

Carotenoids as Flavor & Fragrance Precursors

A Review by John C. Leffingwell. Ph.D.

This is the introduction to our series on aroma materials produced by carotenoid degradation.

Carotenoids are the pigments responsible for the colors of many plants, fruits and flowers. They serve as Light Harvesting Complexes (with proteins) in photosynthesis. Carotenoids are important in human nutrition as a source of Vitamin A (e.g., from beta-carotene) and as a prevention agent for cancer and heart disease (e.g. lycopene). In addition, carotenoids add color to foods and beverages (e.g. orange juice). And in addition, carotenoids are the precursors of many important chemicals responsible for the flavor of foods and the fragrance of flowers.

Carotenoids are a class of hydrocarbons (carotenes) and their oxygenated derivatives (xanthophylls). About 600 carotenoids have been isolated from natural sources.

Where are Carotenoids Found in Nature

For us, the most important source for carotenoids are plants, where often the brilliant colors of the carotenoids are masked by the green chlorophyllic pigments (i.e. in green vegetables and leaves). In a number of cases, as plants mature, the chlorophyll content decreases leaving the carotenoids responsible for the beautiful colors of most fruits (pineapple, oranges, lemons, grapefruit, strawberry, tomatoes, paprika, rose hips) and many flowers (Eschscholtzia, Narcissus). Carotenoids are also responsible for the colors of some birds (flamingo, canary), certain insects, and marine animals (shrimp, lobster and salmon).

Health Aspects of Carotenoids

Carotenoids are important factors in human health and essential for vision. The role of beta-carotene and other carotenoids as the main dietary source of vitamin A has been known for the better part of this century. More recently, protective effects of carotenoids against serious disorders such as cancer, heart disease and degenerative eye disease have been recognized, and have stimulated intensive research into the role of carotenoids as antioxidants and as regulators of the immune response system.

Lycopene, a carotenoid found in tomato products, prevents oxidation of low density lipoprotein (LDL) cholesterol and reduces the risk of developing atherosclerosis and coronary heart disease according to a recent study published in the October 1998 issue of *Lipids* (Agarwal, S., and Rao A.V.; Tomato lycopene and low-density lipoprotein oxidation: a human dietary intervention study. *Lipids*, 33, 981-984 (1998)). This study showed that daily consumption of tomato products providing at least 40 mg of lycopene was enough to substantially reduce low density lipoprotein (LDL) oxidation. High LDL

oxidation is associated with increased risk of atherosclerosis and coronary heart disease. This lycopene level can be achieved by drinking just two glasses of tomato juice a day. Research shows that lycopene in tomatoes can be absorbed more efficiently by the body if processed into tomato juice, sauce, paste and ketchup. The bound chemical form of lycopene found in tomatoes is converted by the temperature changes involved in processing to make it more easily absorbed by the body. Ongoing research suggests that lycopene can reduce the risk of prostate cancer and cancers of the lung, bladder, cervix and skin.

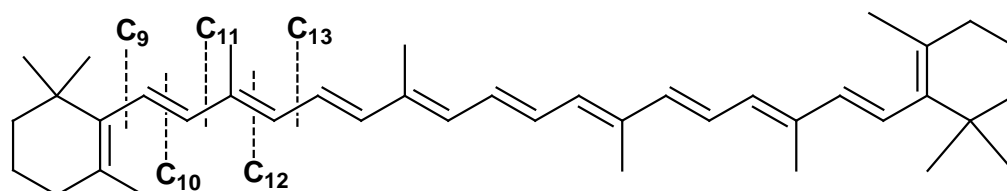
What do Tea, Rose, Osmanthus flowers, Tobacco, Grapes and Saffron all have in common?

The answer: flavor & aroma constituents derived from carotenoids!

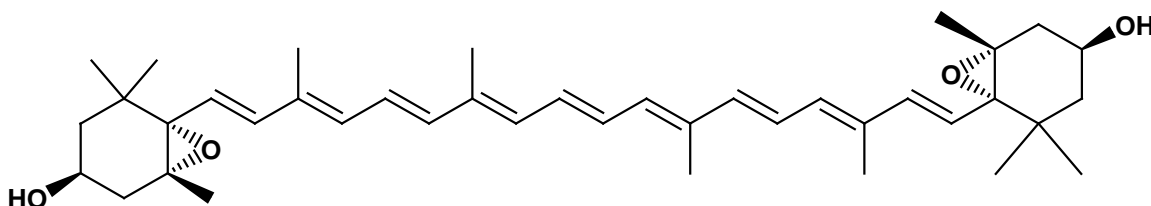
In the discussion of chemical constituents derived from carotenoids in the linked pages we will explore some of the important materials which contribute to the flavor/aroma.

As plants mature, or die, the chlorophyllic pigments rapidly decrease and virtually disappear (one of the normal catabolic changes during plant senescence). The yellow-orange carotenoid pigments of plants also decrease during the senescence or the death phase of plants, but do not always decrease to the point of near extinction as do the chlorophyllic pigments. Thus for plant parts such as the stigma of saffron an intense yellow color (due to carotenoids) remains...and in the green citrus "orange", the fruit turns yellow-orange with maturity.

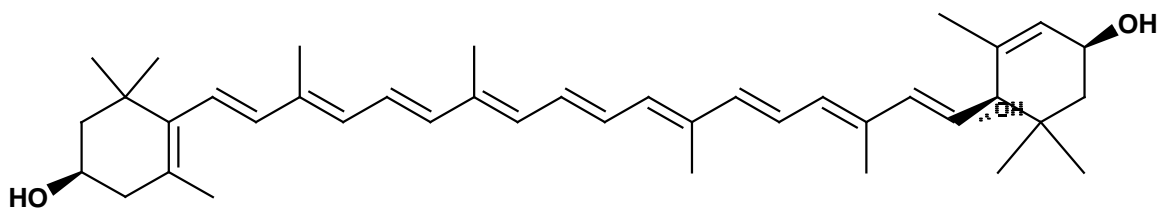
Below you will see four (of the more than 600) common carotenoid structures found in plants and flowers.



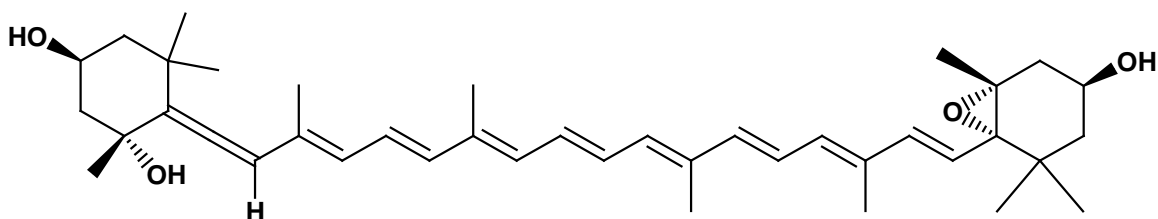
beta-CAROTENE



VIOLAXANTHIN



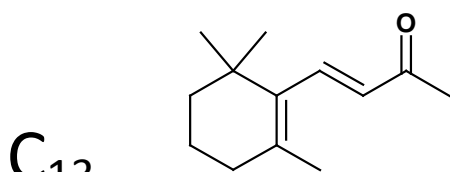
LUTEIN



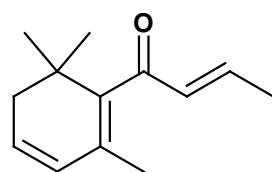
NEOXANTHIN

The primary odor constituents derived from carotenoids are C_{13} - C_{11} - C_{10} - and C_9 derivatives formed via enzymatic oxidation and photo-oxidation of the various carotenoids found in plants, flowers and fruits. While other aroma constituents such as esters, terpenes, pyrazines, etc. are usually also present, these C_9 to C_{13} compounds often are essential to the odor profile. Above you will see a common oxidative fragmentation pattern (shown for beta-Carotene).

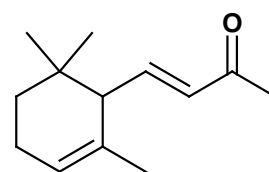
Examples of aroma compounds produced in nature are shown below:



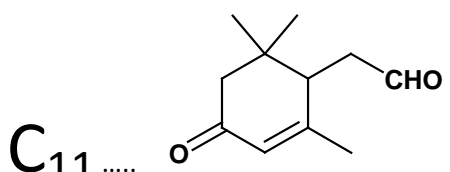
Beta-Ionone



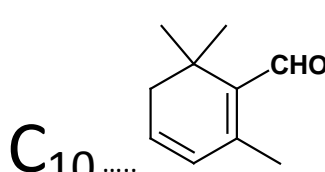
Beta-Damascenone



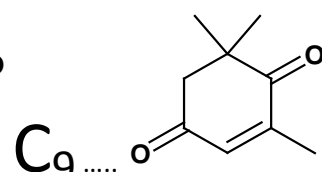
Alpha-Ionone



Isophorone-4-acetaldehyde

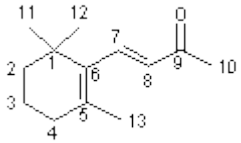
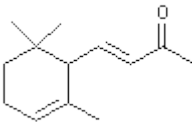
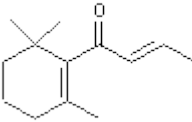
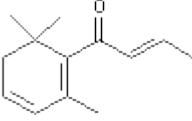
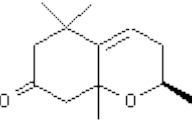
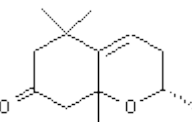
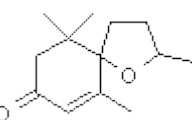
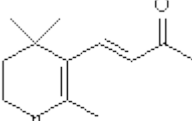
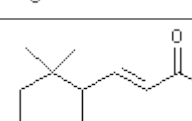


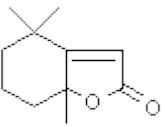
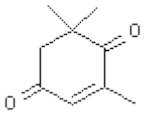
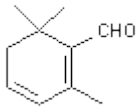
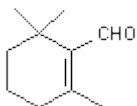
Safranal



4-Ketoisophorone

Common Carotenoid Degradation Products Found in Plants

Name	Structure	Examples of Occurrence
beta-Ionone		Osmanthus, Rose, Black Tea, Tomato, Blackberries, Raspberries, Passion fruit, Carrots, Tobacco, Apricot, Carambola, Cherries, Mango, Bell Pepper, Plum
alpha-Ionone		Black currant, Osmanthus, Black Tea, Blackberries, Raspberries, Carrots, Tobacco, Banana, Cherries, Plum, Celery, Peach, Popcorn, Tomato
beta-Damascone		Rose, Osmanthus, Black tea, Mountain papaya, Rum, Tobacco
beta-Damascenone		Apricot, Rose, Beer, Carambola, Grape, Kiwi, Mango, Tomato, Wine, Rum, Raspberries, Passion fruit, Blackberries
Oxo-Edulan I		Purple Passionfruit, Osmanthus, Burley tobacco, Virginia tobacco
Oxo-Edulan II		Purple Passionfruit, Osmanthus, Burley tobacco, Virginia tobacco
Theaspirone		Yellow Passionfruit, Black Tea, Burley tobacco
4-Oxo-beta-ionone		Red Fox, Black Tea, Osmanthus, Burley tobacco, Freesia flower, Boronia
3-Oxo-alpha-Ionone		Osmanthus, Virginia tobacco,

Dihydroactinodiolide		Osmanthus, Black Tea, Tomato, Cassia, Cassie, Ambergis, Tobacco
4-Oxoisophorone		Osmanthus, Black tea, Saffron
Safranal		Saffron, Osmanthus, Black tea, Grapefruit juice, Mate, Paprika
beta-Cyclocitral		Roasted Mate, Rum, Tea, Tomato, Cantaloupe, Paprika, Peas, Apricot, Broccoli, Melon