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# Citrus Oils: Processing, Technology, and Applications

By R. L. Swaine, Southern Pines, NC and R. L. Swaine, Jr., Procter & Gamble Company, Cincinnati, OH

Citrus fruits have evolved to become an important constituent in the modern diet. Because of the most pleasing, clean, refreshing, and versatile aromas, which connote health and vitality, the volatile byproducts of citrus fruits, i.e. the citrus oils, also have become important in today's society.

It is speculated that plants of the genus Citrus, originated in New Guinea-Melanesia.[1] Evolution of the citrus fruits probably then flourished in Southeast Asia. The cultivation of citrus species extended to India and eventually to the Mediterranean. Ultimately, citrus fruits were brought to the fertile, warm environment of the Americas.

In 1732, Kramer first reported the relationship between citrus fruit and antiscorbutic activity.[2] The inclusion of such citrus fruits as oranges and limes in the diet of seamen in the Royal British Admiralry has been reported and even romanticized, giving rise to the term "limey" for British sailors. Only in about the last century, however, have citrus fruits become an integral part of the human diet. And while they are now associated with nutrition and health, earlier, due to their high cost and appealing flavor, they were probably enjoyed as sweets or desserts. It was not until the advent of modern processing technology, such as the development of the TASTE (thermally accelerated short time evaporator), after the second World War, that the use of citrus fruits flourished.

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Today citrus fruits are, because of their desirable aroma and flavor, as well as their nutritive properties, a significant item in the human diet and in the world economy. To a great extent, the

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volatile or essential oils are responsible for much of the characteristic flavor. These oils may be recovered from the fruit during processing and used to supply the aroma and flavor for countless citrus-scented or flavored products. Indeed these byproducts represent a major portion of the flavor and fragrance industry, and it is these oils that will be discussed. This discussion will include the expressed peel oils obtained from orange, lemon, lime, tangerine, mandarin, and bergamot as well as the distilled oil of lime. Another type of oil that is becoming more important is the oil derived from the juice during evaporation. This, so-called essence oil, also will be discussed.

## Economic Considerations

Citrus oils are a class of essential oils and are employed in a wide range of aromatized products ranging from eau-de-Cologne and household cleansers to soft drinks and confections. The major markets for citrus oils are the United States, Japan, Federal German Republic, United Kingdom, France, and the Netherlands.[3] The major producing regions include:

- USA—Florida, California, Texas, Arizona
- South America—Brazil, Argentina
- Mediterranean—Israel, Spain, Italy, Cyprus
- Mexico
- The Caribbean—West Indies

The annual production figures (for 1985), for several key citrus oils follow.[4]

*Bergamot*—Annual production is 115 metric tons. Italy (80%), Ivory Coast (13%), Guinea (4%), and Brazil (2%) are the major producers.

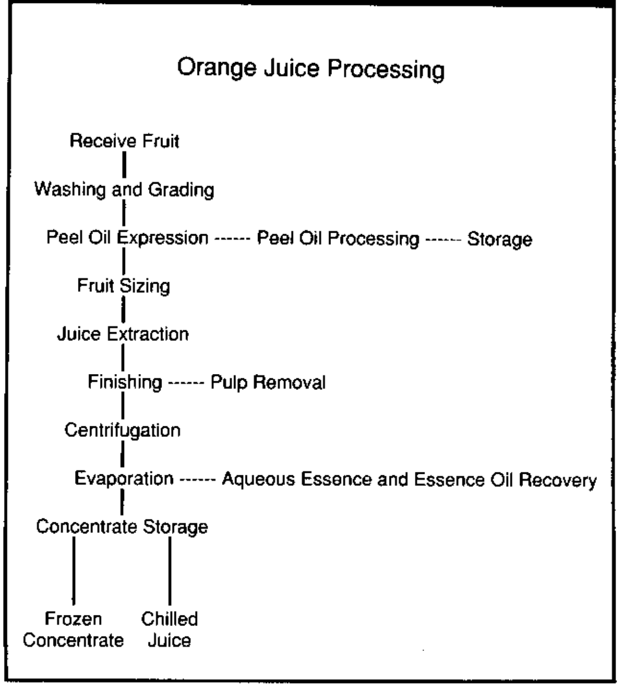
*Grapefruit*—250 metric tons are produced primarily in Israel, Brazil and USA.

*Lemon*—Production of 2500 metric tons is divided among USA (24%), Italy (20%) Argentina (19%), Brazil (8%), Ivory Coast (5%), Greece (4%), Spain (4%) and Israel (3%). Cyprus, Peru, Australia and Guinea also produce small amounts.

*Lime Oil*—The majority of the 1200 metric tons produced annually is distilled lime. Mexico (280 metric tons), Haiti (200 metric tons), and Peru (180 metric tons) are the major producers. Brazil, Cuba, Ivory Coast, Dominica, Guatemala, Jamaica, Ghana, and Swaziland also distill lime oil. Brazil (90 metric tons), USA (40 metric tons), and Mexico (25 metric tons), are the major producers of expressed lime oil.

*Mandarin*—120 metric tons are produced in Italy (40%), Peoples Republic of China (33%). Minor quantities are produced in USA, Argentina and Brazil.

Figure 1




*Bitter Orange*—30 metric tons are produced mainly in Sicily, West Indies, Russia, and Brazil.

*Orange Oil*—The global production is estimated at 12,000-15,000 metric tons. In 1984, the major production regions were: Brazil (7800 metric tons), USA (2500 metric tons), Israel (400 metric tons), Italy (300 metric tons). Minor producers were Argentina, Spain, Morocco, Guinea, Belize, Indonesia, S. Africa, Australia and the USSR.

*Tangerine*—The vast majority of the annual 300 metric tons is produced in Brazil (85%). Spain, Mexico, and the USA also produce minor amounts.

## Production and Technology

During the Middle Ages, the alchemist prepared citrus oils by distillation. It was not until the 1700s that less destructive methods such as grating of peels or pressing of peels were employed to isolate the essential oil from citrus fruits.

The expensive and laborious manual production of citrus peel oils has, in general, given way to the mechanical production of oils. They may be considered byproducts of the juice processing industry. Before examining the production of the oils, an overview of the operation of juice processing will add perspective, specially with regard to the role of oil recovery in an integrated system. Figure 1 illustrates the activities at a typical modern citrus processing facility; in this example, orange juice is being processed. While important to the flavor of the resulting orange juice, the oil, is a byproduct. In this example, the yield of cold-pressed peel oil is 0.27% while 56% of the more costly single strength juice is recovered. Some of the remaining material, such as pulp, is also recovered and as with the oils, either used to formulate a juice or juice drink or sold on the open market. On average, the yields for lemon and orange oils are 0.10-0.35%, grapefruit and tangerine 0.05-0.10% and lime 0.005-0.015%. The mass balance of orange flavorings is shown in Figure 2.

The recovery of peel oil from citrus fruit is effected by the rupture of soft tissue. The essential oil is contained in oval-shaped glands located just below the flavedo. The cold-pressed oils are obtained by the mechanical extraction from these glands, and is much easier than obtaining oils "locked away" in hard tissues as would be the case with cinnamon, for example. In those cases, more intense and destructive measures such as comminution, maceration, and/or distillation are used.

The methods used to recover peel oil include sponge pressing (a labor intensive and costly means), machine pressing,[6] and integrated juice-oil expression. While the sponge method arguably delivers the highest quality essential oil, the dear price associated with oil produced by this method can only be borne in a relatively few, high quality products. Sicilian Lemon Oil, for example, can withstand this higher price.

The majority of the peel oil is, therefore, produced using an integrated juice oil procedure such as the Brown Oil Extractor, (BOE).[7] With the BOE partially submerged (in water), citrus fruit has its flavedo abraded by metal discs containing pointed teeth. The oil is removed as an emulsion. Centrifugation is then used to separate the oil. By removing the oil from the intact fruit prior to the juice extraction process, loss and contamination of oil in juice is avoided.[8] The oil is then winterized by storage for several months at reduced temperatures (0°C) to remove higher molecular weight, non-volatile waxes.

Another type of oil also is being collected, the so-called essence oil or TASTE oil. This oil is becoming increasingly important as it contains the more volatile, fruity topnotes needed by the perfumer and the flavorist to recreate more natural scents and flavors. The recovery of essence oil was pioneered by Dr. Redd. In theory, the TASTE machine is a fractionating distillation unit equipped with multiple condensors. The aromatics are contained in the first 25% of the evaporation process. The vapors from this portion of the TASTE unit are concentrated, condensed and collected. The condensate is then separated into an aqueous and an oil phase.

An overview of the recovery of citrus oils and essences and the material balance is shown in Figure 3 for orange,[9] and Figure 4 for grapefruit.

Although the chemical and organoleptic properties of citrus oils will be discussed in detail later in this paper, remember that there are certain inherent properties possessed by pure citrus oils as described above, that make it advanta-

Figure 2

Mass Balance of Orange Flavorings

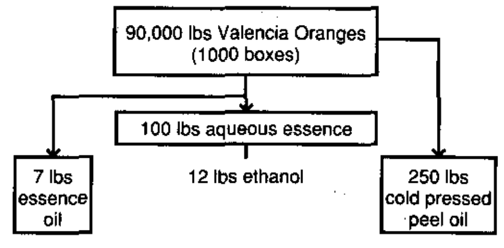
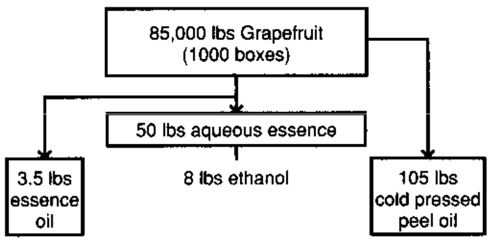


Figure 3

Mass Balance of Grapefruit Flavorings




geous in certain circumstances to further process them. This generally involves removing the terpenes, for purposes of enhancing the stability and solubility and concentrating the oil. Deterpenation is the term applied to a number of processes that result in the partial reduction or the complete removal of terpenes from an essential oil.

Terpenes are prevalent in citrus oils (about 95%). They are part of the full odor profile but due to their relatively weak odor strength, usually not the characterizing part. They are not very soluble in hydroalcoholic mixtures. The high degree of unsaturation renders them labile to oxidative degradation and the formation of deleterious compounds. Their stability with respect to light and to temperature is also bad. Further, in the presence of hydrogen ions, an acid catalyzed hydration-dehydration reaction can take place, with limonene for example, to form potent odorants in the terpenol family. D-limonene is the most prevalent terpene. For these reasons it may, therefore, be desirable to remove or deterpenate an oil.

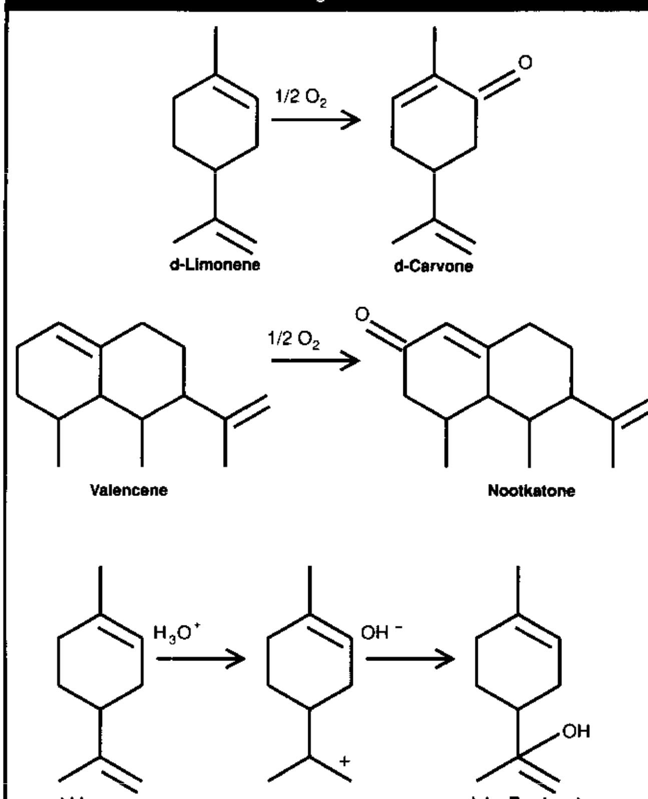
Knowledge of the chemical properties including volatility, solubility, thermal lability and reactivity can be used to help to determine the process for odorant isolation and recovery. For example, if an essential oil contains components that are thermally unstable, it may be wise to use solvent extraction rather than a thermally intensive process such as distillation to recover the oil. The choice of solvent or solvents is now important as this choice can result in selective extraction of components and the tailoring of an odor profile. It should further be noted that solvent extraction is useful in removing less volatile components.

Deterpenation commonly has been affected by fractional distillation. An alternative to distillation is extraction. One process prescribes countercurrent extraction with an appropriate solvent (i.e. alcohol, hexane). This is claimed to be more efficient and, as a lower temperature is used, a less destructive concentration process. This process involves partitioning the citrus oil by pumping against a solvent being pumped in a countercurrent flow. The solvent is later removed under vacuum and by a falling film evaporator. The resultant oil is remarkably free from artifacts and the resultant profile of odor active volatiles is very similar to the feed (i.e. single strength) oil.

The terpeneless oil produced via the countercurrent extraction method has a volatile profile much more akin to the single-fold or feed oil than does the terpeneless oil produced by conventional fractional distillation. Also of note is the fact that of the about 80% d-limonene in the feed oil, only 0.28% remains after deterpenation via extraction while 6% remains in the distilled oil. A comparison of folded oils is shown in Table 1.[10]

One should be mindful that although deterpenation, or folding as it is sometimes called, results in an oil with improved chemical properties (i.e. solubility and stability), the odor profile will be different from the single fold, or feed oil. Although weak, the terpenes do contribute to the profile. Their reduction or removal will alter the

Figure 4



profile somewhat. Further, artifacts may be generated during the processing. These too may alter the profile. Finally, the process most commonly used today removes to some extent the more flavorful and in some cases characterizing "oxygenated compounds." Reprocessing of the terpene fraction to remove the oxygenated compounds that co-distill with the terpenes is becoming increasingly more popular. The more highly valued oxygenated chemicals, such as ethyl butyrate in orange essence oil and octanal in orange peel oil, then can be incorporated into the folded oil to more closely approximate the profile of the single fold oil.

There are distinct chemical and organoleptic differences between the C10 hydrocarbons referred to as terpenes and the more aroma characterizing oxygenated constituents (see Table 2.)[11]

The major method to produce single-fold citrus oils is expression. This method, because of the minimal exposure to high heat and water, produces a high fidelity oil. Expression of citrus oil followed by the prolonged exposure to (acidified) water can result in artifact formation. Specifically, limonene degrades via an acid catalyzed hydration dehydration (ACHD) mechanism to give rise to terpenols. Distilled lime oil is a byproduct of the manufacture of lime juice and has a flavor that is characterized by the ACHD flavor changes. Distilled lime is the exception in the processing of the major commercial citrus peel oils.

### Volatile Composition

It is no coincidence that our growth in knowledge about citrus essential oils has paralleled the tremendous growth in analytical instrumentation and computerization during the past 20 years. While one can marvel at the separation and identification capabilities of modern chromatography and spectroscopy, one must have respect for the pioneers in the field of essential oil chemistry. Just 35 years ago, Ernest Guenther would characterize lemon oil accordingly.[12]

| | |
|---|---|
| Specific Gravity at 25°/25° | 0.849 to 0.855 |
| Optical Rotation at 25° | + 57° 0' to + 65° 36' occasionally below + 57° |
| Refractive Index at 20° | 1.4742 to 1.4755 |
| Aldehyde Content, calculated as Citral (Hydroxylamine Hydrochloride Method) | 2.3 to 3.5% usually around 3% seldom as low as 2.3% |
| Evaporation Residue | 1.5 to 1.8% |
| Solubility | Soluble in 3 vol. of 95% alcohol and more |
| Color | Lemon-yellow |

Only 17 chemicals were identified: four terpene hydrocarbons, two sesquiterpenes, three fatty acids, three alcohols, four aldehydes, and one amorphous unidentified compound! A typical identification would appear as follows:

> Citral: Isolated as bisulite from the oil obtained by steam distillation of the fractionation residue. When decomposed, an optically inactive oil of citral-like odor was obtained: $b_{10}$ 105°-106°, $n^{20}$ 1.4878.
> Identified as α-cirtyl-β-naphthocinchoninic acid m. 199°-200° (corr.), α- and β-citral semicarbazones m. 134°-135°, and α-citral semicarbazone m. 163°-164°.

These methods are incomplete and tedious in comparison to modern analytical instrumental methods.

Before we examine the specific volatile compositions of key citrus oils, bear in mind that the

Table 1

**Aldehyde Composition of Orange Oils (%)**

| | Terpeneless: Countercurrent Extraction | Terpeneless: Fractional Distillation | Singlefold |
|---|---|---|---|
| Octanal | 49 | 0.1 | 41 |
| Nonanal | 3 | 4 | 5 |
| Decanal | 22 | 54 | 29 |
| Dodecanal | 3 | 9 | 3 |
| Geranial | 10 | 12 | 8 |
| Neral | 6 | 7 | 6 |
| Citronellal | 4 | 8 | 5 |
| Perilladehyde | 4 | 6 | 2 |

*Ford (1988)*

Table 2

**Chemical and Organoleptic Properties of Terpenes and Oxygenated Aromatic Chemicals**

| Property | Terpenes | Oxygenates |
|---|---|---|
| Odor Strength | Weak | Strong |
| Character Impact | Little | Significant |
| Naturalness of Essential Oil | Essential | Essential |
| Miscibility: | | |
| Hydrocarbons | Completely | General Good |
| 50% Alcohol | Poor | General Good |
| Volatility | Generally High | Low to Moderate |
| Stability | May Polymerize | Less Reactive (nb. some aldehydes do polymerize.ie. ethanal) |
| Reactivity with Oxygen | Reactive and Deteriorative | Less Reactive (nb. some alcohols and aldehydes will oxidize.) |
| Heat Sensitivity | May Polymerize. (nb. heat accelerates other reactions) | Most are heat sensitive. |
| Reactivity with Water | Anaerobic or neutral pH, not reactive | Reactive, (ie. esters may hydrolize.) |
| Sensitivity to Light | Sunlight may cause polymerization and oxidation | Most are light sensitive |
| Examples | d-Limonene alpha-Pinene | Linalool Neral |

analysis is shown in this text represents data from a specific region and/or season. The volatile profiles and hence the corresponding aroma will vary not only from season to season, but also within the same growing season and region. To illustrate this, consider orange oil. Vora, et al.[13] showed that orange oil processed from midseason fruit had significantly higher color values (20-30%), than late season (Valencia) fruit. Conversely, the late season fruit had a significantly higher concentration of oxygenated aroma components. The late season fruit commands a higher price.

Similarly, Wilson, et al.,[14] using high resolution gas chromatography, examined the aldehydes present in Valencia and midseason orange oils from Florida and those in Navel oils. Their results are summarized in Table 3.

Boelens and Valverde[15] recently demonstrated the effect climatic conditions have in the biogeneration of aromatics. Lemons cultivated in a hot climate yielded a peel oil with a lower citral content than fruit from a more moderate climate, 1.55% and 2.9% respectively. The same relationship was found for the total aldehyde concentration in the peel oil from bitter orange. The fruit cultivated in the hot climate produced a peel oil with 1.0-1.5% total aldehydes while the fruit from a more moderate climate yielded a peel oil with 2.0-3.0% total aldehydes.

*Lemon Oil.* The volatile profile of lemon, as characterized by gas chromatography is summarized in Table 4.[16] Again, it is important to note that the growing region and season are important to the organoleptic and analytical profile.

The California coastal oils typically possess a higher oxygenated fraction, and hence a stronger more characteristic lemon flavor, than Arizona or desert oils. However both pale in comparison to Italian oil in both impact and quality. Much of the quality of lemon oil is dependent on the citral concentration and especially on the ratio of the two isomers. Cis-citral possesses a potent, characteristic lemon aroma, while trans-citral is rather green and fatty.

Table 3

## Aldehyde Composition of Orange Oils (%)

| | Valencia | Mid-Season | Navel |
|---|---|---|---|
| Octanal | 0.393-0.505 | 0.342-0.374 | 0.150-0.172 |
| Nonanal | 0.069-0.075 | 0.057-0.060 | 0.022 |
| Citronellal | 0.090-0.094 | 0.055-0.060 | 0.064-0.081 |
| Decanal | 0.375-0.415 | 0.277-0.338 | 0.131-0.142 |
| Neral | 0.072-0.073 | 0.064-0.065 | 0.045-0.062 |
| Geranial | 0.120-0.180 | 0.113-0.114 | 0.080-0.104 |
| Perillaldehyde | 0.033-0.040 | 0.029-0.031 | 0.013-0.017 |
| Dodecanal | 0.080-0.083 | 0.055-0.067 | 0.030-0.034 |
| beta-Sinensal | 0.056-0.081 | 0.047-0.048 | 0.019-0.026 |
| alpha-Sinensal | 0.037-0.060 | 0.034 | 0.016-0.024 |

*Wilson, et. al., 1984*

Table 4

## Composition of California and Arizona Lemon Oil (%)

| | Coastal | | | Desert | | |
|---|---|---|---|---|---|---|
| | Early | Mid | Late | Early | Mid | Late |
| Heptanal | 0.004 | 0.004 | 0.004 | trace | trace | trace |
| alpha-Thujene | 0.450 | 0.440 | 0.440 | 0.340 | 0.360 | 0.350 |
| alpha-Pinene | 2.110 | 2.140 | 2.150 | 1.410 | 1.500 | 1.490 |
| Camphene | 0.070 | 0.080 | 0.070 | 0.030 | 0.030 | 0.030 |
| Sabinene | 2.480 | 2.610 | 2.680 | 1.090 | 1.110 | 1.170 |
| beta-Pinene | 15.620 | 17.290 | 16.580 | 5.380 | 6.070 | 6.440 |
| Methylheptenone | trace | trace | trace | trace | trace | trace |
| Myrcene | 1.280 | 1.220 | 1.330 | 1.770 | 1.740 | 1.740 |
| Octanal | 0.140 | 0.140 | 0.100 | 0.040 | 0.090 | 0.090 |
| alpha-Phellandrene | 0.040 | 0.040 | 0.040 | 0.040 | 0.040 | 0.040 |
| delta-3-Carene | 0.004 | 0.004 | 0.006 | trace | trace | trace |
| alpha-Terpinene | 0.320 | 0.320 | 0.280 | 0.260 | 0.270 | 0.260 |
| para-Cymene | 0.030 | 0.030 | 0.030 | 0.020 | 0.020 | 0.030 |
| d-Limonene | 60.360 | 58.470 | 59.920 | 76.480 | 75.740 | 76.300 |
| gamma-Terpinene | 9.780 | 9.740 | 9.390 | 7.800 | 8.030 | 7.900 |
| Octanol | 0.020 | 0.020 | 0.030 | 0.030 | 0.010 | 0.010 |
| Terpinolene | 0.390 | 0.380 | 0.360 | 0.370 | 0.360 | 0.350 |
| Linalool | 0.130 | 0.150 | 0.210 | 0.200 | 0.120 | 0.090 |
| Nonanal | 0.210 | 0.270 | 0.210 | 0.060 | 0.060 | 0.060 |
| Citronellal | 0.090 | 0.080 | 0.080 | 0.060 | 0.090 | 0.090 |
| Terpinen-4-ol | 0.070 | 0.160 | 0.100 | 0.060 | 0.060 | 0.060 |
| alpha-Terpineol | 0.170 | 0.270 | 0.260 | 0.230 | 0.130 | 0.090 |
| Decanal | 0.070 | 0.070 | 0.050 | 0.020 | 0.050 | 0.060 |
| Octyl Acetate | 0.006 | 0.007 | 0.004 | trace | 0.002 | 0.003 |
| Nerol | 0.020 | 0.040 | 0.040 | 0.050 | 0.020 | 0.020 |
| Neral | 0.740 | 0.890 | 1.070 | 0.840 | 0.540 | 0.410 |
| Carvone | 0.006 | 0.008 | 0.006 | 0.007 | 0.007 | 0.008 |
| Geraniol | 0.030 | 0.050 | 0.040 | 0.020 | 0.020 | 0.030 |
| Geranial | 1.210 | 1.440 | 1.700 | 1.280 | 0.880 | 0.680 |
| Nonyl Acetate | 0.020 | 0.020 | 0.010 | 0.002 | 0.002 | 0.002 |
| Citronellyl Acetate | 0.030 | 0.020 | 0.010 | 0.010 | 0.030 | 0.040 |
| Neryl Acetate | 0.510 | 0.570 | 0.600 | 0.320 | 0.510 | 0.550 |
| Geranyl Acetate | 0.610 | 0.720 | 0.610 | 0.150 | 0.210 | 0.240 |
| Dodecanal | 0.030 | 0.030 | 0.020 | 0.007 | 0.001 | 0.002 |
| Caryophyllene | 0.230 | 0.230 | 0.260 | 0.270 | 0.220 | 0.210 |
| e-alpha-Bergamotene | 0.400 | 0.400 | 0.350 | 0.340 | 0.420 | 0.410 |
| alpha-Humulene | 0.020 | 0.020 | 0.020 | 0.020 | 0.020 | 0.020 |
| beta-Bisabolene | 0.610 | 0.620 | 0.530 | 0.500 | 0.620 | 0.610 |

*Staroscik and Wilson (1982)*

Table 5

**Comparison of the Volatile Compounds in Mexican and West Indian Limes Oils (Expressed and Distilled) %**

| | Mexican | | West Indian | |
|---|---|---|---|---|
| | Cold Pressed | Distilled | Cold Pressed | Distilled |
| tert-Amyl Alcohol | trace | trace | trace | trace |
| 2-Methyl-3-buten-2-ol | | trace | trace | trace |
| z-3-Hexen-1-ol | | trace | trace | trace |
| Octanol | trace | trace | trace | trace |
| Linalool | 0.31 | 0.18 | 0.25 | 0.12 |
| alpha-Fenchyl Alcohol | | 0.71 | | 0.32 |
| z-beta-Terpineol | | 0.81 | | 0.26 |
| e-beta-Terpineol | | trace | | trace |
| Terpinene-4-ol | 0.53 | 1.75 | 0.32 | 2.39 |
| alpha-Terpineol | | 7.81 | | 6.81 |
| Decanol | trace | trace | trace | trace |
| Geraniol | trace | trace | trace | trace |
| Thymol | trace | trace | trace | trace |
| Decanal | 0.71 | | 0.48 | |
| Neral | 1.50 | | 1.13 | 0.13 |
| Geranial | 2.97 | | 1.70 | 0.31 |
| Neryl Acetate | 0.16 | 0.03 | 0.07 | 0.04 |
| Geranyl Acetate | 0.36 | 0.10 | 0.16 | 0.56 |
| n-Nonane | 0.04 | 0.04 | 0.02 | 0.02 |
| alpha-Thujene | 0.55 | | 0.54 | |
| alpha-Pinene | 3.72 | 1.14 | 2.37 | 1.69 |
| Camphene | 0.18 | 0.75 | 0.17 | 0.37 |
| beta-Pinene | 23.81 | 1.75 | 24.23 | 9.49 |
| Myrcene | 2.10 | 1.38 | 1.40 | 0.86 |
| alpha-Phellandrene | | trace | | trace |
| para-Cymene | | 0.59 | | 0.21 |
| d-Limonene | 34.30 | 49.20 | 44.17 | 47.25 |
| gamma-Terpinene | 14.00 | 8.42 | 11.88 | 8.86 |
| Terpinolene | 0.76 | 9.00 | 0.83 | 7.24 |
| alpha-Elemene | 0.77 | 0.07 | 0.54 | 0.11 |
| beta-Elemene | 0.53 | 0.07 | 0.33 | 0.05 |
| beta-Caryophellene | 1.36 | 0.68 | 0.70 | 0.51 |
| alpha-Bergamontene | 2.16 | 0.81 | 1.34 | 0.61 |
| Guaiene | 0.78 | 0.46 | 0.42 | 0.34 |
| beta-Bisabolene | 5.70 | 2.49 | 3.18 | 2.12 |
| 1,4-Cineole | | 1.92 | | 0.21 |
| 1,8-Cineole | 0.35 | 0.74 | 0.26 | 0.29 |

*Azzouz, Reineccius (1976)*

*Lime Oil.* Again, a comparison of major producing regions is necessary. The expressed Mexican oil contains less of the monoterpene d-limonene and more oxygenated aroma compounds than West Indian. Processing methods can greatly influence the profile of an oil. There is no better example than lime. There is less $\beta$-pinene and citral in the Mexican oil. However, the greater disparity is between the expressed and the distilled oils. Expressed oil contains more aldehydes (especially citral), and $\beta$-pinene than the distilled oil. Conversely, the distilled oil contains magnitudes more $\alpha$-terpineol, the ACHD product formed from d-limonene. These data are summarized in Table 5.[17]

*Bergamot.* Bergamot oil is highly prized, in fact, it is known to connoisseurs as the "king of citrus fruits." This is rather remarkable since the oil comes from the peel of fruit considered too sour to consume.

The majority of bergamot is produced in Italy; the gas chromatography profile of a typical oil is shown in Table 6.[18] More recently, Huang, et al.,[19] identified additional components in Chinese bergamot oil. Bergamot oil also contains phototoxic agents that must be removed by distillation prior to use in perfumes. This subject is covered later in greater detail.

*Tangerine & Mandarin Oils.* Because of their botanical similarity, many people tend to use tangerine and mandarin interchangeably. As shown by the analysis in Table 7,[20] numerous differences exist. The price of mandarin is about five times that of tangerine!

Table 6

**Composition of Bergamot Oil (% w/w)**

| | Italian | Chinese |
|---|---|---|
| alpha-Pinene | 1.51 | 0.52 |
| Camphene | 0.04 | 0.01 |
| beta-Pinene | 7.07 | 2.90 |
| Sabinene | 1.23 | 0.58 |
| Myrcene | 0.90 | 0.95 |
| alpha-Phellandrene | 0.04 | 0.01 |
| d-Limonene | 35.64 | 35.42 |
| gamma-Terpinene | 7.63 | 4.80 |
| para-Cymene | 0.34 | 0.11 |
| Terpinolene | 0.17 | 0.16 |
| Nonanal | 0.03 | 0.03 |
| Citronellal | 0.02 | 0.03 |
| Decanal | 0.09 | 0.08 |
| Linalool | 12.67 | 17.38 |
| Linalyl Acetate | 32.71 | 31.15 |
| Terpinen-4-ol | 0.29 | 0.05 |
| Bergamotene | 0.32 | 0.15 |
| Neral | 0.23 | 0.04 |
| alpha-Terpineol | 0.08 | 0.07 |
| Geranial | 0.35 | 0.14 |
| Bisabolene | 0.60 | 0.95 |
| Geranyl Acetate | 0.26 | 0.77 |
| Nerol | 0.05 | 0.09 |
| Geraniol | 0.02 | 0.15 |
| "1,8-Cineol" | | 0.16 |
| Octanal | | 0.11 |
| Hexyl Acetate | | 0.11 |
| Methylheptenone | | 0.01 |
| z-Linalool Oxide | | 0.02 |
| Octyl Acetate | | 0.19 |
| Nonyl Acetate | | 0.91 |
| e-beta-farnesene | | 0.57 |
| undecanal | | 0.08 |
| beta-Caryophyllene | | 0.53 |
| Citronellyl Acetate | | 0.13 |
| Decyl Acetate | | 0.05 |
| alpha-Terpenyl Acetate | | 0.19 |
| Neryl Acetate | | 0.91 |
| Citronellol | | 0.05 |

*Huet (1981) Huang, et al 1987*

Table 7

**Comparison of Tangerine and Mandarin Oils (%)**

| | Florida Tangerine | Italian Mandarin |
|---|---|---|
| alpha-Pinene | 1.00 | 3.93 |
| Camphene(+unknown) | 0.01 | 0.02 |
| beta-Pinene(+unknown) | 0.44 | 2.16 |
| Myrcene | 2.03 | 1.80 |
| alpha-Phellandrene | 0.03 | 0.03 |
| alpha-Terpinene | 0.05 | 0.42 |
| d-Limonene | 91.23 | 67.10 |
| "1,8-Cineole" | 0.63 | 0.54 |
| gamma-Terpinene | 3.09 | 20.14 |
| para-Cymene + Ocanal | 0.38 | 1.34 |
| Terpinolene | 0.13 | 0.89 |
| Methyl Heptenone | trace | |
| z-3-Hexenol | trace | |
| Nonanal(+unknown) | 0.02 | 0.01 |
| Heptanol | trace | 0.01 |
| Sabinene Hydrate(+unknown) | 0.01 | 0.02 |
| Citronellal | 0.04 | 0.01 |
| Decanal | 0.10 | 0.03 |
| Linalool | 0.62 | 0.13 |
| Nonanol + Caryophyllene | 0.02 | 0.07 |
| Decyl Acetate | 0.03 | 0.01 |
| Neral + Terpineol | 0.05 | 0.15 |
| Neryl Acetate + Dodecanal | 0.04 | 0.01 |
| "Citronellol, Geranial, Decanol" | 0.03 | 0.01 |
| Geranyl Acetate(+unknown) | 0.05 | 0.10 |
| carvone + Nerol | 0.03 | 0.01 |
| Geraniol | trace | trace |
| e-Carveol | 0.01 | trace |
| Perillaldehyde | 0.03 | 0.04 |
| z-Carvoel | trace | trace |
| Benzyl Alcohol | trace | 0.01 |
| Undecanol | trace | trace |
| Dodecanol | trace | trace |
| Methyl-N-Methylanthranilate | | 0.33 |
| Thymol | 0.03 | 0.03 |
| alpha-Sinesal | 0.07 | 0.11 |

*Hussein and Pidel (1976)*

*Grapefruit Oil.* Table 8[21] compares the volatile profiles of commercial grapefruit oils. While today's common wisdom is to grade grapefruit oils by the nootkatone concentration, nootkatone exists as sterioisomers. The properties of the two isomers are vastly different. (+)− nootkatone has a grapefruit aroma and the threshold in air is 30 ppm. The taste threshold is 0.8 ppm in water and the resultant taste is bitter. This is sharply contrasted to (−)−nootkatone which is virtually tasteless and has a soft woody aroma.[15]

The workers in the Firmenich Laboratories have elucidated the structures of what they consider to be compounds important to the quality, impact, and the character of grapefruit juice.[22] These include (+) −8, 9-didehydronootkatone and 1- P-menthene-8-thiol. The latter compound is reported to display an authentic, fresh grapefruit juice aroma at the ppb level or less.[23]

*Bitter Orange Oil.* Table 9 is a composite of the compositional data for Bitter Orange Oil.[24] Again, one marvels at the wide range of data within one aroma camp.

*Orange Oil.* The vast majority of the citrus oil used in the fragrance and flavor industry is orange oil. Table 10 contains the analysis for commercial peel oils, and data for essence or TASTE oils.[25] The higher ester and sesquiterpene fraction of the essence oils makes them more applicable for products requiring natural or fruity aromas.

Also of note is the lower aldehyde content in Brazilian oil and to a lesser degree in Navel oil as compared to Valencia. While the Valencia is more prized than the Brazilian oil, the Navel oil is an appealing and under-utilized oil. Essence oils are subjected to thermal abuse during juice evaporation resulting in the destruction of the naturally occurring antioxidants, tocopherols. Extra precaution is, therefore, warranted in storage and handling.

*Malodors.* A discussion of the citrus volatiles would not be complete without the mention of malodorous volatiles that may form as a result of processing, mishandling, or improper storage. Oxidative and acid catalyzed reactions are responsible for the most noticeable undesirable aromas in citrus oils.

Citrus peel oils, predominantly unsaturated terpenes, and essence oils, unsaturated terpenes and sesquiterpenes are particularly susceptible to oxidation. The formation of malodorous artifacts d-carvone and nootkatone from limonene and valencene is shown in Figure 4. The formation of α-terpineol from d-limonene via the ACHD mechanism is also described in Figure 4.

Of particular concern to products containing lemon oil or isolates is the generation of a turpentine off-odor. It is generally agreed that p-cymene is the offensive compound. Several mechanisms have proposed the formation of p-cymene.[26-27] These mechanisms are shown in Figure 5.

## Application in Fragrances & Flavorings

Citrus oils can impart a fresh, light effect, or give a characteristic aroma and taste to perfumes and flavorings. Their high volatility as compared to other fragrance materials used for middle and base notes, makes citrus oils ideally suited for use as topnotes in a wide array of applications. Citrus oils are useful as they blend well with a diverse range of aromatic compounds such as spice oils, vanilla, and fruity esters. Some appli-

Table 8

## Grapefruit Oils (%)

| | Singlefold Peel Oil | Five Fold Peel Oil | Singlefold Essence Oil |
|---|---|---|---|
| alpha-Pinene | 0.38 | trace | 0.38 |
| beta-Pinene | 0.02 | trace | 0.02 |
| Sabinene | 0.42 | 0.02 | 0.36 |
| Myrcene | 1.37 | 0.34 | 1.60 |
| e-2-Hexenal | trace | 0.03 | trace |
| d-Limonene | 83.40 | 52.60 | 86.00 |
| Ethyl Butyrate | trace | trace | 0.04 |
| gamma-Terpinene | 0.01 | 0.21 | 0.02 |
| para-Cymene | 0.02 | 0.16 | 0.02 |
| Octanal | 0.62 | 0.11 | 0.69 |
| Nonanal | 0.07 | 0.19 | 0.08 |
| z-3-Hexenol | trace | trace | 0.01 |
| Citronellal | 0.09 | 0.32 | 0.05 |
| Decanal | 0.40 | 2.01 | 0.41 |
| Linalool | 0.10 | 0.32 | 0.13 |
| Octanol | 0.09 | 0.36 | 0.10 |
| beta-Caryophellene | 0.24 | 1.55 | 2.11 |
| Neral | 0.04 | 0.20 | 0.04 |
| alpha-Terpineol | 0.04 | 0.44 | 0.05 |
| d-Carvone | 0.06 | 0.07 | 0.04 |
| Geranial | 0.06 | 0.31 | 0.06 |
| Dodecanal | 0.02 | 0.11 | 0.03 |
| Valencene | trace | 0.04 | 0.15 |
| Geraniol | trace | 0.03 | trace |
| Nootkatone | 0.10 | 2.11 | 1.10 |

*Myers (1988)*

cations may use the natural citrus oil while some may benefit from, or in fact may require, a derivative or isolate from the native oil. The practitioner should remember that compounded recreations or isolates may be recognized and functional, but they may lack the true natural character necessary for certain fine applications. Reasons for this include:

1. Natural oils contain many trace impurities not identified or not available in synthetic mixtures or isolates.
2. Synthetic aroma chemicals with sites of asymmetry are usually optically inactive and the resulting aroma may be different from the D or L isomers of the chemicals present in nature.

In many cases, such as the rigorous processing of flavorings or functional fragrances, citrus oil facsimilies, isolates or derivatives aid in overcoming inherent instability or infer special properties. Examples include the Schiff's Base of citral and methyl anthranilate which gives tenacity and strength to household cleaners[28] or orange juice carbonyls which reinforce the natural orange character in orange juice.

Table 9

## Bitter Orange Oil (%)

| | |
|---|---|
| alpha -Pinene | 0.36-1.25 |
| beta-Pinene | 0.03-6.15 |
| Sabinene | 0.05-1.25 |
| Myrcene | 1.90-2.10 |
| d-Limonene | 48.42-96.89 |
| gamma-Terpinene | 0.07-8.76 |
| para-Cymene | <0.83 |
| Decanal | <0.41 |
| Citronellol | <1.10 |
| Linalool | <12.85 |
| Linallyl Acetate | <9.72 |
| Bornyl Acetate | <0.15 |
| alpha-Terpineol | 0.03-03.07 |
| Neral | <1.75 |
| Geranial | <2.58 |
| Nerol | <0.30 |
| Geraniol | <0.52 |
| Camphene | 0.40-0.90 |
| 1,8-Cineole | 0.80-8.10 |
| Octanal | 1.40-2.20 |
| Nonanal | 0.10-0.40 |
| Citronellal | 0.30-0.40 |
| Citronellyl Formate | 0.10-1.10 |
| Citronellyl Acetate | 0.20-0.60 |
| Isopulegol | 0.30-0.40 |
| Geranyl Formate | 0.30-0.60 |
| Terpinen-4-ol | 0.30-0.40 |
| Nootkatone | 0.01 |

Table 10

## Orange Oils (%)

| | Florida: | | Calif.: | Florida: | Calif.: |
|---|---|---|---|---|---|
| | Valencia CP | Brazil CP | Navel CP | Essence | Essence |
| Ethyl Butyrate | 0.006 | 0.005 | 0.004 | 0.052 | |
| alpha-Pinene | 0.454 | 0.523 | 0.513 | 0.494 | 0.394 |
| beta-Pinene | 0.010 | 0.010 | 0.031 | 0.022 | 0.042 |
| Hexanal | | 0.002 | 0.004 | 0.028 | 0.028 |
| Myrcene | 1.773 | 1.530 | 1.890 | 1.690 | 1.590 |
| e-2-Hexenal | | | 0.002 | 0.007 | 0.022 |
| d-Limonene | 90.600 | 91.071 | 77.600 | 88.600 | 88.500 |
| gamma-Terpinene | 0.002 | 0.002 | 0.031 | 0.015 | 0.036 |
| para-Cymene | 0.002 | | 0.016 | 0.033 | 0.351 |
| Octanal | 0.590 | 0.356 | 0.196 | 0.375 | 0.003 |
| Hexanol | 0.096 | | 0.002 | | 0.055 |
| Nonanal | 0.077 | 0.054 | 0.032 | 0.066 | 0.044 |
| Citronellal | 0.087 | 0.073 | 0.052 | 0.036 | 0.510 |
| Decanal | 0.523 | 0.336 | 0.202 | 0.285 | 0.430 |
| Linalool | 0.372 | 0.443 | 0.228 | 0.379 | 0.075 |
| Octanol | 0.039 | 0.043 | 0.012 | 0.042 | |
| beta-Caryophellene | 0.045 | 0.032 | 0.027 | 0.018 | 0.040 |
| Neral | 0.077 | 0.043 | 0.052 | 0.044 | |
| alpha-Terpineol | 0.064 | 0.048 | 0.046 | 0.047 | |
| d-Carvone | 0.012 | 0.005 | 0.009 | 0.047 | |
| Geranial | 0.122 | 0.065 | 0.048 | 0.061 | 0.067 |
| Dodecanal | 0.068 | 0.056 | 0.026 | 0.033 | 0.053 |
| Valencene | 0.058 | 0.036 | 0.079 | 0.241 | 0.620 |
| Geraniol | 0.006 | 0.004 | 0.007 | 0.003 | 0.005 |
| Nootkatone | 0.014 | 0.010 | 0.012 | 0.090 | |

*Myers and Lee (1988)*

The formulations included in this review are skeletal in nature and are intended to demonstrate the effect citrus oils have on basic flavor and fragrance types. Unless otherwise referenced, they are modifications of formulas from the laboratories of Procter & Gamble or the authors.

*Bergamot.* The expressed oil of bergamot is extremely sweet-fruity and fresh with a sharp lemon-like topnote. This is followed by a sweet, rich, oily, herbaceous aroma. Also present are rich floral, balsamic notes. The flavor is somewhat reminiscent of bitter orange.

Bergamot is used extensively in perfumery because of its sweetening and freshening qualities. It is an integral part of eau-de-Cologne formulations, and finds further use as a topnote in chypre and fougere compositions (see Table 11, 12 and 13). It is also used in floral bouquets, and floral compositions such as cyclamen, gardenia, muget de bois, and magnolia. Oriental and leather compositions also benefit from the rich aroma of bergamot. Bergamot is used more in extract perfumes than in chemistry stressed functional fragrances.

The use of bergamot in flavorings is somewhat more limited. It functions as a topnote, and can act as a blender or modifier, especially in combination with other citrus oils. Typical flavor applications are cola, orange and other citrus. An interesting use is in tobacco flavorings.

*Grapefruit.* Grapefruit oil has a characteristic aroma and flavor. It has a fresh citrus aroma, one that Arctander[29] characterized as having notes common to both the sweet and bitter orange. This has an interesting woody base note.

The primary application for grapefruit in perfumes is as a modifier for other citrus compositions; bergamot, for example.

However, grapefruit is used more in the flavor industry as a useful blender and modifier. It adds body to a number of citrus (see Table 18, number 5) and non-citrus flavorings. Single fold grapefruit oil is used in concentrations of 50-200 ppm in soft drinks. The use of the oil derived from the evaporation of grapefruit juice is becoming more popular in an attempt to recreate fresh and natural grapefruit juice. It is blended in a ratio of 3:1 with cold-pressed grapefruit and used at 60-120 ppm in juice products. The increasing popularity of this flavorant and its limited supply from Florida make this oil quite dear. The price has risen from $19 to $35 per pound this year alone!

*Lemon Oil.* The oil expressed from the lemon rind has a characteristic lemon aroma—sweet, fresh, and sharp. The refreshing, sweet traits of lemon oil make it amenable to many fragrance applications, such as eau-de-Colognes (see Table 11), citrus fragrances, chypre-types (see Table 12) and household cleaning products. Lemon adds a refreshing topnote to almost any fragrance.

Lemon is used in flavorings as a blender or modifier as well as for its characterizing flavor. Beverages and confections consume the greatest quantities of lemon oil. Lemon is also used to mask off-odors.

*Distilled Lime Oil.* Distilled lime oil is fresh and sharp. It is characterized as citrusy and terpeny as

Table 11

**Eau de Cologne Formulations (% w/w)[36]**

| | circa 1885 | Modern |
|---|---|---|
| Bergamot Oil | 22.22 | 1.30 |
| Lemon Oil | 22.22 | 5.00 |
| Orange Oil | 22.22 | 2.00 |
| Rosemary Oil | 16.67 | |
| Neroli Brigarade Oil | 5.56 | 5.00 |
| Petitgrain Oil | 11.11 | 5.00 |
| Citrus Aldehydes(C9,C10,C11) | | 0.10 |
| Lavender Oil | | 10.00 |
| Linalool-Linalyl Acetate | | 25.00 |
| Floral Blend:Jasmine | | 10.00 |
| Floral Blend:Rose | | 5.00 |
| Floral Blend:Lilac | | 10.00 |
| Geranium Oil | | 5.00 |
| Citronellol | | 5.00 |
| Amber Blend | | 1.00 |
| Animal Blend | | 0.10 |
| Resinous Blend | | 2.00 |
| Orris-Ionone Blend | | 4.00 |
| Woody Blend | | 2.00 |
| Sweet Blend | | 2.00 |
| Musk | | 0.50 |

Figure 5

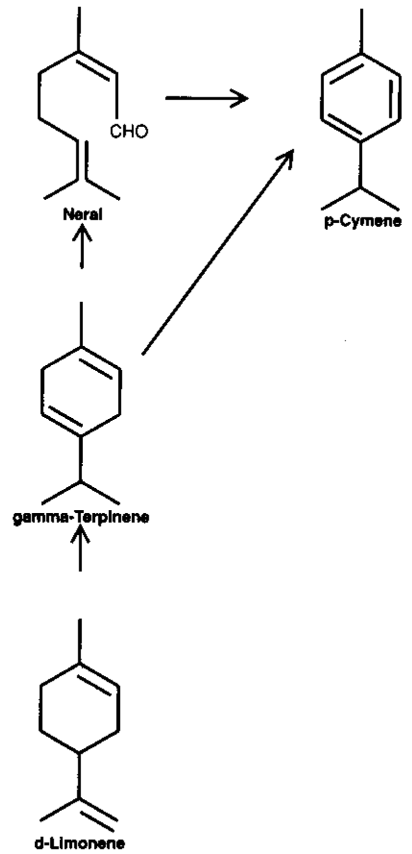



Table 12

**Chypre-Type Formulations (% w/w)**

| | 1 | 2 |
|---|---|---|
| Bergamot Oil | 24.00 | 24.00 |
| Orange Terpene Free | 2.00 | |
| Lemon Terpene Free | | 2.00 |
| Anisic Blend | 1.20 | 1.20 |
| Clary Sage Oil | 3.60 | 3.60 |
| Floral Blend:Jasmine | 18.10 | 18.10 |
| Floral Blend:Rose | 10.90 | 10.90 |
| Moss Blend | 2.40 | 2.40 |
| Sweet Blend | 14.80 | 14.80 |
| Animal Blend | 1.20 | 1.20 |
| Amber Blend | 4.80 | 4.80 |
| Orris-Ionone Blend | 6.10 | 6.10 |
| Resinous Blend | 1.20 | 1.20 |
| Woody Blend | 6.10 | 6.10 |
| Musk | 3.60 | 3.60 |

Table 13

**Fougere-Type Formulation (% w/w)**

| | |
|---|---|
| Orange Oil | 3.0 |
| Bergamot Oil | 11.5 |
| Lemon Oil | 2.0 |
| Linalool | 10.0 |
| Lavender Oil | 7.0 |
| Methyl Salicylate | 2.5 |
| Floral Blend:Rose | 6.0 |
| Geranium Oil | 10.0 |
| Floral Blend:Ylang Ylang | 2.0 |
| Anisic Blend | 1.0 |
| Moss Complex | 7.0 |
| Resinous Blend | 1.0 |
| Amber Blend | 1.0 |
| Woody Blend | 3.0 |
| Sweet Blend | 14.0 |
| Floral Blend:Jasmine | 11.0 |
| Floral Blend:Muget de Bois | 2.0 |
| Musk | 6.0 |

Table 14

## Aldehydic Formulation (% w/w)

| | |
|---|---|
| Expressed Lime Oil | 2.43 |
| Bergamot Oil | 10.30 |
| Aldehyde C10 | 0.20 |
| Aldehyde C11 | 0.20 |
| Aldehyde C12-MNA | 0.20 |
| Linalool | 7.30 |
| Floral Blend:Ylang-Cananga | 9.73 |
| Floral Blend:Jasmine | 12.17 |
| Floral Blend:Rose | 2.43 |
| Floral Blend:Carnation | 4.87 |
| Floral Blend:Muget de Bois | 4.87 |
| Moss Blend | 0.49 |
| Animal Blend | 0.61 |
| Musk | 10.95 |
| Amber Blend | 0.61 |
| Ionone-Orris Blend | 14.84 |
| Resinous Blend | 0.24 |
| Sweet Blend | 12.70 |
| Woody Blend | 4.87 |

Table 15

## Masculine Fragrance (% w/w)

| | |
|---|---|
| Expressed Lime Oil 2X * | 5.0 |
| Bergamot Oil | 39.0 |
| Petitgrain Oil | 8.0 |
| Woody Blend | 10.0 |
| Floral Blend:Rose | 8.0 |
| Floral Blend:Jasmine | 8.0 |
| Floral Blend:Carnation | 4.0 |
| Ionone-Orris Blend | 8.0 |
| Sweet Blend | 6.0 |
| Amber Blend | 2.0 |
| Musk | 2.0 |

** Citronova 200-Firmenich*

Table 16

## Moss Complex (% w/w)

| | |
|---|---|
| Bergamot Oil | 10.00 |
| Woody Blend | 12.50 |
| Linalool | 12.00 |
| Floral Blend:Hyacinth | 10.00 |
| Musk | 10.00 |
| Sweet Blend | 25.00 |
| Amber Blend | 5.00 |
| Orris-Ionone Blend | 2.00 |
| Resinous Blend | 5.00 |
| Benzyl Salicylate | 5.00 |
| Mandarin Oil Select-Italian | 3.50 |

Table 17

## (Bitter) Orange Oil Blend for Liqueurs (% w/w)

| | |
|---|---|
| Saigon Cinnamon Bark Oil | 0.63 |
| Clove Bud Oil | 0.47 |
| Corinder Oil | 0.16 |
| Bergamot Oil | 0.31 |
| Neroli Brigarade Oil | 0.47 |
| Cold Pressed Lemon Oil | 3.92 |
| Cold Pressed Valencia Peel Oil | 54.86 |
| Bitter Orange Oil | 39.18 |

well as fruity-perfumy. There is a distinct floral (lilac) note. The odor is much more harsh and sharp than expressed lime. The character is extremely dependent on the growing area and method of production.

The use of lime oil in perfumery is rather limited as compared to the other citrus oils. Eau-de-Colognes, toilet waters, and masculine fragrances are the main applications. Distilled lime is used to flavor soft drinks, especially cola and lemon-lime types, and confections, mainly hard candies. It is also used as a modifier in citrus formulations (see Table 18, number 5).

*Expressed Lime Oil.* The aroma of this oil is considered by many to be the "champagne" of citrus oils. The limited quantity produced makes it highly valued. It has a fresh, rich, sweet, citrus peel odor. Expressed lime oil is much smoother and less harsh than the distilled lime, and in fact, has an odor more akin to lemon peel oil. It is more mellow and full, even perfumy to some.

Expressed lime oil is used in eau-de-Cologne and toilet waters. It enriches and modifies citrus blends and adds a refreshing, rich topnote to aldehyde compositions, such as in Table 14. It can also be the dominant note in masculine fragrances (see Table 15).

The rather expensive price severely limits the use of expressed lime in flavorings. However, new processing methods are making the oil from the small soft fruit more accessible. It does blend well with and modify other citrus notes especially lemon. It, like lemon, is a good masking agent.

*Mandarin Oil.* In contrast to tangerine, mandarin oil has an amine-type (i.e., fishy) topnote. Although sweet, one would not consider the aroma fresh or refreshing as with other citrus oils. It possesses a rich floral undertone.

The use of mandarin in perfumes is reserved mainly as a modifier for other citrus oils.[30] Arctander also claims its use in nerolic bases, and in fantasy moss notes. The latter is demonstrated in Table 16.

Again, its application in flavorings is mainly as a modifier for citrus compositions, especially with orange and bitter orange. It enhances, intensifies and enrichens orange character. The major application is in citrus beverage compositions.

*Bitter Orange Oil.* This oil possesses fresh citrus topnotes, but is considered less sweet, and even bitter and dry.[31] It has floral and aldehyde characteristics. The tenacity is greater than most other citrus oils.

Table 18

**Orange (and other natural oils) blends for foods and beverages (% w/w)**

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Cold Pressed Valencia Oil | 83 | 80 | 72 | 80 | 73.25 |
| 5X Orange Oil* | 12 | 12 | 10 | 10 | 10 |
| Terpenefree Orange Oil** | 5 | 5 | 5 | 5 | 5 |
| Terpenefree Lemon Oil*** | | 3 | | | |
| 4X Lemon Oil**** | | | 13 | | 0.25 |
| Mandarin Oil-Italian | | | | 5 | |
| Cold Pressed Grapefruit Oil | | | | | 10 |
| Lime oil Distilled | | | | | 0.5 |
| Tahiti Lime Oil ***** | | | | | 1 |

** Citronova 533-Firmenich*
***Templar C1809-Felton*
****Templar C1592-Felton*
*****Citronova 400-Firmenich*
******Citronova 501-Firmenich*

The classic application for bitter orange oil is in eau-de-Cologne. It is also used in chypre and fougere compositions and provides a fresh top-note in aldehydic, floral, and fruity perfumes. Bitter orange oil may be used in the reconstitution of jasmine and bergamot.

In flavorings, this oil can be used to provide a citrus topnote or act as a modifier in a citrus blend. The major application is in citrus flavorings for beverages, especially liqueurs (see Table 17). It also intensifies the orange character in soft drinks.

*Orange Oil.* The most widely used citrus oil is cold pressed orange oil. It possesses a light sweet, fresh topnote with fruity and aldehydic characters. It is characteristic of the rind of the fruit. The essence oil recovered during the evaporation of the juice has fruity, and green characters in addition to the natural orange note.

Many masking fragrances for household products make use of orange oil due to its pleasing character, ability to blend with other aromatics, low cost and availability. It also finds use in eau-de-Colognes, chypre, aldehydic, fougere, and fruity perfume compositions. Several prototypes in Tables 11, 12 and 13 demonstrate the versatility of sweet orange in perfumery.

Orange oil is widely used in the flavor industry, especially in beverages, and candies. It can provide the topnote for citrus flavorings as well as the characteristic and most universally accepted flavor. The essence oil is used almost exclusively in the juice industry as it introduces many of the fresh, natural, fruity notes lost during processing. Table 18 contains several basic orange and citrus prototypes:

1. This fundamental orange flavoring uses deterpenated oils for character, strength and the clarity needed in finished beverages (up-types), gelatin desserts, and hard candies.
2.3. The use of lemon modifies the primary flavoring and gives added strength and character.
4. The use of mandarin results in a richer, fuller and sweeter flavor, reminiscent of blood orange. Formulations such as this are useful in cake mixes, as they withstand the rigors of heat.
5. This complex blend represents an orange predominant citrus punch.

*Tangerine Oil.* Tangerine should not be used interchangeably with mandarin. Tangerine has a sweeter, fresher quality, especially in the topnote. It has a thinner body and lacks the richness and perfumy character of mandarin.

Used only to a minor degree in perfumes, tangerine is mainly a modifier in eau-de-Colognes or a novel topnote for aldehydic perfumes. Tangerine is used more in commercial flavorings, but primarily as a modifier. It is used in candy and soft drinks, as well as citrus (example, lemon-lime) soft drinks.

### Safety Considerations

Citrus essential oils by definition are natural products, thereby connoting health and well

# Table 19

## CITRUS OILS

| Essential Oil | Botanical Source | Geographical Source | Flavor (Odor) Characteristics | Chemical Constituents | Utility | Volatility | Chemical Characteristics | Sensitivities Heat | Light | Oxygen | Acid | Alkali | Storage |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Bergamot | C.aurantium: bergamia: rind | S.Calabria, Italy | sweet, fresh, lemon-bitter orange topnote. rich, herbaceous, floral | limonene, linalool linallyl acetate nerol, a-terpineol 4-terpineol | topnote blender modifer | high | less reactive than other citrus | high | high | high | low | high | cool inert headspace protect from light |
| Lemon | Citrus limornum: rind | Calif., Florida Sicily S.Africa Spain, Isreal | fresh, sharp, sweet, Lemon-Citrus clean refreshing | limonene, citral (neral:geranial), octanal, decanal, neryl acetate, geranyl acetate | modifier blender body character | high | rapid deterioration on exposure to heat, air, & light increase in viscosity upon aging | high | moderate | high | moderate | high | cool inert headspace protect from light antioxidants |
| Orange (Bitter) | C.aurantium, amara: rind: semi-ripe fruit | West Indies Guinea Spain, Italy | fresh, citrus:floral aldehydic | limonene, citral decanal, linalool, a-terpineol | body modifier topnote | high | rapid deterioration on exposure to heat, air, & light increase in viscosity upon aging | high | high | high | moderate | high | cool inert headspace protect from light antioxidants |
| Orange (Sweet) | C.aurantium, dulcis: rind | Florida, Calif. Brazil, Italy S.Africa, Israel | fresh, citrus orange sweet, fruity aldehydic | limonene, citral, octanal decanal, linalool methyl anthranilate | body modifier topnote character | high | rapid deterioration on exposure to heat, air, & light increase in viscosity upon aging | high | high | high | moderate | high | cool inert headspace protect from light antioxidants |
| Lime (Distilled) | Citrus aurantifloria Swingle: steam distillation | West Indies, Mexico, Guatemala | fresh-sharp citrus-terpeny floral-lilac -"lime"- | limonene, dipentene citral, octanal nonanal, decanal linalool, geraniol, a-terpineol | blender modifier topnote body | high | rapid deterioration on exposure to heat, air, & light increase in viscosity upon aging | high | moderate | high | low | moderate | cool inert headspace protect from light antioxidants |
| (Expressed) | C.aurantifolia, Swingle: rind | | fresh citrus-lemon | | | mod-high | | high | moderate | high | moderate | high | |
| Grapefruit | Citrus paradisi: rind | Florida, Texas, West Indies, California, Brazil | fresh-citrus bitter-sweet grapefruit | waxes, octanal decanal, geraniol citral, dimethyl anthranilate nootkatone 1-p-menthene-8-thiol | body blender modifier character | mod-high | rapid deterioration on exposure to heat, air, & light increase in viscosity upon aging | high | high | high | moderate | high | cool inert headspace protect from light antioxidants |
| Mandarin Tangerine | Citrus reticulata: rind | Mediterranean Florida, Brazil | sweet-citrus fresh, orange-like | decanal, p-cymene linalool, a-terpineol nerol, terpenyl acetate, octanal, nonanal, dodecanal, citronellal dimethyl anthranilate | modifier topnote character | high | rapid deterioration on exposure to heat, air, & light increase in viscosity upon aging | high | high | high | high | high | cool inert headspace protect from light antioxidants |

being. There are, however, some constituents contained in these oils with toxicological implications of which the perfumer especially should be aware. Specifically, certain phototoxic agents are known to be present in bergamot oil expressed, lime oil expressed, lemon oil expressed, and bitter orange oil. The distilled or rectified versions of the above oils, and all grapefruit, mandarin and orange oils exhibit no phototoxic effects.

IFRA has developed the following guidelines:[5]

- Bergamot oil should not be used at levels that will result in a level of 5-methoxypsoralen (bergapten) in the fragrance oil of 75 ppm or greater. Assuming a 5-MOP content of 0.35% this translates to about 2% bergamot oil in the fragrance compound.
- Bitter orange oil should not be used at levels greater than 7% in the fragrance compound.
- Lemon oil cold pressed should not be used at levels greater than 10% in the fragrance compound.
- Lime oil expressed should not be used at levels greater than 3.5% in the fragrance compound.

## Summary

Table 19 summarizes some of the key topics which have been discussed in this article.[32-33] In an industry of ever increasing complexity and sophistication, citrus oils and their isolates retain a key position on the palate of the perfumer and flavorist. One can expect however that a new sophistication will become a part of future augumen chemistry. Biochemical and genetic regulation of secondary metabolites responsible for citrus aroma appears on the horizon.

Technology, such as taught by Japikse, et al.[34-35] is already being employed to modify the volatile profile of citrus oils. Japikse prepares concentrated orange aroma compositions characterized by enhanced concentrations of desirable aromatics and decreased concentrations of undesirables by using dense gas solvent extraction. These new isolates and oils deliver, as do traditional oils, characterizing aromas, fresh topnotes, and harmonious blends.

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Address correspondence to Robert L. Swaine, Jr., 12061 Chardon Lane, Cincinnati, OH 45246.


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