Natural Aroma Chemicals from Oranges and Other Botanical Sources*

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The production of natural chemicals from essential oils is an exciting and interesting business. There are many chemicals today that are produced primarily from essential oils, as this is the most economic method. And, there is plenty of potential for new products from both traditional and new sources.

In this article, I will focus on the production of aroma chemicals from orange. But I will also mention other essential oils that are sources of aroma chemicals.

The Market for Oranges

The orange processing industry worldwide has an annual turnover of approximately US$2 billion. The market has been dominated by Florida and Brazil since the mid-1970s. It is important to remember that concentrated orange juice is six-and-a-half times single strength and is the main product of processing. The frozen concentrated orange juice is shipped around the world in refrigerated bulk tanker vessels containing 15,000 tons. It is the by-products of juice processing that interest the flavor and fragrance industry.

Brazil has more than 150 million orange trees and Florida has 60 million trees. This would equate to 3 million acres. We estimate that, worldwide, there are 400-500 million orange trees covering a landmass the size of Connecticut.

Orange Processing

In an orange juice plant, due to the volumes involved, every piece of the fruit is utilized. After extraction of oils and juices, the orange is dried and sold as cattle pellets on the common market at prices as low as $65 per ton F.O.B. Rotterdam. Cattle pellets represent a multibillion dollar business.

Once in the plant, oranges are fed through machines and washed. Cold-pressed oil is liberated from the peel by pressing or rasping. The juice is then squeezed from the orange, normally by an FMC (Food Machinery Company) or by a Brown extractor machine. This juice is then passed to a six-stage taste evaporator where the juice is concentrated and most of the water is removed.

During the concentration of this juice, orange oil phase essence ex juice and orange water phase aroma (also called orange aroma) are removed and captured. After the oil has been extracted from the peel, the peel is passed to a d-limonene feedmill where the peel is dried and pelletized and the limonene is recovered, normally at a minimum 93% pure. The fact that 75,000 tons of d-limonene and orange oil cold pressed are produced annually from the approximately 500 million trees in the world will give an idea of the volume of fruit required.

Products and By-Products from Oranges

Table I shows the average percentage yield of products and by-products from oranges.

Orange oil cold pressed: According to many people in the flavor industry, orange oil cold pressed is the natural citrus turpentine; that is to say, the starting material for the production of many aroma chemicals. For octanal and decanal, this is one of the cheapest natural FEMA/GRAS sources. One of the benefits of orange oil as a production source is that its by-products or terpenes can be priced at approximately the same level as the starting or raw material oil.

d-Limonene ex peel/feedmill: This d-limonene is normally sold as minimum 93% pure, as a by-product from the

Table I. Average percentage yield of products and by-products from oranges

Product or by-products	Yield (%)
fresh single strength juice	53.00
cattle pellets	5.00
orange oil cold pressed	0.27
d-limonene	0.27
orange water phase aroma	0.11
orange oil phase essence ex juice	0.03

*This article is adapted from Hugo Bovill's presentation at the International Citrus Symposium, January 29, 1996, in Orlando, Florida.

0272-2666/96/0003-0009$04.00/0

feedmill. It should not be confused with what are sold commercially as orange terpenes, which are normally 95% d-limonene, and result from the distillation/concentration of orange oil cold pressed and orange oil phase essence ex juice.

Orange water phase aroma: Traditionally, orange water phase aroma has been used to add flavor back to orange juice. There is a somewhat limited market for natural orange alcohol from this source, at present some tens of tons per year. This alcohol is a key to certain natural-orange-derived aroma chemicals such as acetaldehyde, which is found at parts per million in orange water phase aroma.

Orange oil phase essence ex juice: Orange oil phase essence ex juice has been produced since the mid-1960s, when Dr. Redd commercialized the essence trap. This oil is recovered from the concentration of the juice and has been used primarily to flavor concentrated orange juice—to add back some of the flavor that was lost during concentration. It is also used to some extent in the perfumery industry for fragrancing detergents and similar low-cost products. The production of this is approximately one tenth of the production of orange oil cold pressed.

Extracted Aroma Chemicals from Oranges

If you looked at a gas liquid chromatography trace of orange oil cold pressed, you'd see a d-limonene peak representing 95% of the oil. But there are other aroma chemicals that are or could be obtained from this oil by physical extraction. I'll discuss them in order of volatility.

1. ***Aldehyde C8 octanal:*** This product can be obtained by distillation and extraction from orange oil cold pressed, where it is normally found at about 0.4% by weight though this varies slightly from season to season. Octanal is fairly volatile and is not normally recovered when concentrating oils unless low-temperature cold traps are used.
2. ***Myrcene:*** This product, which elutes on most standard gas chromatographic traces at the same point as octanal, is found at 1.5-2.0% in orange oil cold pressed. Myrcene could be used in some natural tropical fruit flavors, but generally is considered an unwanted product in citrus beverages.
3. ***d-Limonene/orange terpenes:*** The major component (95%) of orange oil cold pressed, d-limonene/orange terpenes was traditionally considered a by-product. But, since the mid-1980s, with ever increasing green awareness on the part of consumers and governmental bans on chlorinated solvents, the demand for d-limonene/orange terpenes has been increasing considerably. d-Limonene can be redistilled to 99% minimum purity and can be produced to give an extremely low odor. The product has many industrial uses in, for example, electronics, cleaning and degreasing. The highest grade is relatively expensive and can cost as much as five times the cost of the crude limonene which normally sells for the same price as orange oil cold pressed.
4. ***δ-3-Carene:*** In d-limonene/orange terpenes, δ-3-carene is present at extremely low levels: 0.1-0.15%. It is an important flavor constituent of tropical fruit flavors, but it is extremely difficult to fractionate from d-limonene.
5. ***Linalool:*** This can be obtained from orange oil. It is present at approximately 0.5% in orange oil cold pressed. The nonanal (aldehyde C9) is also present in this fraction. Some flavorists find the linalool fraction of great interest, as the nonanal flavor contribution is fairly strong.
6. ***Decanal:*** Decanal (aldehyde C10) is found at 0.5% and is the major orange aldehyde. Terpeneless orange oil cold pressed is normally standardized at a level of 25-30% decanal. The term "orange oil cold pressed minimum 1.2 aldehyde" means 1.2 total aldehydes by classical analysis (i.e., decanal plus octanal plus other minor aldehydes).
7. ***Sinensal:*** This is found at around 0.05% in orange oil cold pressed and is a mixture of alpha and beta isomers; in tangerine/mandarin, alpha predominates. Sinensal is a heavy sesquiterpene aldehyde and in pure form is unstable. It has a very high tenacity and could be used in fragrances as well as flavors. As many as 750,000 kilos of oranges (4.1 million individual oranges) are required to obtain 1 kilo of sinensal.
8. ***d-Limonene 95%:*** This d-limonene (unlike the d-limonene/orange terpenes which is also 95% but obtained from orange oil cold pressed) is obtained from distillation/concentration of orange oil phase essence ex juice. The aroma differs noticeably from the aroma of d-limonene/orange terpenes because nature has given orange oil phase essence ex juice a fruity character, whereas orange oil cold pressed has a peely aldehydic octanal character.
9. ***Ethyl butyrate:*** Ethyl butyrate is found as the light volatile fraction of orange oil phase essence ex juice and can be extracted from the orange essence oil phase at levels of up to 30% purity. The hexanals and hexenals present around the ethyl butyrate can lead to some difficulty during separation. These hexanals and hexenals give the flavor some green notes that are considered important in orange. The ethyl butyrate could also be used in other natural flavors, but normally this ethyl butyrate would be used solely for orange flavors due to its cost.
10. ***Valencene:*** Valencene can be extracted from orange oil phase essence ex juice by distillation, and concentrated to levels of 70-80%. Valencene is used in some small way as a flavor component, but is normally used as a precursor chemical for the production of nootkatone in the United States and Israel. Nootkatone is a major grapefruit component

and is considered of great importance when valuing cold-pressed and distilled grapefruit oils. Nootkatone has been produced from valencene via an oxidation process since the 1950s.

Carbonyls are also produced from orange oil phase essence ex juice, normally as a by-product of valencene production. "Carbonyls," a term given to the aldehydes that are offered ex oil phase, is a very loose term and the composition will vary considerably from supplier to supplier.

Other Botanical Sources

Apart from orange as a source, it is interesting to see what other natural aroma chemicals can be produced from essential oils. In this age of increasing trends toward naturals, many essential oils are now being looked at as new sources of raw materials. Here are a few examples.

- Terpinyl acetate could be produced from cardamon oil distilled in India or Guatemala. Terpinyl acetate is normally found in these oils at 50%. This can be used in natural flavorings of berry and fruits-of-the-forest type products.
- Ylang ylang oil, normally used in the fragrance industry, contains germacrene D at 20-25%. This chemical, found in many fruits, was most recently identified in grapefruit and, in particular, Japanese yuzu fruit. Germacrene D, which to my knowledge is not available artificially, can be obtained from ylang ylang oil and is used in fruit flavors, giving a subtle, unique character.
- Asafetida oil, distilled from Iranian gum, could be used to make many sulfides and similar products.
- Galbanum gum (also from Iran) has traditionally been used in the fragrance industry. This gum could be used as a starting material for the production of natural pyrazines.
- Lavender/lavandin oils, of which there are abundant supplies in France, could be used for the production of natural linalool and linalyl acetate, and even octen-3-ol (also known as mushroom alcohol), which is found in certain strains of lavender. The trace chemicals that make up its unique floral bouquet could be used to make other exotic flavors.

It should be well noted that it is often the impurities that give the most important effect to the character of the desired natural fraction. More often than not, flavorists and perfumers purchase for the impurities rather than the pure molecule. A good example is the demand for some of the minor C9 aldehydes in linalool ex orange.

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