Chapter 1

Natural Raw Materials

Introduction

When I joined the flavor industry, my first reference books were the six volumes on Essential Oils by Guenther[1]. Even then the analytical information was way out of date, but I was enthralled by the enthusiasm of the writer for such an inexhaustible subject. Essential oils and other natural raw materials are often relatively simple examples of nature at work. This makes them ideal subjects for training. Understanding the relationships between essential oil components forms the best starting point for the novice or trainee flavorist.

Types Of Natural Flavor Raw Materials

Essential Oils: Essential oils are normally only isolated from herbs, spices and foods that contain high levels of flavoring components. The most common method of isolation is steam distillation.

Steam, generated in a separate boiler, is blown through the botanical material on grids in the still. The essential oil and the water are immiscible, each exerting its own vapor pressure as if the other were absent. The mixture boils when the combined vapor pressures equal the surrounding pressure. The steam and essential oil are condensed and separated. Most, but not all, essential oils are lighter than water and form a layer at the top of the separator. The excess water is removed continuously. Some oils are heavier than water and the function of the separator must be reversed. The attractions of steam distillation are its relative simplicity and the fact that components of the oil with boiling points up to 300°C are distilled at temperatures well under 100°C. The process also carries a number of disadvantages. Many chemicals are not steam volatile and are not

carried over in the oil. This applies particularly to many chemicals responsible for taste and antioxidant effects. Some very volatile chemicals are lost during distillation and the process itself may induce chemical changes such as oxidation or hydrolysis.

Water distillation employs the same principle but involves contact between the water and the material to be distilled. This method is often better for flowers and fine powders than steam distillation because steam forms channels in powders and clumps flowers. Water distillation can involve an increased risk of burnt "still odor." This burnt character will gradually dissipate on storage of the oils. Steam and water distillation together combine some features of both methods, but restricts the choice to low pressure steam. The botanical material is separated from boiling water in the lower part of the still by a grid. If the still is heated carefully this method reduces the danger of "still odor." Hydrodiffusion is a variant on the normal steam distillation process where the steam enters from the top of the vessel, and the oil and water mixture is condensed from the bottom. This method reduces distillation time and is especially suitable for distilling seeds.

Dry distillation involves the distillation of the botanical without added water. It is rarely used but can provide a simple way of distilling the oil from plant exudates.

Destructive distillation results in combustion of the botanical in the still. It produces essential oils, such as cade oil from juniper wood, which are not strictly natural and, in any case, should not be used on safety grounds.

Citrus oils are usually isolated from the peel by expression or "cold pressing." This process involves abrasion of the peel and removal of the oil in an aqueous emulsion, which is subsequently separated in a centrifuge. Cold-pressed oils are not heated during processing and have finer aromas and greater stability than distilled oils because of the absence of heat during the process and the inclusion of components that are not steam volatile, especially antioxidants. The only disadvantage to cold-pressed oils is the small loss of polar chemicals into the water used in the process.

Extraction of essential oils with supercritical or liquid carbon dioxide also incorporates the advantage of a cold process and includes some nonvolatile components.

Most essential oils are produced at source. Third world producers often use small traditional stills of variable quality. Small quantities of high quality oils are produced in the United States and Europe from imported botanicals.

Processed Essential Oils: Redistillation can be carried out to remove coarse impurities, such as iron (and the odd rock), from essential oils.

Rectification is the selection of fractions during redistillation. This may simply involve the removal of one or more undesirable fractions from the start and the end of the distillation. It may, at the extreme, involve the removal of most of the terpene hydrocarbons from the oil. In many oils, terpene hydrocar-

bons contribute little flavor and cause problems of instability and poor solubility.

When an oil contains large quantities of terpene hydrocarbons, the removal of some or all of the hydrocarbons is referred to as concentration. The oil remaining in the still after the removal of terpene hydrocarbons is called a concentrated oil. The disadvantages of this process are the effects of heat and the loss of desirable components with similar boiling points to the hydrocarbons. The profile of the oil will be changed and the degree of flavor concentration will not match the physical concentration.

Terpeneless oils are produced by distilling, under vacuum, the volatile fractions of a concentrated oil from the still residues. If the sesquiterpene hydrocarbons are removed during this process the final product is a sesquiterpeneless oil. The main disadvantage of this process is the loss of desirable components in the still residues.

Fractionation can also be taken to its logical extreme to isolate a single component from the oil. This is commonly done to purify a major component, but it can also produce very interesting minor components as by-products from oils that are processed in bulk.

Extraction and chromatography offer cold processes, which achieve the same objective of selecting desirable parts of the oil. Extraction generally provides superior results because vital components are not lost, but it has the twin disadvantages of poor efficiency and a weak end product. Chromatography is expensive and sometimes produces unbalanced concentrated oils.

Liquid Extracts and Tinctures: Edible solvents, such as alcohol and water mixtures, can be used to extract the flavor from many botanicals. The raw material is ground and then percolated with the solvent for up to a week. The mixture may be heated to improve the level of extraction, but this will result in some flavor degradation. Filtration removes the remaining botanical.

Solid Extracts: Solid extracts are often called oleoresins or prepared oleoresins, but this term is more correctly applied to a type of exudate. The process is the same as that for liquid extracts, except that the solvent is removed. The range of extraction solvents used expands to include a number that would not be acceptable in liquid extracts.

Production of solid extracts has shifted from the United States and Europe to the countries of production but quality problems have slowed this trend.

Exudates: Tree or plant exudates are categorized by composition, including gums, gum resins, oleo gum resins, resins, oleoresins and balsams. These respective exuded matters may be processed in a number of different ways. Prepared resins are oleoresins with the essential oil removed. Resinoids are prepared by extraction of resins with a hydrocarbon solvent followed by removal of the solvent. Resin absolutes are produced by alcohol extraction of resinoids and subsequent removal of the solvent.

Concretes: Concretes are prepared by the extraction of plant or animal material, or distillation waters, with a hydrocarbon solvent, commonly hexane.

The solvent is then removed by distillation. Concretes are used in high quality fragrances but are usually not soluble in flavors. In three instances concretes may be preferred to absolutes in flavors. Firstly, when the level of use is very low and solubility considerations are less important. Secondly, when the concrete only contains small quantities of insoluble hydrocarbons. Finally, when the botanical contains some unstable components they are more likely to be retained in the concrete than in the absolute. In these cases the finer odor characteristics of the concrete can give it the edge over the corresponding absolute.

Absolutes: Absolutes are produced by the extraction of concretes, resinoids or essential oils with alcohol at room temperature. The extract is chilled and filtered, and the solvent removed under vacuum. Absolutes were originally developed for use in alcoholic fragrances and are soluble in most flavor solvents at normal use levels. This normally makes them much more practical for flavor applications than concretes, but the additional extraction process results in some loss of odor quality.

Absolute Oils: Prepared by the steam distillation of absolutes, these products are mainly of academic and analytical interest and are not usually commercially available.

Fruit Juices, Concentrates and Distillates: Single strength fruit juices and pulps are sometimes used as flavorings but normally require concentration to be a practical proposition. The first part of the water removed during the concentration process contains some of the volatile aroma of the fruit. These "esters" are also used in flavors, often in conjunction with the concentrated juice. The "fold" of the esters is their concentration relative to the starting juice. The "esters" may be further concentrated by reverse osmosis to produce a highly concentrated and expensive oil. Essence oils are the oil fractions of citrus esters and normally consist of a mixture of true juice oil present in the cells together with some distilled peel oil. Most of the fresh juice character of citrus esters resides in the aqueous fraction.

Other Products: Oil concretes and ottos are simply alternative names for essential oils. Oil concretes acquired their name because precipitated hydrocarbons gave the oils a similar appearance to concretes. Otto is derived from Attar, which has its origins in the Arabic perfume oils.

Quality and Legislation

Many natural flavoring materials, particularly essential oils, are subject to oxidation, polymerization and hydrolysis over time. They should be stored in full glass or metal containers in a dark, cold area. Ideally the headspace in the container should be an inert gas, such as nitrogen.

Adulteration is rife and the traditional physical and chemical standards are out of date. GC analysis is normally the most reliable way of ensuring authenticity.

Many natural flavoring materials are specifically listed in the United States by the Flavor and Extract Manufacturers Association (FEMA) as GRAS, an industry list of raw materials that are Generally Recognized As Safe. These listings are given in the section of this book on Important Natural Flavoring Materials. Most of these materials are also listed in Chapter 21 of the United States *Code of Federal Regulations*. specifically 21 CFR, which also covers a number of raw materials that are not specifically listed by FEMA. These cases are also noted in the same section. The European Union permits a much wider range of natural flavoring materials but has maximum levels set for toxic components (deriving from added flavoring) in finished foods (including beverages). Higher limits are sometimes set for historical reasons in specific foods, e.g., alcoholic beverages. Council of Europe listings have no legal force in most European Union countries (except Denmark), but they are influential.

Markets

The major markets for essential oils and oleoresins are, in descending order, the United States, Europe and Japan. Problems of quality, price and supply, coupled with the ready availability of synthetic alternatives, have led to a steady decline in the use of essential oils. Interest in natural flavors has slowed this trend a little. Oleoresins are not so easily replaced and demand has remained constant.

Uses Of Natural Flavoring Materials

The uses of natural flavoring materials can be grouped into three broad categories.

The first use is to give a characteristic flavor to an end product. The flavor may be simple or, as is the case with cola, part of a blend. Some natural raw materials are also used in nature identical flavors to contribute their own recognizable character. The most common examples of this use of natural raw materials are the citrus oils. Orange oil in particular is a vital part of many nature identical orange flavors. Nature identical chemicals are added to give fresh or juicy characteristics and impact.

Unfortunately many natural raw materials are not recognizable in a finished food. Strawberry juice is typical of many fruit juices. It tastes very weak and burnt in most end products.

The second, and more challenging use of natural flavoring materials is in the creation of blended natural flavors. They sometimes contain key characteristics of flavors and can be used to enhance those characteristics. Coriander oil, for example, contains linalol, which is an important component of the natural aroma of apricots, and is used to good effect in natural apricot flavors. The main disadvantage of this practice is that other, less desirable components of the oil can detract from the overall flavor. This problem can be reduced by isolation of the key component from the oil.