

Citrus Oils in Perfumery and Cosmetic Products

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It does not take an anthropological genius or decades of research to surmise that citrus was used long before any written history as either a food or for fragrance value. For those with a passion for written history, it appears that lemon was introduced to Europe by the Arabs around 10 CE. Sweet orange appeared some 500 years later.¹

Since that time, the world has embraced citrus and has consumed or utilized citrus in grand style. Citrus fruit, juice or peel oils are currently used in everything from food or food preparations, soft drinks, ice cream, candy, pharmaceutical preparations, air fresheners, cleaning products and solvents as well as colognes and fine perfumes. More than 80,000 metric tons of orange, tangerine, lemon, lime, and grapefruit, alone, are consumed annually.²

Natural Citrus Notes

Table 1 lists the types of citrus oils expressed from the peel of the fruit commercially available to the fragrance and flavor industry. The columns indicate the percentage of major components commonly found in these various oils.

If we examine Table 1, we see that it is organized by groups, beginning with the highest percentage of limonene. One might think that these products would smell and taste quite similar to one another. This is clearly not the case. Citrus products are a clear case where the major components are not responsible for the character of the oil. If they were, there would be little difference between

Table 1. Types of citrus oils in commercially available percentages

Citrus Oil	Pinene alpha %	Pinene beta %	Limonene %	Terpinene gamma %	Linalool %	Linalyl Acetate %	Citral %
Orange	0.5	0.2	96.0				
Grapefruit	0.5	2.0	95.0				
Tangerine	0.8	2.0	91.0	3.3	0.5		1.5
Mandarin	2.2	1.8	72.0	19.0	0.6		
Lemon	1.8	12.0	69.0	8.0			1.5
Lime	2.2	13.5	57.0	14.0			3.5
Bergamot	1.6	7.0	36.0	6.4	14.0	31.0	0.1
Neroli	0.6	15.0	15.0		34.0	9.0	
Orange Flower	0.1	0.4	5.0		32.0	17.0	
Petitgrain	0.2	2.5	2.5	2.0	23.0	50.0	0.2
Lemon Leaf	0.1	0.1	33.0	7.0	1.0		1.8

orange, grapefruit and tangerine, which are nearly identical at first glance. It is probably best to think of limonene, (the major component) as primarily a solvent for the important odor-characterizing components.

The trace components that characterize orange are various low-to-medium molecular weight aldehydes, unsaturated aldehydes, ketones, and esters and alcohols. For as much as we have learned about the constituents of orange (over 100 components), the fragrance and flavor industry cannot make a good orange flavor without using the natural product.

- Grapefruit is characterized by specific sulfur-containing components in addition to the woody, sesquiterpenic section that provides a very rich long-lasting character.
- Tangerine and mandarin are characterized by different unsaturated trace aldehydes and amino esters like methyl anthranilate.

- Lemon is characterized by citral (neral and geranial) and other aldehydes, both saturated and unsaturated. These, along with trace sulfurous notes, contribute significantly to the character that defines good fresh lemon character. However, these very important materials are unstable and short-lived.
- Lime has a very distinctive aroma and flavor that are imparted by terpinolene, α -fenchyl alcohol and various cyclohexadienes. Unfortunately, at this point in time we have not adequately identified the real characterizing components of lime. There are many important sulfurous materials waiting to be discovered in lime that will enhance our ability to create a more natural version.
- Bergamot oil, expressed from the peel of *Citrus aurantium linnaeus*, is one of the most beautiful oils in the citrus family. However, as can be seen in Table 1, it is a hybrid of citrus and floral notes. The main components, terpenes, terpene alcohols and esters, are all enhanced by traces of aldehydes, lactones, and trace sulfurous components so wide ranging that bergamot is practically a fragrance by itself. Bergamot oil is a great example of a marvelously blended and complemented citrus bouquet
- Neroli oil is steam-distilled from the flowers of *Citrus aurantium linnaeus*. This is an increasingly rare and expensive oil. While it is related to orange flower absolute and petitgrain, there is nothing like it. It is a hybrid character with unique citrus, floral, green, and nearly bread-like notes that has a performance all its own. This is due to the combination of terpenes, aldehydes, alcohols, esters and perhaps, most importantly, pyrazines and sulfurous moieties.
- Orange flower absolute is a solvent/alcohol extract of the *Citrus aurantium linnaeus* flower. This is characterized by linalool, linalyl acetate and various esters blended with methyl anthranilate, (an important note in mandarin and tangerine) in addition to indole and lactones. This is a decidedly floral, yet complex note that adds dimension and longevity to any citrus composition.
- Petitgrain oil is derived by steam distillation of the leaves and twigs of *Citrus aurantium linnaeus* (bitter orange), a byproduct of the pruning process. It is a very beautiful and inexpensive material that is used in a wide variety of applications ranging from men's and women's colognes to cosmetic and functional products. This material is characterized by terpenes, linalool and linalyl acetate, various other acetates, aldehydes, and, most importantly (as in neroli oil), pyrazines and sulfurous components. Petitgrain is a beautifully complex and economical natural raw material that has few economic rivals. It is a wonder that leaf oils from other citrus species are not used in the same quantity.
- d-Limonene is the dominant constituent of citrus oils. While limonene itself is not the most significant odor-characterizing component in citrus oils, it is still an odor contributor. It has a very fresh pleasing aroma that can be described as citrus and somewhat piney. It is interesting to note that d-limonene that has been isolated from orange peel retains its orange character, due mainly to all the trace components from orange peel. How do we know this? When we examine d-limonene from a totally synthetic source (e.g. from alpha pinene), we notice that the typical orange character is completely absent. At this point one can begin to appreciate the true nature of d-limonene.

In Table 1 we can see that α - and β -pinene and other terpenes begin to appear. γ -Terpinene in tangerine, mandarin, lemon and lime is an unsaturated hydrocarbon, which introduces additional character to nature's citrus composition. It is somewhat citrus-like in character, but is differentiated by a sharp pungent character that can be described as somewhat spicy (similar to black pepper or thyme). This adds a new dimension to the tangerine, mandarin, lemon and lime, putting a "tang" in all citrus products.

Products from *Citrus aurantium* have a very different composition. There are large amounts of linalool and linalyl, which enhance the floral element. If one were to describe the character of linalool, it would fall into the category of both lemon-like citrus and lily-like floral.

There is an orange-juice oil that is separated from the fresh juice by high-vacuum distillation. While the two oils, peel and juice, are related, they are quite different. The peel oil is highly lipophilic and oil soluble, composed largely of hydrophobic hydrocarbons. The juice oil is composed of small amounts of hydrocarbons and other polar aldehydes, alcohols and esters that have a higher degree of water solubility. It is highly likely that the first uses of these juices and oils were to flavor foods or improve the taste of water.

How are citrus products used today? We still make real lemonade by squeezing the juice into water, sometimes adding a little sugar. This is for immediate consumption because it is not a stable mixture. People outside the flavor and fragrance industry may not realize that almost all of our carbonated soft drinks utilize lemon, lime and orange oils. The greatest examples are cola flavors like Coke and Pepsi. Such flavors are so expertly blended that the citrus character is not obvious. In such blendings, citrus elements are mixed with spice ingredients to assume a unique identity. It has always been interesting to observe people adding a twist of lemon to Coca-Cola. This may be an instinctive need to "freshen-up" a lemon character that has lost its freshness.

Synthetic Citrus Notes

There are many synthetic chemicals available to produce citric notes for use in perfumery. These include synthetic aldehydes, alcohols, acetals and, to a limited extent, ketones. There are also some nitrogenous and sulfur components that are available for enhancement and stability purposes. When I examine our database on the above, I can quickly point to approximately 200 synthetic components that are primarily citrus in character.

Dihydro myrcenol is a synthetic ingredient that possesses a fresh lemon-lime character and is structurally similar to linalool. While they are somewhat related as unsaturated tertiary alcohols, their odor and stability is quite different. While linalool, a major component of bergamot, has a somewhat citrus floral character, dihydro myrcenol is decidedly more lemon-lime like and extraordinarily stable.

Aside from the intrinsic quality of the odor character of dihydro myrcenol, the real value is its extraordinary stability in a variety of media. It does not easily oxidize or deteriorate in any environment. This problem of oxidation and deterioration is common to all citrus products. To have a material that does not deteriorate is a tremendous tool for the perfumer.

Another important synthetic citrus note is dimetol (2,6 Dimethyl heptan-2-ol). It possesses a stable lemon-like aroma with a bit more floralcy than dihydro myrcenol.

Because aldehydes exhibit a citrus character and enhance any citrus performance, they are almost always used in tandem with citrus products. However, they are not as stable as needed in a variety of circumstances including functional products like soap and detergents, or other products where oxidation or reactivity presents a problem.

To replace the use of unstable aldehydes, the perfume industry has resorted to the use of nitriles, which are less prone to oxidation and are less reactive under a variety of circumstances. Some examples of these are geranyl and neral nitriles, citronellyl nitrile, and decyl and dodecyl nitrile. At this point in time we are aware of at least 60 synthetic nitriles, many of which possess a citrus character.

Another choice in this arena is the use of acetals. One might say these are aldehydes in which the reactivity has been deactivated by reacting the aldehydes in advance. Many of these acetals have a citrus character, albeit somewhat different and unique from their aldehyde progenitors. Some examples of these materials are citral dimethyl and diethyl acetals, citronellal dimethyl acetal, octanal dimethyl, and diethyl acetals. We currently use over 70 various acetals.

Longevity of Citrus Character

Up to this point, we have only addressed the issues of oxidation and reactivity in citrus products. We have not yet addressed the issue of longevity or lasting ability for citrus character. We constantly hear customers say, "We love the fresh lemon character of your fragrance, but it does not last long enough."

The intrinsic character of citrus is to be light and fresh. As a consequence, it is often short-lived. This answer never satisfies our clients. We are often expected to spin straw into gold and, just as often, we may come close.

In order to satisfy customer needs, we often turn to Schiff's bases for the solution. Many Schiff's bases of aldehydes, both straight chain and unsaturated, citral, and other branched or cyclic aldehydes, are reacted with amines like methyl anthranilate. This provides an unusual character peculiar to Schiff's bases, yet related to citrus. This can be viewed in the following way. Citrus products like mandarin, tangerine and orange blossom contain methyl anthranilate and several other aldehydes. It can be surmised that Schiff's bases are probably naturally occurring,

but often break down to their respective aldehyde and amine components during analysis by gas chromatography. The main point, however, is that these Schiff's bases possess a particular citrus-like character that has tremendous longevity and enhanced stability in air fresheners and functional products. These materials do not provide the fresh citrus top notes that we have all come to love. However, they do impart an undertone that is quite long-lasting and, in effect, mimic the peel-like character.

Fragrances

Some of the earliest world-famous colognes used citrus products of some sort. Imperial (1850) and Eau Imperiale (1861) by Guerlain included the use of bergamot, lemon, lime, mandarin, orange and orange blossom oils.⁷ The earliest European fragrances were based on citrus oils like lemon, lime, bergamot, orange, mandarin and petitgrain. The classic accords like Eau de Cologne (1750) and 4711 have been the foundations for many fragrances in history, eventually evolving into modern citrus blends. Looking at the history of the fragrance industry we can pick the popular fragrances of each decade and take a cursory look at the construction very nearly at random.

Women's Fragrances

In 1921, Chanel 5 utilized lemon, bergamot and synthetic aldehydes. The quantities used were (perhaps for the first time ever) in amounts exceeding the norms of both the industry and nature. Whenever natural products such as citrus are used, a portion of their performance and beauty is a result of the naturally occurring aldehydes that are part of their complex. This is true for other natural products as well, but it is particularly true for citrus products. The use of synthetic aldehydes, saturated and unsaturated, impart and enhance a citrus character and provide a fresh character to the overall composition. The additional effect of this is to introduce unparalleled power and performance. This was especially unusual in 1921.

In 1927, Arpege by Lanvin used bergamot and neroli on top of a heavier oriental chypre and amber complex. The citrus section was also supported by the use of the now very popular synthetic aldehydes, which enhance the citrus section. Other important milestones in the use of citrus elements are:

- Muguet de Bois by Coty (1936) used bergamot and orange to enhance the natural floralcy of the muguet character.
- Vent Vert by Balmain (1945) used lemon, lime, bergamot orange and mandarin to enhance the vetivert and natural green notes.
- L'air du Temps by Nina Ricci (1947) was a light floral muguet that was extended and enhanced by bergamot, lemon and orange. This light "springtime" fragrance

accord is still very popular today. Many fragrances both old and new have followed this formula of light floral notes blended with judicious amounts of citrus. This blend creates universally accepted fragrances.

- Diorissimo by Dior (1956) was a wonderful floral muguet blend that was enhanced by bergamot and lemon, much in the same way as L'air du Temps.
- O de Lancôme by Lancôme (1969) utilized bergamot, lemon and petitgrain.
- Charlie by Revlon (1973) contained bergamot and touches of other citrus notes to enhance the underlying floralcy of jasmine, tuberose and gardenia.
- Cristalle by Chanel (1974) owed its top note to lemon and bergamot, providing a fresh, clean fragrance.
- Lauren by Cosmair (1978) was a most beautiful fruity muguet heightened by bergamot and orange blossom.
- Giorgio by Giorgio Beverly Hills (1981) had a powerful tuberose floral foundation combined with bergamot and orange blossom.
- Allure by Chanel (1996) was a modern floral using the time tested combination of lemon and bergamot.
- Contradiction by Calvin Klein (1997) was a complex woody amber blend that became fresh and clean with the use of bergamot, lemon, mandarin and orange.

Men's Fragrances

The following is a short list of historically important points of men's-fragrance evolution:

- English Leather by Mem Corp. (1949) contained bergamot, lemon, orange and petitgrain, providing a bright and fresh top note to an oriental oakmoss blend.

The 3 following fragrances can be thought of as modern versions of the nearly antique 4711, which is based on citrus products like bergamot, lemon, lime, orange, mandarin and petitgrain. These products feature citrus products almost exclusively:

- Eau Sauvage by Dior (1966) contained bergamot, lemon, lime, orange, mandarin and petitgrain.
- Eau de Guerlain (1974) contained bergamot, lemon, lime, orange, mandarin and petitgrain.
- Eau de Cologne by Hermes (1982) contained bergamot, lemon, lime, orange, mandarin and petitgrain
- Polo Sport by Ralph Lauren (1995) was a modern, sophisticated fragrance that employed lemon and bergamot very skillfully.
- Cool Water by Davidoff (1988) used bergamot and lemon among some new synthetic materials such as dihydro myrcenol.

Table 2. Top-selling fragrances (1999)

Citrus blends	Woody blends	Floral blends	Oriental blends
CK One	Polo	Pleasures	Obsession
Eternity for Men	Bobsession Mens	Eternity	White Diamonds
Polo Sport	Aromatics Elixir	Tresor	
Tommy	Safari Mens	Allure	
Polo Sport Women		Jessica McLintock	
Cool Water		White Linen	
Hugo		Chanel 5	
Drakkar Noir		Tommy Girl	
Escape (Men)		Contradiction	
		Beautiful	

By now it can be seen that citrus products are widespread throughout the fragrance industry. It is difficult to say how important these materials are. Do not be deceived into thinking that all the above fragrances are the same or even similar because of the widespread and repeated use of the same materials. It is the very nature of citrus products to absorb, enhance and modify the identity of any fragrance in which they are used. This is also due to the artistic skill of the creative perfumers who use these wonderful items. With this in mind, I feel the top selling fragrances in 1998 have a story to tell. If we examine them, organize them into odor categories and look at them philosophically, we may see a pattern.

Table 2 contains the top-selling fragrances for 1998 from the categories of unisex, women and men. I have organized them, most importantly, by odor category. As can be seen, the two most popular categories are floral blends and citrus blends. It is difficult to identify any fragrance appearing in Table 2 that does not contain some citrus. Almost every fragrance created or designed for almost any product utilizes at least one citrus ingredient.

More often than not, several citrus oils are combined. What is the reason for this? Citrus products have the ability to lift the character of the fragrance and extend and enhance those notes that are present and create a fresh and lively aroma profile. As previously noted, limonene, linalool and linalyl acetate do not themselves impart the character of the fruits. It is the trace ingredients that are doing all the work. A great example of this is Shalimar. Upon examination by the newly initiated, this seems like a balsamic, vanilla and powder-like fragrance. The fact that Shalimar has a high percentage of bergamot and other citrus may not seem obvious. This situation is typical in perfumery.

CK One (1994) is an extremely popular top-selling fragrance worldwide. This universal appeal is in part attributable to the prodigious use of bergamot, lemon and mandarin. It is a fresh citrus cologne artfully blended with

other ingredients to create a new entity with its own unique identity. Notes of pineapple and papaya are applied for the fruity character, cardamom and amber for the spice section, jasmine, lily, rose and freesia for floralcy, and cedar, orris, sandalwood and oakmoss for the woody section. These are all supported by amber and musk. This is great example of how commonly available ingredients can be utilized in a unique way to create a successful fragrance with universal appeal. This can be said for all successful fragrances cited above and those not stated here.

Eternity for Men (1989) utilizes mandarin, lemon, and notes of orange blossom and petitgrain for an Old-World twist. This citrus blend is supported by basil, tarragon, sage and coriander for a spice section, geranium and lavender for a herbal section, cedar, vetivert, oakmoss, rosewood with a hint of jasmine amber, and oakmoss for a classic blend which is still popular and well-received today.

Polo Sport (1993) uses lemon and bergamot in addition to jasmine, rose, cyclamen and tagette for the fruity floral character. Geranium, lavender and artemesia form the herbal section, while oakmoss, cedar sandal and guaiacwood rest on a base of musk and amber. These, combined with a hint of nutmeg, form a classic blend of forest and deep, rich woody notes that are lifted as a result of the citrus section.

Tommy Hilfiger (1995) employs the use of bergamot, lemon, lime, mandarin and grapefruit. In addition to wild berry notes, there is an herbal section using lavender and mint in addition to spices, including nutmeg and cinnamon. These are blended with an amber and musk foundation rounded out with sandalwood and cedar. While this is a sophisticated and complex fragrance, it is the citrus section that makes the whole composition fresh and lively.

Cool Water (1988) blends bergamot, lemon and orange blossom with dry woody and amber notes. This combination is fresh, unique and long-lasting. This amber- and musk-based composition combines the fresh aroma of herbs like rosemary, lavender, mint, sage and coriander with geranium, jasmine, honeysuckle and lily. The foundation is composed of woody components like orris, sandalwood and cedar. It also uses dihydro myrcenol, which has an important synthetic fresh citrus character. This enhances the lemon note and provides a unique twist to the citrus core. We will examine the use of this material in citrus compositions later on in this chapter.

Hugo for Men (1995) combines lemon, lime, orange and bergamot with oakmoss and other deep, rich, woody forest notes that are very Old-World like in this modern era. These notes are blended with lavender, geranium,

mint, sage and other spices. These are further blended with touches of jasmine and muguet. Cedar, sandalwood and vetiver support these notes, which magnify and enhance the grapefruit character.

Drakkar Noir (1982) utilizes mandarin, lemon, bergamot and (like Cool Water) a generous portion of dihydro myrcenol. This is bolstered by a spice blend of basil, cinnamon and cardamom. This blend is linked to a foundation of patchouli, pine, cedar, sandalwood and oakmoss. We will examine the importance of dihydro myrcenol shortly.

Escape for Men (1993) is a classic type, blending bergamot, lemon and grapefruit with new and synthetic citrus-like ozone and fresh notes that extend and enhance the citrus character. This modern fragrance is blended with birch, juniper, eucalyptus and pine, all of which complement the citrus section. The foundation is based on artemesia with touches of rose and cyclamen, which has an element of citrus character by itself.

It has often been said, and this author agrees, that the prestige market often leads the way for popular trends. This is due in large part to the massive advertising and marketing campaigns that are launched for each fragrance or product. A good fragrance will have a tremendous effect for second purchase and continued long-term success. However, a mediocre product with great advertising, packaging and distribution will win every time over a great product that no one knows about. After a new type (or a similar type) of fragrance has been introduced, a second tier of related functional products such as soap, hair care, creams, lotions, candles and air-freshener products can be expected to follow close behind.

Can any pattern be seen from the above examples? It should be clear that citrus notes are ubiquitous in the fragrance industry. The few isolated examples that have been extracted for illustration are only the tip of a very large iceberg. It should also be remembered that the very few examples shown in this text are only a one-person view.

The Future

What will be the future of citrus use in fragrance? It is inevitable that change will occur. The fragrance industry has seen many changes; some good, some not. Many products have been eliminated or drastically reduced for toxicological reasons. The best example of this is natural, cold-pressed bergamot. There is a presence of bergaptene and a class of chemicals (methoxy psoralenes) that exhibit phototoxic effects. As can be seen by the preceding examples, bergamot is used in many fragrances. This beautiful material is restricted from skin use. This seems a shame because the effects and consequences of using this material may be questionable. When one thinks of the centuries of use without any real incident, one has to question if the use of this material should have been restricted at all.

Whenever I use the bergaptene free or distilled version of bergamot, I always feel disappointed with the lack of depth and beauty of natural, cold-pressed bergamot. I think of the many people who are making lemonade or hand-squeezing fresh lemon and lime (which are also restricted) into tea and other food preparations throughout the world and are not complaining of photo-sensitization. The amount that is deposited directly onto the skin from this activity is often many hundreds of times the exposure that anyone would receive from a cologne and thousands of times more than any functional product. Our industry, through science, has chosen to err on the side of safety, not practicality or artistic sensibility.

Many chemists around the world are doing great research on natural products. This is an area where many newly identified products will enhance our understanding of nature. As indicated throughout this text, the area of greatest importance is the sulfur and nitrogen components that abound in nature. These are critically important in citrus products. New gems are waiting to be identified, synthesized and brought into commercial use. This is the least understood and probably the most important area in the fragrance and flavor industry at this point in time. They are part of the reason that the natural products smell and taste so great.

Synthetic fragrances and flavors do not smell or taste bad (different) because they are synthetic. They taste bad (different) because they are much simpler and less complete than nature. There is always new information and materials that are being introduced to the fragrance industry as well as new challenges in new products. New products always require new ideas. I feel very certain that the continued use of citrus products both synthetic and natural (I hope), will be assured for many centuries to come.

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