

Dendrobium Essential Oil

Subjects: **Plant Sciences**

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A detailed chemical composition of Dendrobium essential oil has been only reported for a few main species. This article is the first to evaluate the essential oil composition, obtained by steam distillation, of five Indian Dendrobium species: *Dendrobium chrysotoxum* Lindl., *Dendrobium harveyanum* Rchb.f., and *Dendrobium wardianum* R.Warner (section *Dendrobium*), *Dendrobium amabile* (Lour.) O'Brien, and *Dendrobium chrysanthum* Wall. ex Lindl. (section *Densiflora*). We investigate fresh flower essential oil obtained by steam distillation, by GC/FID and GC/MS. Several compounds are identified, with a peculiar distribution in the species: Saturated hydrocarbons (range 2.19–80.20%), organic acids (range 0.45–46.80%), esters (range 1.03–49.33%), and alcohols (range 0.12–22.81%). Organic acids are detected in higher concentrations in *D. chrysanthum*, *D. wardianum*, and *D. harveyanum* (46.80%, 26.89%, and 7.84%, respectively). This class is represented by palmitic acid (13.52%, 5.76, and 7.52%) linoleic acid (*D. wardianum* 17.54%), and (Z)-11-hexadecenoic acid (*D. chrysanthum* 29.22%). Esters are detected especially in species from section *Dendrobium*, with ethyl linolenate, methyl linoleate, ethyl oleate, and ethyl palmitate as the most abundant compounds. Alcohols are present in higher concentrations in *D. chrysanthum* (2.4-di-tert-butylphenol, 22.81%), *D. chrysotoxum* (1-octanol, and 2-phenylethanol, 2.80% and 2.36%), and *D. wardianum* (2-phenylethanol, 4.65%). Coumarin (95.59%) is the dominant compound in *D. amabile* (section *Densiflora*) and detected in lower concentrations (range 0.19–0.54%) in other samples. These volatile compounds may represent a particular feature of these plant species, playing a critical role in interacting with pollinators.

Dendrobium

essential oil

steam distillation

mass spectrometry

pollinator

1. Introduction

The Orchidaceae family, with its huge number of species that evolved different pollination systems, is known for the variety and complexity of its floral scents, which according to Kaiser (1993), could potentially cover all the spectrum of fragrances occurring in nature [1]. Floral scent, which derives from the composition of volatile organic compounds emitted by the flowers' tissues (floral VOCs), is fundamental for the defense against pathogens/herbivores and pollinator responses [2]. This trait, together with other characteristics of flowers, such as the color, the presence of nectar, and other peculiarities of the reproductive portions, contributes indeed to defining pollination syndromes [3]. The genus *Dendrobium* Sw., 1799 (Epidendroideae; Dendrobiinae), which accounts for about 1100 species distributed in Pacific Islands, Asia, and Australia, is one of the largest of the family [4]. As potted and cut flowers, *Dendrobium* species and hybrids are of great economic interest, being at the top ten among the most commercially traded orchid taxa [5]; several species are also grown and sold for medicinal purposes [6][7]. A large number of taxa, the great morphological diversity, and the wide distribution range have contributed to taxonomic ambiguities that are currently under debate [4][8][9]. In the phylogenetic revision of the genus, Takamiya et al. (2014)

considered the presence of papillae on the flower's lip in entities belonging to different clades. They demonstrated that this character evolved as an adaptation to bee pollination by *Dendrobium* species [4]. As stated in previous studies, bee-pollinated orchid flowers exhibit papillose carpets, identified as osmophores, structures of accumulation of substances responsible for floral fragrances [10][11]. Takamiya et al. (2014) recorded odor-producing cells in all species of Section *Densiflora* and the majority of the Section *Dendrobium*, thus hypothesizing that this character has probably been acquired after the divergence between the Asian and the Australasian Superclades [4]. Despite the great number of studies aimed at optimizing in vitro propagation protocols (i.e., Marting and Madassery, 2006; Teixera da Silva et al., 2015; Calevo et al. 2020; and references therein) [12][13][14], and at characterizing anatomical and chemical traits (Carlsward et al., 1997; Xu et al., 2013; Devadas et al., 2016 and references therein) [15][16][17], the genus *Dendrobium* has been little investigated from the point of view of the reproductive biology, and even less is known about floral volatilome [18]. To the best of our knowledge, only a few authors had carried out characterizations of floral volatiles from *Dendrobium* species. Flath and Ohinata (1982) investigated the VOCs of *D. superbum* Rchb. f. (syn. *D. anosmum* Lindl.), which is pollinated by the melon fly (*Dacus cucurbitae*), finding a significant amount of 4-phenylbutan-2-one, whose structure is closely related to another known fly attractant [19]. Brodmann et al. (2009) worked on *D. sinense* Tang and F.T.Wang and reported that this species emits (Z)-11-eicosen-1-ol (a molecule present in the alarm pheromone of honeybees) to attract hornets for pollination [20]. Silva et al. (2015) recognized terpenes as the most abundant class of compounds in the floral volatiles of *D. nobile* Lindl. [21]. Julsrigival et al. (2013) found a prevalence of 2-pentadecanone in *D. parishii* Rchb.f. [22]. Robustelli della Cuna et al. (2017), instead, compared the essential oil of different portions of *D. moschatum* (Buch.-Ham.) Sw., including the inflorescence: They observed differences among the volatile compositions, and then hypothesized that compounds like ketones or long-chain methyl and ethyl esters play a role as pollinator attractants [23]. The few reports dedicated to reproductive biology have stated that there are various ways for which *Dendrobium* species attract pollinators: There are cases of shelter mimicry [24][25][26][27][28], nectar rewarding [18], chemical and visual attraction [29], rest and mating place offering, or generalized food deception strategies like a simulation of other co-flowering species occurring in the same habitat [30]. In this work, we aimed to characterize and compare the floral volatiles of five *Dendrobiums* belonging to sections *Dendrobium* and *Densiflora* of the Asian Superclade [4][9]. In particular, we characterized the volatile fractions of the inflorescences of *D. chrysanthum* Wall. ex Lindl. (Figure 1A), *D. harveyanum* Rchb. f. (Figure 1B) and *D. wardianum* R.Warner (Figure 1C) from section *Dendrobium*, Core subclade of Clade A, and *D. chrysotoxum* Lindl. (Figure 1D) and *D. amabile* (Lour.) O'Brien (Figure 1E) from Clade A and C, respectively, of section *Densiflora* (according to Takamiya et al. 2014) [4].



Figure 1. *Dendrobium chrysanthum* (A), *D. harveyanum* (B), *D. wardianum* (C), *D. amabile* (D), and *D. chrysotoxum* (E), greenhouse-grown plants cultivated in Turin (Italy).

2. Current Researches and Results

The yields of *D. amabile*, *D. chrysanthum*, *D. chrysotoxum*, *D. harveyanum*, and *D. wardianum* essential oils obtained by steam distillation from fresh flowers were evaluated as 0.09%, 0.34%, 0.33%, 0.39%, and 0.33% (weight/dry weight basis), respectively. **Table 1** shows the results of qualitative and quantitative oil analyses on the Elite-5MS column. The compounds are listed in order of their elution and are reported as percentages of the total essential oil. Differences in the qualitative and quantitative compositions of the obtained essential oils have been observed. As shown in the Venn's diagram (**Figure 2**), only palmitic acid was shared by all five taxa. On the other hand, 30 compounds were uniquely identified in *D. chrysotoxum*, and nine, eight, four, and three in *D. wardianum*, *D. harveyanum*, *D. chrysanthum*, and *D. amabile*, respectively. Furthermore, 21 compounds were found shared by *D. chrysotoxum* and *D. wardianum*. Below, the qualitative and quantitative description of essential oils for each taxon. The Pie chart (**Figure 3**) shows that the essential oils were different depending on the different species: It can be observed that the main constituents were compounds belonging to saturated hydrocarbons, acids, esters, coumarin, and alcohol classes.

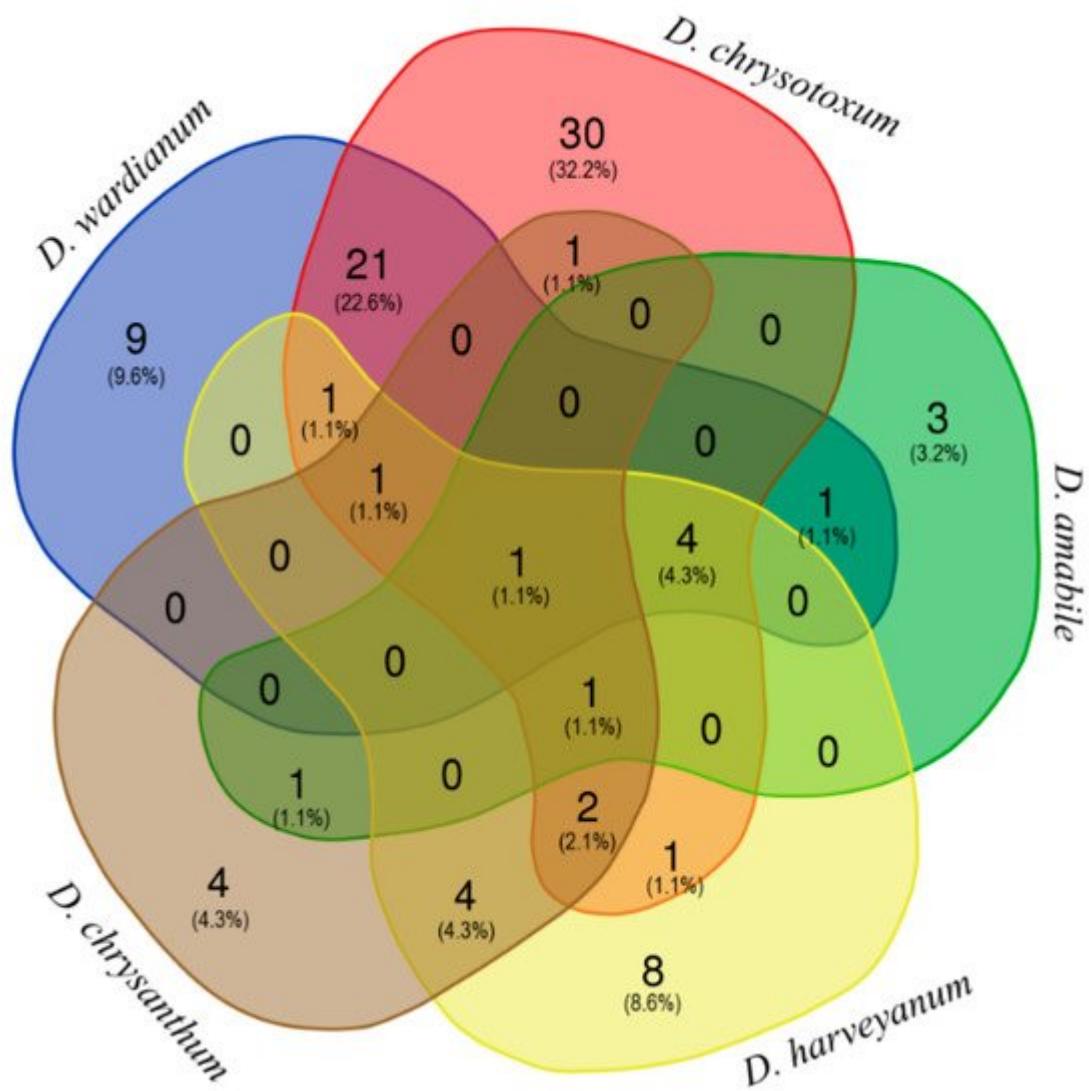


Figure 2. Venn's diagram shows both the number of compounds shared and unshared/peculiar among the five *Dendrobium* species. Percentages are referred to the total number of compounds found, not to the relative abundance.

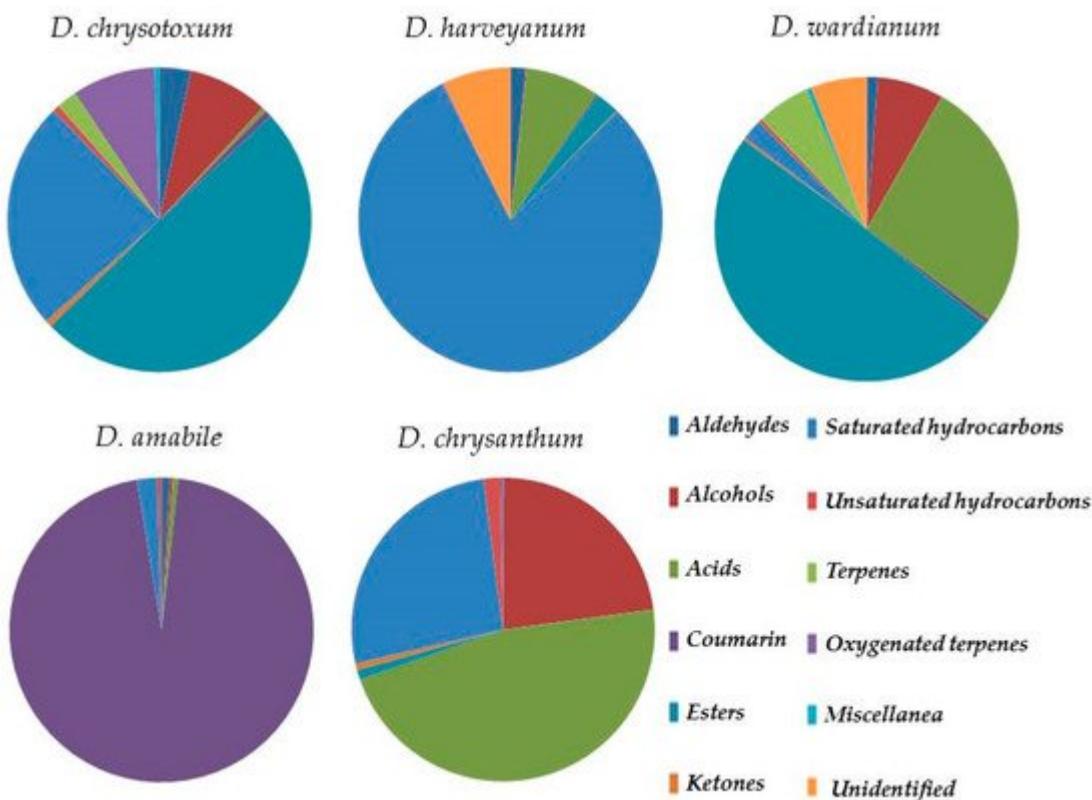


Figure 3. Pie chart of distribution of the classes.

Table 1. Essential oils composition of inflorescences from the five *Dendrobium* species.

Compound ^a	RI ^b	RI ^c	Section <i>Dendrobium</i>				Section <i>Densiflora</i>		Identification ^d
			D. chrysotoxum %	D. harveyanum %	D. wardianum %	D. amabile %	D. chrysanthum %		
Octane	800	800	-	0.15	-	-	-	-	RI, NIST
Hexanal	802	801	0.73	0.06	0.02	-	-	-	RI, NIST
2-hexanol	804	808	-	0.12	-	-	-	-	RI, NIST
Diacetone alcohol	841	841	-	-	-	-	0.68	-	RI, NIST
α-pinene	939	931	0.21	-	-	-	-	-	MS, NIST
Benzaldehyde	960	958	0.14	-	-	-	-	-	RI, NIST
β-pinene	979	973	0.03	-	-	-	-	-	MS, NIST
Caproic acid	1005	1003	0.06	-	-	-	-	-	RI, NIST
α-terpinene	1017	1015	0.10	-	-	-	-	-	RI, NIST
o-Cymene	1026	1023	0.09	-	-	-	-	-	RI, NIST

Compound ^a	RI ^b	RI ^c	Section <i>Dendrobium</i>			Section <i>Densiflora</i>			Identification ^d
			<i>D. chrysotoxum</i>	<i>D. harveyanum</i>	<i>D. wardianum</i>	<i>D. mamame</i>	<i>D. bimaculatum</i>	<i>D. chrysanthum</i>	
Limonene	1029	1027	0.17	-	-	-	-	-	RI, NIST
Benzyl alchol	1032	1035	0.21	-	0.52	-	-	-	RI, NIST
β -Isophorone	1042	1041	0.51	-	-	-	-	-	RI, NIST
Phenylacetaldehyde	1042	1043	0.84	-	0.06	-	-	-	RI, NIST
2-octenal	1056	1058	-	0.13	-	-	0.06	-	RI, NIST
γ -Terpinene	1060	1059	0.76	-	0.04	-	-	-	RI, NIST
Unidentified	-	1065	-	-	2.89	-	-	-	-
<i>cis</i> -sabinene hydrate	1070	1067	0.27	-	-	-	-	-	MS, NIST
dihydromyrcenol	1073	1073	-	0.04	-	-	0.06	-	RI, NIST
1-octanol	1070	1074	2.80	-	0.41	-	-	-	MS, NIST
<i>trans</i> -sabinene hydrate	1098	1098	0.20	-	-	-	-	-	RI, NIST
Linalool	1097	1101	0.34	0.08	-	-	-	-	MS, NIST
Nonanal	1102	1105	-	0.16	-	-	-	-	RI, NIST
2-phenylethanol	1107	1115	2.36	-	4.65	-	-	-	MS, NIST
Methyl octanoate	1127	1127	0.04	-	-	-	-	-	RI, NIST
<i>cis</i> -verbenol	1141	1142	0.92	-	-	-	-	-	RI, NIST
<i>trans</i> -verbenol	1145	1148	4.60	-	-	-	-	-	RI, NIST
Camphor	1150	1157	-	0.12	-	-	-	-	MS, NIST
Nonenal	1162	1161	0.41	-	0.17	-	-	-	RI, NIST
α -phellandren-8-ol	1170	1169	2.15	-	-	-	-	-	RI, NIST
Terpinen-4-ol	1177	1179	1.53	-	-	-	-	-	RI, NIST
Diethyl succinate	1182	1184	0.33	-	-	-	-	-	RI, NIST
<i>p</i> -cymen-8-ol	1183	1186	0.29	-	-	-	-	-	RI, NIST

Compound ^a	RI ^b	RI ^c	Section <i>Dendrobium</i>			Section <i>Densiflora</i>			Identification ^d
			D. <i>chrysotoxum</i> %	D. <i>harvejanum</i> %	D. <i>wardianum</i> %	D. <i>mamabile</i> %	D. <i>chrysanthum</i> %		
α-terpineol	1189	1192	0.18	-	-	-	0.28	RI, NIST	
Ethyl octanoate	1196	1199	0.20	-	-	-	-	RI, NIST	
Decanal	1202	1206	-	-	0.04	-	-	RI, NIST	
Verbenone	1205	1210	0.20	-	-	-	-	MS, NIST	
2,4-nonandienal	1212	1214	-	-	0.03	-	-	RI, NIST	
4-vinylphenol	1224	1221	-	-	0.52	0.08	-	RI, NIST	
3-phenyl-1-propanol	1232	1231	-	-	0.08	-	-	RI, NIST	
Phenylacetic acid ethyl ester	1247	1247	0.15	-	0.72	-	-	RI, NIST	
Nerol	1254	1256	0.06	-	-	-	-	RI, NIST	
2,4-decadienal (<i>E,E</i>)	1291	1295	0.40	0.39	0.39	0.16	-	RI, NIST	
2-methoxy-4-vinyl-phenol	1315	1315	-	-	0.24	-	-	RI, NIST	
2,4-decadienal (<i>E,Z</i>)	1319	1317	0.63	0.88	0.48	0.72	-	RI, NIST	
2-nonenoic acid-γ-lactone	1345	1344	0.39	-	0.49	-	-	RI, NIST	
Capric acid	1359	1359	-	0.32	-	-	-	RI, NIST	
Eugenol	1367	1366	-	-	-	0.10	-	RI, NIST	
1-tetradecene	1390	1393	-	0.07	-	-	0.57	MS, RI	
3,4-dihydrocoumarin	1398	1399	-	-	-	0.10	-	RI, NIST	
Coumarin	1434	1436	0.71	0.19	0.54	95.49	-	RI, NIST	
9-epi-(<i>E</i>)-caryophyllene	1466	1458	-	-	1.32	-	-	MS, NIST	
Ethyl-cinnamate	1467	1468	-	-	0.55	-	-	RI, NIST	

Compound ^a	RI ^b	RI ^c	Section <i>Dendrobium</i>			Section <i>Densiflora</i>		Identification ^d
			<i>D. chrysotoxum</i>	<i>D. harveyanum</i>	<i>D. wardianum</i>	<i>D. mambibile</i>	<i>D. chrysanthum</i>	
2,4-di-tert-butylphenol	1494	1489			-	0.12	22.81	MS, NIST
β-selinene	1494	1489	0.25	-	1.30	-	-	MS, NIST
9-oxo-ethyl-nonanoate	1507	1510	1.28	-	-	-	-	MS, NIST
Lauric acid	1566	1568	0.23	-	-	-	-	RI, NIST
Ethyl laurate	1593	1596	0.15	-	-	-	-	RI, NIST
Unidentified	-	1658	-	5.16	-	-	-	-
Pentadecan-2-one	1667	1667	-	-	0.26	-	-	RI, NIST
Heptadecane	1700	1700	0.31	-	0.54	-	-	RI, NIST
Unidentified	-	1767	0.39	-	3.04	-	-	-
Myristic acid	1780	1776		-	3.59	-	-	MS, NIST
1-octadecene	1790	1796	0.32	-	0.41	-	-	MS, RI
Methyl pentadecanoate	1820	1828	0.04	-	-	-	-	MS, NIST
Unidentified	-	1879	5.74	-	-	-	-	-
Ethyl pentadecanoate	1890	1896	0.36	-	0.19	-	-	MS, NIST
Heptadecan-2-one	1902	1903	0.11	-		-	-	RI, NIST
Methyl palmitate	1927	1928	0.34	-	0.44	-	-	RI, NIST
<i>cis</i> -9-hexadecenoic acid	1942	1943	-	-	-	-	4.06	RI, NIST
Z-11-Hexadecenoic acid	1953	1953	-	-	-	-	29.22	RI, NIST
Palmitic acid	1958	1960	0.05	7.52	5.76	0.61	13.52	RI, NIST
Neocembrene	1960	1966	0.52	-	3.07	-	-	MS, NIST
Ethyl palmitate	1992	1997	3.05	-	0.99	-	-	MS, NIST

Compound ^a	RI ^b	RI ^c	Section <i>Dendrobium</i>			Section <i>Densiflora</i>			Identification ^d
			<i>D. chrysotoxum</i> %	<i>D. harveyanum</i> %	<i>D. wardianum</i> %	<i>D. nummularia</i> %	<i>D. mambabile</i> %	<i>D. chrysanthum</i> %	
Octadecan-1-ol	2074	2071	0.17	-	0.60	-	-	-	MS, NIST
Eicosane	2000	2000	-	40.42	-	-	0.55	RI, NIST	
Unidentified	-	2037	-	2.06	-	-	-	-	
Methyl linoleate	2051	2068	7.48	2.50	13.17	-	1.03	MS, NIST	
10-Heneicosene	2060	2073	-	-	-	0.43	-	MS, RI	
Heneicosane	2100	2100	1.01	2.92	1.66	0.25	-	RI, NIST	
Linoleic acid	2144	2147	0.12	-	17.54	-	-	RI, NIST	es et al. e volatile te a first ctions of thogens, isolation
Ethyl linolenate	2169 [33][34]	2171	26.98	-	32.24	-	-	RI, NIST	
Ethyl oleate	2179	2181	5.39	-	0.72	-	-	RI, NIST	
Ethyl octadecanoate	2193 [35][36]	2198	0.80	-	0.31	-	-	RI, NIST	
Docosane	2200	2204	1.66	26.82 [37][38][39][40]	-	1.94	17.53	RI, NIST	e in the (.) Clairv. nding on dditional
9-Triacosene	2279 [41]	2275	0.31	-	-	-	-	MS, RI	
Tricosane	2300	2307	9.33	-	-	-	-	RI, NIST	
Tetracosane	2400	2401	0.40	0.90	-	-[3]	2.07	RI, NIST	
9-Pentacosene	2474	2475	0.07	-	-	-	-	MS, RI	
Pentacosane	2500	2501	0.95	6.53	-	-	6.40	RI, NIST	lied. The nitic acid tilome of
Hexacosane	2600	2600	-	2.46	-	-	-	RI, NIST	
9-Eptacosene	2676	2676	-	[23][35][42]	-	-	1.15	MS, RI	at it was
Heptacosane	2700	2701	0.18	-	-	-	-	RI, NIST	(5.76%),
Aldehydes			3.15	1.62	1.20	0.88	0.06		
Alcohols			7.97	0.12	7.02	0.30	22.81		esters in
Acids			0.45	7.84	26.89	0.61	46.80		organic
Coumarin			0.71	0.19	0.54	95.59	-		any fruits

[43]. High content of volatile esters has been linked with the strong flavor of the 'Snow Chrysanthemum' cultivar of *Coreopsis* by Kim et al. (2020) [44]. In *D. moschatum*, a putative role as semiochemicals involved in pollinator attraction has been hypothesized for methyl and ethyl esters by Robustelli della Cuna et al. (2017) [23]. According to da Silva et al. (1999) and Cseke et al. (2007), terpenes are more abundant in flower VOCs of species pollinated by food-seeking bees [45][46]. As shown in **Table 1**, *D. wardianum* had the highest level (5.73%) of terpenes in the essential oil, followed by *D. chrysotoxum* (2.04%), but this class of compounds was not the predominant one in these two species. Conversely, oxygenated terpenes have been detected only in *D. chrysotoxum* (8.31%), while they were present in lower percentages in *D. harveyanum* and *D. chrysanthum*. Therefore, due to their ester and

Compound ^a	RI ^b	RI ^c	Section Dendrobium			Section Densiflora			Identification ^d
			D. chrysotoxum	D. harveyanum	D. wardianum	D. nummularia	D. mambibile	D. chrysanthum	
		[19]	%	%	%	%	%		
Esters			46.59	2.50	49.33	-	1.03		
Ketones			0.62	0.12	0.26	-	0.68		
Saturated hydrocarbons			22.84	80.20	2.20	2.19	26.55		
Unsaturated hydrocarbons			0.69	[23]	0.07	0.41	0.43	1.72	
Terpenes			2.04	-	5.73	-	-		
Oxygenated terpenes			8.31	0.11	-	-	0.34		
Miscellanea			0.48	-	0.49	-	-		
Unidentified			6.13	7.22	5.92	-	-		[47]

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