The 'Halo' Effect of Amides in Mandarin and Tangerine

Mandarin has a peculiar aroma that can be described as somewhat "fishy," which might be due to an unidentified amine compound.

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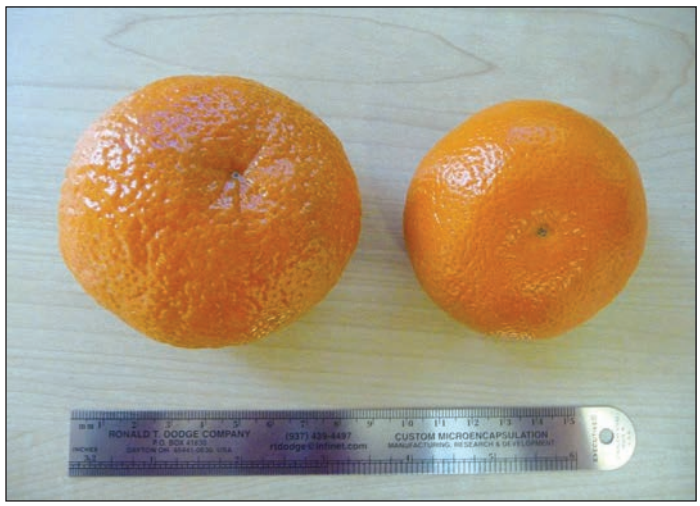
All citrus oils have a great deal in common. Their major components are nearly identical. Orange, grapefruit, tangerine and mandarin all have d-limonene, myrcene and pinenes as their major constituents (more than 95%). It is fascinating that these citrus oils are so easily distinguished by their odor alone. Why is this the case?

In particular, mandarin or tangerine oils (*Citrus reticulata*) are quite distinctive and have been the subject of studies for years.[1,2] There has been a recent push to develop and market a hybrid of mandarin and sweet orange, so-called Halos[a], that is set apart from the previously well-known brand called Cuties[b]. The new hybrid is significantly larger, seedless, a bit sweeter and easier to peel. While these advantages are obvious to a consumer, the real flavor components that contribute to its character are not well-known or understood.

Those in the flavor and fragrance industry agree the major components of limonene, myrcene, and α- and β-pinenes are *not* the character-donating ingredients. The character, in fact, comes from the delicate balance and blend of some 100 additional components that occur in both the peel and the juice. While no commercial peel oil extract of the new hybrid[a] is available, the recent market appearance of its fruit provided an opportunity for exploration and research. In unpublished work, this author previously examined the smaller variety of clementines[b] and here, compares the new hybrid along with sweet and sour orange, mandarin orange and tangerine.



The new Halo[a] hybrid (left) is significantly larger, seedless, a bit sweeter and easier to peel than the well-known clementine.

Odor Contributions

T-1 shows similarities as well as differences between the samples. For ease of comparison and a general understanding, a simple one-word odor character contributor is listed immediately to the left of each item. Note that these are not always the only character contribution, but indeed the main characters; also, there are always differences of opinion, and the author's may vary from other experts in the field.

The sweet orange, mandarin and tangerine extracts were all good commercial qualities, but the clementine and new Halo[a] hybrid, both peel and juice, were extracted in-house. Methylene chloride was used for the extractions in all cases. Previous unpublished work on clementine as well as sour orange[c] had elucidated the different profiles of peel direct, peel extract, juice direct and juice extracts. Peel direct and juice direct refer to analysis of the expressed peel oil and juice direct injections into a GC-MS system[d] using a variety of polar and non-polar capillary columns.

As can be seen in **T-1**, the distribution of components among samples is significantly different, but qualitatively similar. Significant differences in the juices versus peel oils are clear. In particular, the acids, while barely detectable in the peel, are significant in the juice section. Conversely, the limonene concentration in the peel is major, while it is minor in the juice. The new hybrid also contained a significant amount of waxes in the juice, contributing more to the mouthfeel than the flavor imparted by the acids.

Examining the components, in particular the levels of γ-terpinene, one can see the effect of hybridization between the mandarin and sweet oranges. Mandarin has approximately 20%, while the hybrids have 2-4%, and the sweet and sour oranges have practically none. The noted differences, however, do not effectively or accurately describe or account for the major character difference in mandarin or tangerine, as opposed to sweet or sour orange.

[a] Halos are a registered trademark of Paramount Citrus.
[b] Cuties are a registered trademark of Sun Pacific.
[c] *Citrus aurantium*, Seville Orange
[d] Gas chromatograph 6890A, coupled to a 5975C mass spectrometer, Agilent

T.1 Orange hybrid, clementine, tangerine component comparison

			New hybrid peel	New hybrid juice XT	New hybrid juice direct
Odor	**Material**	**CAS**			
Citrus	Acetaldehyde	75-07-0			1.47
Acidic	Formic acid	64-18-6			2.79
Low odor	Ethanol	64-17-5			6.41
Fruity	Ethyl acetate	141-78-6		0.33	
Acidic	Acetic acid	64-19-7			8.63
Wine	Acetyl methyl carbinol	513-86-0	0.02	0.66	
Wine	2-Propanone, 1-hydroxy	116-09-6			1.80
Honey	Furfural	93-01-1			2.84
Green	Hexenol, *cis*-3-	928-96-1	tr		
Honey	Furfuryl alcohol	93-00-0			1.37
Citrus	α-Thujene	2867-06-2			
Citrus	α-Phellandrene	99-83-2	0.29		
Pine	α-Pinene	80-56-8	1.55		
Pine	Camphene	79-92-5	0.01		
Low odor	Citric acid	77-92-9			1.61
Honey	Methyl furfural	620-02-0			0.20
Citrus	Sabinene	8008-82-4	0.26		
Pine	β-Pinene	127-91-3	0.54		
Citrus	β-Myrcene	123-35-3	3.61		
Citrus	Aldehyde C-8 (n-octanal)	124-13-0	0.11		
Citrus	α-Phellandrene	99-83-2	0.13		
Citrus	α-Terpinene	99-86-5	0.10		
Caramel	Cyclotene	765-70-8			0.12
Low Odor	**Limonene**	**5989-27-5**	**76.84**	**1.34**	**0.20**
Honey	**Phenyl acetaldehyde**	**122-78-1**			**0.05**
Celery	Ocimene, *cis*-	13877-91-3			
Pepper	**γ-Terpinene**	**99-85-4**	**7.61**		
Citrus	Sabinene hydrate	15826-82-1	0.02		
Waxy	Alcohol C-8 (n-octanol)	111-87-5	0.03		
Caramel	Furaneol	3658-77-3		0.88	
Honey	Furyl hydroxymethyl ketone	17678-19-2			0.34
Lime	Terpinolene	586-62-9	0.36		
Citrus	Sabinene hydrate isomer	15826-82-1	0.01		
Floral	**Linalool**	**78-70-6**	**0.30**		
Citrus	Aldehyde C-9 (n-nonanal)	124-19-6	0.06		
Low odor	Mentha-2,8-dienol, *trans*-p-	7212-40-0	0.01		
Earthy	Limonene oxide, *trans*-	4959-35-7	0.02		
Vanilla	Pyranone, 3,5 dihydroxy, 6-methyl	28564-83-2		9.90	
Lemon	Citronellal	106-23-0	0.02		
Waxy	Alcohol C-9 (n-nonanol)	143-08-8	0.01		
Hay	Terpinen-4-ol	562-74-3	0.02		
Floral	α-Terpineol	98-55-5	0.10		
Caramel	**Maltol, 5 hydroxy***	**1073-96-7**			**0.85**
Citrus	Aldehyde C-10 (n-decanal)	112-31-2	0.24		

**Also found in honey*

	Clementine peel XT	Clementine peel direct	Clementine juice	Sour orange peel XT	Sour orange juice	Orange (sweet) peel oil	Commercial tangerine peel oil	Commercial mandarin peel oil
		0.48						
		3.07						
		0.66	0.07					
				tr				
	0.18		0.04	tr			0.19	0.58
		0.50	0.17	0.45		0.92	1.11	1.75
				0.01			0.01	
							0.38	0.24
	0.29	0.92	0.07	0.77			0.39	1.13
	1.77	1.40	0.50	1.65	0.07	2.89	1.95	
	0.06			0.13		0.43		
	0.06			0.03				
	0.09							0.26
	90.60	**71.76**	**27.50**	**87.19**	**4.59**	**92.00**	**88.03**	**72.32**
				0.27			0.21	
	3.51		**1.29**			**0.10**	**4.50**	**19.14**
						0.09		
	0.17			0.03				0.80
			0.06				0.27	
	0.17		**0.15**	**0.16**		**0.59**	**0.94**	**2.40**
				0.01				
				0.01				
	0.01			tr		0.09	0.07	
				0.10			0.02	
							0.13	0.20
	0.10	0.16		0.17		0.52	0.20	0.10

T.1 Orange hybrid, clementine, tangerine component comparison (Cont.)

			New hybrid peel	New hybrid juice XT	New hybrid juice direct
Odor	**Material**	**CAS**			
Waxy	Acetate C-8 (n-octyl acetate)	112-14-1	0.01		
Floral	Geraniol	106-24-1	0.02		
Lemon	Neral (citral)	5392-40-5	0.01		
Citrus, floral	Linalyl acetate	115-95-7			
Honey	2-Hydroxymethyl 5-furfural*	67-47-0			29.30
Citrus rind	Decenal, *trans*-2-	3913-71-1	0.05		
Lemon	Geranial (citral II)	5392-40-5	0.03		
Waxy	Perilla aldehyde	2111-75-3	0.06		
Low odor	Limonen-10-ol	3269-90-7	0.07		
Floral	Indole	120-72-9			
Thyme	Thymol	89-83-8			
Citrus	Aldehyde C-11 (n-undecanal)	112-44-7	0.03		
Clove	Vinyl guaiacol	7786-61-0			
Waxy	Decadienal, *trans*-2,*trans*-4-	2363-88-4	0.02		
Citrus	Neryl acetate	141-12-8	0.05		
Woody	α-Copaene	3856-25-5	0.11		
Citrus	Geranyl acetate	105-87-3	0.05		
	β-Elemene	33880-83-0	0.03		
Floral	**Dimethyl anthranilate, N-methyl methyl anthranilate**	**85-91-6**	**0.01**		
Citrus	Aldehyde C-12 (n-dodecanal)	112-54-9	0.05		
Woody	β-Caryophyllene	87-44-5	0.03		
	Perilla acetate	15111-96-3	0.01		
Woody	Humulene α-	6753-98-5	0.04		
Citrus rind	Dodecenal, *trans*-2-	20407-84-5	0.01		
	Germacrene D	23986-75-5	0.06		
	Bicyclogermacrene 8	24703-35-3	0.02		
Woody	α-Cadinene	82468-90-4	0.02		
Woody	Valencene	4630-07-3			
Woody	α-Farnesene	502-61-4	0.18		
Woody	δ-Cadinene	483-76-1	0.12		
	Elemol	8015-64-4	0.05		
Citrus	Sinensal	60066-88-8			
Woody	Nerolidol	7212-44-4			
No odor	Octacosane	630-02-4		0.52	
No odor	Eicosane	112-95-8		1.99	
No odor	Tricosane	638-67-5		9.57	
No odor	Tetracosane	646-31-1		5.67	
Waxy peel	**Hexadecanamide**	**629-54-9**	**2,0**		
No odor	Pentacosane	629-99-2		18.25	
Waxy peel	**Unknown amide (?)**			**2.00**	
Low odor	Unknown other waxes, 6 pks min			30.00	
Waxy peel	**Oleyl amide**	**301-02-0**	**2.00**		
Low odor	Flavone, 4,5,6,7,8-pentamethoxy	481-53-8	1.17		
Low odor	Flavone, hexamethoxy tentative		3.62		

**Also found in honey*

Clementine peel XT	Clementine peel direct	Clementine juice	Sour orange peel XT	Sour orange juice	Orange (sweet) peel oil	Commercial tangerine peel oil	Commercial mandarin peel oil
					0.04		
					0.08		
			0.79				
0.01			0.01				
0.01			0.10			0.01	
0.02						0.03	
0.01							
			0.02				
						0.07	
0.01			0.01				
	1.80						
0.01							
0.02			0.06		0.13		
0.06					0.3 6		
0.01			0.22				
0.02			0.04				
0.01							**0.61**
0.02					0.10		
0.02			0.13				
			0.07				
			0.03				
			0.02				
			0.17		0.33	0.01	
			0.02				
			0.01		0.42		
					0.41		
						0.05	0.17
					0.19	0.25	0.27
			0.13				
	5.88			9.29			
				4.47			
		2.21	5.13	5.46			
	15.00	50.00		50.00			
				1.35			
			0.30				

The new Halo[a] hybrid was compared with clementine, sweet orange, tangerine and sour orange (unripe specimens shown here).

Amides in Citrus

With more than 30 years' experience, this author has long noticed that mandarin has a peculiar aroma that can be described as somewhat but not exactly "fishy." This might be due to some unidentified amine compound. To this author's knowledge, primary amines have never been reported in any citrus oils as impacting aroma or donating character; the most relevant studies report on amides in seedlings.[3-12] Dimethyl anthranilate, of course, is an aromatic amino ester and occurs in many mandarin varieties.[13]

Interestingly, for the first time, researchers have identified hexadecanamide and oleamide, with a few related amides in the citrus hybrid[a] and sour orange juice. All of these have precious little odor impact and smell more waxy and peel-like than the fishy amine aroma that seems to characterize mandarin orange. However, their presence provides a clue: that there are amides, and very likely amines, in the juice or peel at low levels. The molecular weight that could best fit the fishy aroma profile would be in the $C_{10\text{-}12}$ amide or amine range. These could be unsaturated as well, which adds another aroma character dimension.

Such amine entities would likely be high enough in molecular weight that they do not smell fishy or amine-like but have the hybrid quality of being waxy and peel-like with a hint of the amine odor, which would produce a mandarin effect. It is precisely this type of molecule, present at very low concentrations, that provides a distinctive character and imparts an overall "halo effect" on any composition, providing an identifiable and recognizable signature.

Honey and Caramel

A few other compounds worthy of mention are 5-hydroxymaltol and phenyl acetaldehyde, which are contributors to the "honey-like," sweet character of the new hybrid[a]; in fact, they are referred to as "honey tangerines." On a related note, in previously unpublished work, this author has independently found both of these components in manuka honey.

Finally, it is worth noting that the furan and pyran compounds, found in honey and vanilla at low levels, contribute to the candy caramel-type sweetness that is only suggested in the

new fruit. Perhaps this is the reason why orange Creamsicles[e] seem like such a natural combination; flavor chemists have only slightly enhanced nature.

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[e] Creamsicle is a registered trademark of Unilever.

[f] Author's note: Herein, the authors report, "Eighty percent of the total polyamine content in fully developed flowers is localized in the reproductive organs and only 20% is localized in the petals and the calyx. This study relates changes in conjugated and free polyamines to citrus flower growth." The polyamine content found was from the petals and calyx, not the peel or fruit.

[g] Author's note: Palmitoylethanolamide [N-(2-hydroxyethyl) hexadecanamide] is a ubiquitous lipid in plants, particularly in seeds. This reference supports their natural and known existence.