as a constituent of the *Citrus* essential EOs, However, it has been used in some cases to recognize the authenticity of mandarin EOs in several parts of the world [9]. n-Hexadecanoic acid as a compound with high boiling point identified in these EOs usually is a minor component, but sometimes it can be used as a biomarker to distinguish different peel EOs of C. *reticulata* Blanco. In many situations, alkanes were neglected or undetected in EOs of mandarin. Alkanes weren't used as biomarkers of EOs from *Citrus* previously, but some of them can be used as potential biomarkers like Tricosane, which was firstly suggested by us.

Antioxidant Activities

At the same time, the antioxidant activities of these EOs and those biomarkers were studied correspondingly [3, 5-7, 10-14].The EOs from C. *reticulata* Blanco demonstrated moderate activity to eliminate free radicals, which mainly due to the d-limonene with high content [3]. The studies in vivo and in vitro both demonstrated that d-limonene has some anti-oxidant activities [3,10].

γ-Terpinene showed strong scavenging abilities against DPPH (1,1-diphenyl-2-picrylhydrazyl), and effective restraining on lipid peroxidation, while oxygenated compounds like α-Terpineol, and Terpinene-4-ol, showed weak scavenging abilities to free-radical like DPPH [7].

Linalool acts mainly as an anti-lipoperoxidant agent [11]. Antioxidant activity is more significant in case of linalool-containing essential oils, most probably due to the synergy between components. At relatively high concentrations (120 mg/kg) and long-time exposure, linalool protects guinea-pig brain tissue against hydrogen peroxide oxidative stress, its effects being similar to those exhibited by lipoic acid and vitamin E [11]. However, in thiobarbituric acid reactive species assay, linalool behaves as a pro-oxidant; in micellar system with linoleic acid, its antioxidant activity has not been demonstrated [6,12]. Inhalation of linalool by subjects with no underlying disease significantly improved antioxidant activity. And, it was found that the relationships between linalool and antioxidant level, not only in subjects without underlying disease but in patients with Carpal tunnel syndrome. These results therefore indicated that inhalation of linalool enhanced antioxidant activity, regardless of the presence of increased oxidative stress [15].

The antioxidant activity of thymol was superior to that of carvacrol, possibly due to greater steric hindrace of the thymol phenolic group. In addition, positive results were obtained for all migration extracts by the antioxidant activity study performed by the DPPH method, showing thymol a higher antioxidant capacity [16]. It is worth mentioning that the reaction mechanism between phenolic antioxidant (e.g., thymol) and peroxyl radical was historically believed to be an H-atom transfer (HAT) mechanism but recently it has been revised as a proton-coupled electron transfer (PCET) [5].

CONCLUSION

In this paper, 14 biomarkers selected from the identified compounds in *Citrus reticulata* Blanco peel EOs and the antioxidant activities of these EOs and some biomarkers has been reviewed. In fact, there are some other biomarkers summarized in other researches [2,4,6]. In the following researches, these compounds should be discerned if they can be included into this system or not. If some can, their antioxidant activities need to be summarized or studied in depth also.

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