Citrus essential oils

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The term "essential oil" originated when the earliest practitioners of medicine spoke of the *Quinta essentia* (quintessence) of a drug that was, to them, the most sublime extractive. It represented the efficient part of the drug.[1] In time, the term "essential oil" was used to represent that part of the plant or fruit necessary for the characteristic flavor or other useful property of the natural product. A citrus essential oil is the part of the fruit (located in the peel) necessary for the characteristic flavor of that particular fruit. In recent years other flavor fractions such as distilled oils or distilled aqueous aroma solutions (essences) have been developed for use in flavoring citrus products. But the essential oil from the peel still remains a basic flavor ingredient in most citrus products.

The major cold-pressed citrus peel oils recovered commercially and listed in order of their increasing commercial value are orange, grapefruit, mandarin, lemon, and lime; cold-pressed lime oil is only slightly more valuable than lemon oil. In commercial methods of peel oil recovery, the oil sacs are mechanically ruptured and the oil is washed away from the peel with water; some pressing action usually is involved. The resulting oil-water emulsion is separated by centrifugation. Sometimes enzymes, emulsion-breaking agents (e.g. Dupanol), and heat are used for maximum yield of the valuable oils of lemon and lime.

In the United States, citrus peel oils usually are extracted commercially by use of either the FMC in-line extractor or the Brown International Corp. peel shaver. In the FMC process, a fine spray of water washes the oil from the mashed peel at the same time the juice is being extracted through a center tube that cores the fruit. In the Brown process, peel halves expelled from the juice extractor are shaved to remove the flavedo. The flavedo then mixed with water and put through a knurled roll to transfer the oil to the water in an emulsion. In either process, the volatile water-soluble components of the oil are partitioned between the oil and water. Use of excess water can significantly decrease the total aldehydes in the finished oil.[2]

A new whole fruit oil extraction system from Brown International Corp. is advantageous because its use of recycled water improves disposal of waste water by decreasing the volume generated during oil recovery. The oil extractor consists of a bed of rolls covered with needle-like projections that are mounted in a shallow tank (see figure 1). Whole fruit advances in a single layer across the rolls which are rotating in the same direction as the fruit movement. The rolls pierce the oil cells located in the outer portion of the peel to release the oil. An overhead paddle conveyor maintains uniform flow of fruit. Water enters at the fruit discharge end and flows countercurrent to the fruit flow, forming an emulsion with the released oil. The oil-water emulsion discharges over a weir which maintains liquid level. The emulsion is screened in a paddle finisher and then centrifuged in two stages. The low solids content of the emulsion permits high efficiency in the first stage of centrifugation and recycling of water from the centrifuge back to the oil extractor without further purification.

When the juice for canning operations is deoiled by partial distillation in a vacuum deoiler, an oil is separated by centrifugation before the aqueous condensate is returned to the juice. The oil obtained is a distilled juice oil that differs markedly from peel oil because it lacks the high-boiling components of the peel oil. Its composition has been altered during distillation when important flavor components are partitioned between oil and water.

Other distilled oils (usually sold as d-limonene) are produced during pasteurization of peel for pectin recovery, in waste heat evaporators, in preparation of concentrated (folded) oils by distillation, and by distillation of the aqueous discharge from the oil centrifuge. These distilled oils have not been widely used as flavorings but those from lemon and lime oils might have potential use. Development of uses

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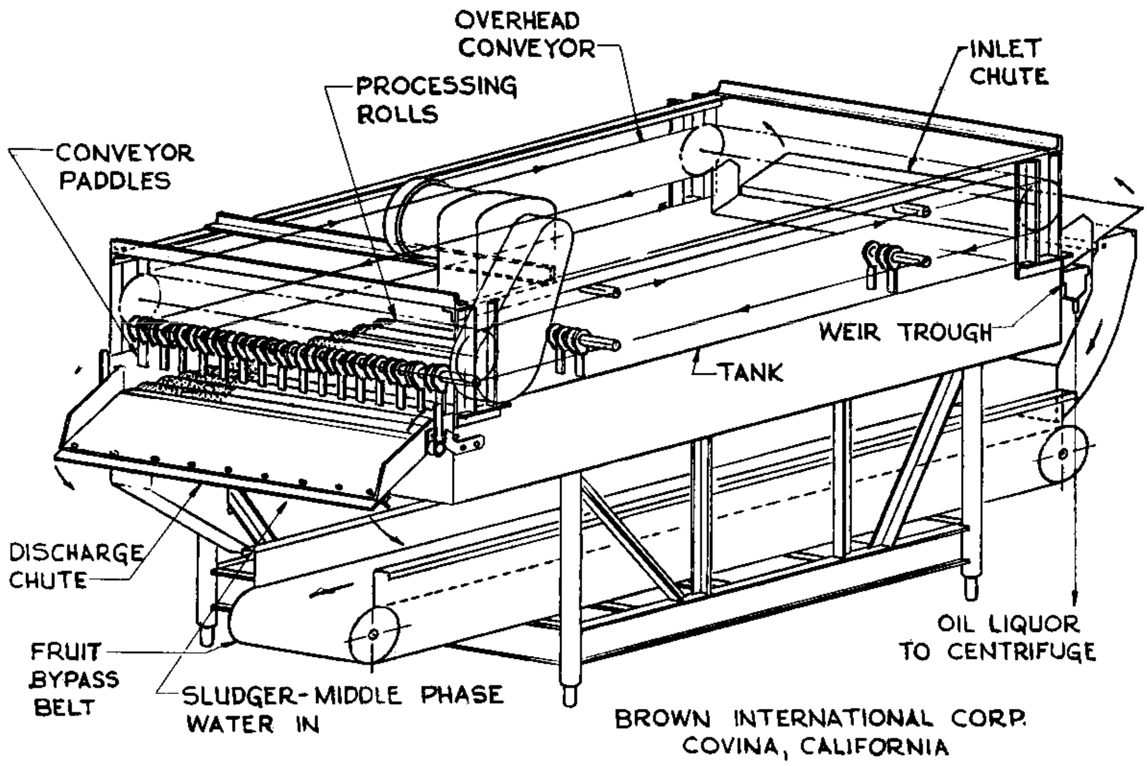
Figure 1

BROWN OIL EXTRACTOR



for distilled oils could indirectly facilitate disposal of waste water because the oil in effluent interferes with bacterial growth in some waste disposal processes.[3] However, many citrus processing plants use spray fields for their heavy wastes and find that certain soil organisms can break down high levels of citrus oils. Additional distilled oils, as well as distillates from aqueous fractions, are produced during the commercial processing of citrus juices and are widely used in flavoring citrus products.

Orange Oil

It has been more than three decades since frozen concentrated orange juice was first produced commercially in Florida. In that time, both the size of the Florida orange crop and the percentage of the crop that is processed have grown steadily until processed products have become the dominant use for oranges grown in Florida. However, large plantings have been made in Florida of orange varieties that mature early, thus allowing an earlier start and a larger fresh fruit marketing season. Some of the biggest processing problems connected with fruit varieties are caused by these fruit grown for the fresh market that are not well-suited to processing.

California has continued to grow oranges primarily for the fresh fruit market so that "packinghouse eliminations" from this market make up a significant portion of the fruit used in processing. Early season juice of one of the two primary varieties grown in California, the Washington navel orange, develops intense bitterness after extraction and much research has been conducted to try to minimize or remove the bitter principles in this variety to make it better-suited to processing.[4] This juice is generally blended with nonbitter juice from other varieties.

From late season navel oranges, California processors produce considerable bulk concentrate that is not bitter. It has very good color and can be used in orange drinks and breakfast beverages. A limited amount of navel orange concentrate can be blended in frozen concentrated orange juice. The limiting factor is not necessarily bitterness but may be a characteristic "navel concentrate flavor."

Certain areas of Florida, such as the Indian River section, produce fruit primarily for the fresh market. However, the juice from packinghouse eliminations of the Washington navels, from certain orange-mandarin crosses, and other hybrids can be blended with juice from processing oranges because these that have objectionable flavors constitute such a minor portion of the total fruit processed. If juice from the hybrid varieties is blended much above the legal 10% level, flavor differences can be detected in the product.

In Florida, most of the peel oil from late-season (Valencia) oranges and from early- (mostly Hamlin and Parson Brown) and mid-season (Pineapple) fruits is recovered if the price is sufficiently high and there is not a large carryover of oil from the previous season. A few processors lack the efficient equipment that would make recovery of oil from early- and mid-season oranges profitable. They recover peel oil in the peel-drying process as a distilled, low quality oil and sell it as d-limonene. Valencia peel oil brings a premium price and it is used to flavor much of the frozen concentrated orange juice. However, early- and mid-season oils also are used in frozen concentrated orange juice and in frozen concentrate for breakfast orange beverages. Orange oils are dewaxed by storage in large cooled tanks (the smaller processors use 50 gal drums) and most of the oil is decanted from the precipitated wax. The small amount of remaining oil is separated from the wax in a centrifuge.

The major California orange oil is from the Valencia cultivar although Washington navel orange is also produced. Kesterson and coworkers showed that Florida and California orange oils are similar in specific gravity, refractive index, evaporation residue, and optical rotation but California oils generally have a higher ester content and a deeper color than Florida oils.[2]

Quantitative comparison of Florida mid- and late-season oils showed no significant differences in composition even though flavoring properties of late-season oil are regarded as superior.[5] Cold-pressed orange oil contains about 96% terpene hydrocarbons (mostly (+)-limonene), 1.6% aldehydes (largely octanal and decanal), 0.8% alcohols (mostly linalool), 0.3% esters (largely octyl and neryl acetates), and 1% nonvolatile high-boiling components that cannot be detected by gas chromatography.[6,7,8] The oxygenated components, especially the aldehydes, are most important to the flavor of orange oil and the total aldehyde content is used as one measure of oil quality. Besides octanal and decanal, one high-boiling aldehyde, sinensal, is believed to contribute significantly to orange flavor. Its instability in the pure form has hampered taste panel evaluations of this aldehyde which is found in two isomeric forms (α- and β-sinensals) in orange oil. Both isomers have similar aromas and the β-isomer predominates. The small amount of citral (neral and geranial) present in orange oil seems important to orange flavor.[9] Basic orange flavor has not been attributed to any one single component of orange oil. Apparently, a combination of components in certain proportions is responsible for the basic flavor of orange.[6]

The terpene hydrocarbons make some contribution to the flavor of orange and other citrus oils as well. Thus, concentrated (folded) oils that contain the oxygenated components from cold-pressed oils but have greatly diminished percentages of terpene hydrocarbons have somewhat different flavoring properties than the cold-pressed oils from which they were made. This difference is attributed primarily to the absence of the terpenes that serve as carriers for other (oxygenated) components in cold-pressed oils. During the folding process, however, the proportions of different oxygenated constituents also change and this may account for some of the differences in flavor between folded and cold-pressed oils.

Cold-pressed orange oil provides the basic flavor for orange products. However, increasing numbers of orange products are being fortified with other natural flavor fractions to enhance the fresh "floral" note that is associated with fresh orange juice but is lacking in most processed orange products. Aqueous orange essence was the first flavor fraction (other than good quality fresh juice) that was added to frozen concentrated orange juice to try to enhance its fresh floral flavor notes. Aqueous orange essence is a concentrated aqueous distillate from the first stage of an evaporator used in preparing frozen concentrated orange juice. The aqueous essence must first be separated from an oily layer (essence oil) before it is added to the frozen orange concentrate. Aqueous essence continues to be the fraction most widely used for this purpose and now is added to about half the pack of Florida frozen concentrated orange juice. Aqueous essences is added to some single-strength juice but it is much less stable in single-strength than in frozen concentrated juice.

Orange essence oil contains many of the same components as aqueous essence that provide fresh floral notes in juice and this oil is becoming more widely used in flavoring orange products. This distilled oil lacks the natural high-boiling antioxidants that stabilize cold-pressed orange oil and so it is usually mixed with cold-pressed orange oil (33-50% essence oil in the mixture) to increase its stability. Due to the addition of aqueous essence and essence oil along with cold-pressed peel oil, highly acceptable frozen concentrated orange juice can now be made without the need to add any high quality fresh juice to enhance the flavor.

Fixed flavors for use in dry beverage mixes are now being produced in considerable volume and citrus flavors are by far the most popular. Cold-pressed oil, folded oil, and essence oil are all used. Sometimes "exotic" imported oil or mandarin oil is added to orange flavors and Italian oil (hand-pressed) is added to lemon flavors. The oils are fixed (prepared in a dry or granular state) by spray drying with gum acacia, "plating" on sugar, or by the Sunkist "Permastable" process.

Grapefruit oil

For grapefruit juice of acceptable flavor, cold-pressed oil should be present at about the 0.010% level. The major white varieties grown and processed in Florida are the Marsh seedless and the Duncan. No attempt is made to separate the two varieties during processing either for the juice or the oil and the mixed oil is used to flavor frozen concentrated grapefruit juice. In Florida, pink and red varieties of grapefruit are produced primarily for the fresh market and small quantities of these varieties can have detrimental effects on the quality of processed juice and oil. Unless special precautions are taken, pink grapefruit juice turns an undesirable "muddy brown" color, has a low color score, and possibly a low grade rating. The color of pink grapefruit is due mainly to the lycopene in the endocarp although some lycopene is also present in the peel. Contamination of white grapefruit oil with small amounts of pink or red grapefruit oil gives it a pink tint; such oil is difficult to sell. In Texas, pink and red grapefruit varieties are widely grown for the fresh market and their pleasing color and sweet flavor bring a premium price. However, processing of pink grapefruit juice requires special care to preserve the pink color during processing and storage.[10]

White grapefruit oil contains about 89% terpene hydrocarbons (mostly (+)-limonene), 1.8% aldehydes (largely octanal and decanal), 0.5% alcohols (mostly linolool), 0.3% esters (largely octyl and decyl acetates), 0.5% ketones (mostly nootkatone), and 7.5% nonvolatiles.[7, 11] In grapefruit oil, as in orange oil, total aldehyde content is a measure of oil quality. More esters are present in significant quantities in grapefruit than in orange oil and they may play an important role in grapefruit flavor.[12] The sesquiterpene ketone, nootkatone, has an intense grapefruit-like aroma and flavor and is a component of some grapefruit oils. However, many good quality grapefruit oils have been found to have only a trace of nootkatone. Thus, a combination of components in the right proportions is apparently necessary for the full flavor of high-quality grapefruit oils.

Nootkatone is an effective compound for flavoring synthetic grapefruit-flavored beverages. One popular grapefruit-flavored beverage was originally formulated with grapefruit oil. However, the supply of grapefruit oil varied so the beverage was flavored with nootkatone and its volume of sales did not decrease. Nootkatone is synthesized from the sesquiterpene, valencene, which can be isolated from orange essence oil in reasonably pure form (70-90% valencene) by distillation.

Aqueous grapefruit essence and essence oil both have good, full-bodied aromas unless collected in the early part of the season. Currently, some aqueous essence and essence oil are used to flavor single-strength juice reconstituted from frozen concentrated grapefruit juice.

Tangerine (mandarin) oil

The term "mandarin" is commonly used to denote all loose skin varieties; the majority are crosses between tangerine and some other fruit. Tangerine oil is by far the most valuable of the mandarin oils. For maximum use of tangerine juice, it is usually blended up to the 10% legal level in orange juice. Only small volumes of pure single-strength tangerine (and some temple) juice and frozen concentrate are produced because the unusual flavor is not readily accepted by consumers. Tangerines are usually processed separately from oranges so that the tangerine juice can be blended with orange juice that has a low color score and because tangerine oil brings a premium price (approximately 10 times that of a late-season Florida orange oil). The other mandarin oils (tangelo, murcott, temple) only return two to three times the value of orange oil. Tangerine oil is used to flavor the small amount of frozen concentrated tangerine juice that is produced but it is also widely used in flavoring tangerine-flavored desserts, candies, and other products.

Because there are many mandarin varieties, quantitative values for components of their oils vary more widely than for oils of any of the other four major kinds of citrus.[13] Dancy tangerine oil contains about 94% terpene hydrocarbons (mostly (+)-limonene), 1.1% aldehydes (largely octanal, decanal, geranial, α-sinensal), 0.5% alcohols (mainly linalool), 0.25% esters, and 4% nonvolatiles.[7,14] As with orange oil, no single component has been identified as the source of the basic tangerine aroma and flavor. However, α-sinensal is present at approximately 0.2% of the oil and is believed to contribute to tangerine flavor. Thymol, thymol methyl ether, and dimethyl anthranilate are also believed important to tangerine flavor but have not been evaluated by definitive taste tests.[14,15]

Aqueous tangerine essence and essence oil can be separated during the preparation of frozen concentrated tangerine juice. However, they are rarely collected because they often have "fishy" aromas and do not enhance the flavor of tangerine concentrate. This fishy aroma is very labile and disappears when anhydrous essence extract is prepared for gas chromatographic analysis.[16]

Lemon oil

Cold-pressed lemon oil is a valuable commodity used not only in food flavorings but also in cosmetics and liquid cleansers because the aroma and flavor are widely accepted by consumers. The lemon processing industry developed primarily for collection of the valuable cold-pressed peel oil and frozen concentrated lemonade was produced in part to dispose of the juice in some profitable manner. The California citrus industry has produced large quantities of lemons for the fresh market for many years and packinghouse eliminations are diverted to processed lemon products. The Florida citrus industry has only recently made large plantings of lemon trees. As in California, the major lemon varieties planted in Florida are those that are desirable for the fresh market rather than for processing. Most lemons processed in Florida are those the packinghouse eliminated from the fresh market (usually because of fruit size). Only 40-50% of the lemons entering packinghouses are acceptable for the fresh market.

Composition differs markedly between the oil of lemon and that of other citrus. The main hydrocarbon (+)-limonene is present in much lower quantity in lemon oil (approximately 65%), but other monoterpene hydrocarbons, especially β-pinene and γ-terpinene (approximately 8-10% each), are present in relatively high quantities. The most important contributors to lemon oil flavor are neral and geranial (together called citral) and lemon oil quality is judged on its citral content. Some lemon oils contain up to 13% citral but a range of 2-4% citral is optimum for a high quality oil. The primary esters in lemon oil are neryl and geranyl acetates and they are believed important in providing a desirable full-bodied lemon flavor. Alcohols in lemon oil, especially α-terpineol and terpinen-4-ol, can vary considerably. A high level of these two alcohols could indicate abuse of the oil during preparation. The high acidity of lemon juice can cause the formation of these compounds by hydration of the major terpene hydrocarbons present in the oil. Nonvolatiles in lemon oil comprise about 2% of the oil and they are reported to stabilize the oil during storage.

The aromas of aqueous lemon essence and essence oil are very pleasant and are more characteristic of the aroma of the fruit than are the aromas of orange, grapefruit, or mandarin essences or essence oils. Aqueous lemon essence was used experimentally in lemon-flavored beverages but it probably has greater potential than has been realized. Lemon essence oil is used in flavoring some lemon products.

Lime oil

Cold-pressed lime oil is usually prepared from the Persian (Tahitian) cultivar. Because of the number of oil glands in the peel, cold-pressed peel oil can be recovered profitably with commercial extractors and other peel oil recovery equipment. The volume of cold-pressed oil produced is small compared to that of distilled lime oil recovered from the Mexican (West Indian or Key) cultivar but the cold-pressed oil brings the highest price of any major citrus oil. The Mexican lime contains such a small amount of peel oil that the only profitable way to recover the oil is to mash the entire fruit and distill the oil from the mixture. Then the peel oil is in intimate contact with the acidic juice and is profoundly changed during distillation. Those changes alter the composition of the oil sufficiently to give it a strong "reverted" flavor that has been accepted by consumers throughout the world as the typical lime flavor. In fact, the flavor and composition of cold-pressed lime oil resembles that of lemon oil more closely than distilled lime oil. Distilled lime oil is widely used in preparing lime-flavored candies and other food products. Even producers of synthetic lime flavors seek to mimic the flavor of distilled rather than cold-pressed lime oil.

The composition of cold-pressed lime oil is similar to that of lemon oil in that it has relatively high quantities of β-pinene and γ-terpinene (approximately 10% each) and a limonene content of 50-65%. The percentages of citral and of neryl and geranyl acetates seem to be higher in cold-pressed lime than in lemon oil. The percentage of nonvolatiles is considerably higher in lime (7%) than in lemon oil and is due mainly to the presence of one coumarin, limettin.

Composition differs markedly between cold-pressed and distilled lime oils. Citral, β-pinene, and γ-terpinene are much lower and *p*-cymene, 1,4-cineole, 1,8-cineole, terpinen-4-ol, and α-terpineol are much higher in distilled than in cold-pressed oil. The latter five compounds are formed by degradation of the former three compounds during the extraction and distillation. Distilled lime oil has virtually no nonvolatile constituents to protect it from oxidation during storage whereas cold-pressed lime oil has high-boiling components.

Aqueous lime essence and essence oil are highly aromatic with the good aromas characteristic of the fresh fruit. However, these fractions have not been widely used to flavor citrus products. Perhaps it is because the stronger flavor of distilled lime oil is so firmly entrenched as the typical lime flavor.

Conclusions

Cold-pressed citrus oils are widely used to flavor both natural and synthetic citrus-flavored foods. Some of the oils are also used as bases for partly synthetic oils wherein certain chemicals are added to the natural oils to emphasize specific flavor notes. The recent trend toward natural ingredients in foods should increase the use of natural citrus oils and aqueous essences. They provide a wide range of flavors and solubility characteristics for use in foods, cosmetics, and cleansers and can be declared as natural ingredients on the label.

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