Natural Oil of Bitter Almond

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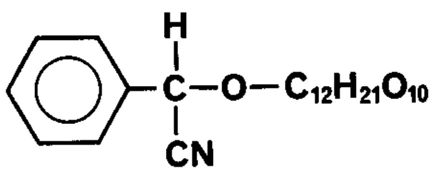
Oil of bitter almond,[1-4] *amygdalia amarae*, is the volatile oil derived by steam distillation of the dried, ripe kernels of bitter almonds (*Prunus amygdalus*), peaches (*Prunus persica*), apricots (*Prunus armenica*) or other kernels containing amygdalin, e.g., cherries (*Cerasus* species) and plums (*Prunus domestica*). Prior to distillation, the fixed fatty oil is freed from the kernels by expression, then the powdered cake is macerated in water to split the glucoside amygdalin (mandelonitrile gentiobioside).



Amygdalin

The glucoside amygdalin,[5] which is present at a level of about 2-4% in the dried kernels, is cleaved enzymatically (enzyme emulsion), to yield benzaldehyde, hydrocyanic acid (also known as prussic acid) and d-glucose as shown in Reaction I.

The freed poisonous hydrocyanic acid is chemically treated with ferrous sulfate and calcium hydroxide. The oil of bitter almond is then distilled, dried and immediately stored under nitrogen. This oil is termed FFPA, or Free From Prussic Acid.

The bitter almond tree is widely cultivated in North Africa (Morocco, Algeria, Tunisia and Egypt), Spain, Asia Minor and, more recently, in the western region of the USA (California). Other lower priced and higher yielding kernels of other fruit trees which contain amygdalin are also used, which yield large quantities of high quality essential oil. The ever-expanding fruit canning industry has yielded huge quantities of kernels as by-products. The kernels from the peaches and apricots grown in North Africa are particularly abundant and useful for the production of oil of bitter almond (see Table I).

Table I. Production of apricots in North Africa

Country	Area (hectares)	Apricot (tons)	15% Kernels (tons)	30% Almonds (tons)	50% Oil (tons)
Algeria	3100	25000	3750	1125	560
Morocco	2700	22000	3300	990	495
Egypt	1960	15700	2350	700	350
Tunisia	1500	12000	1800	540	270

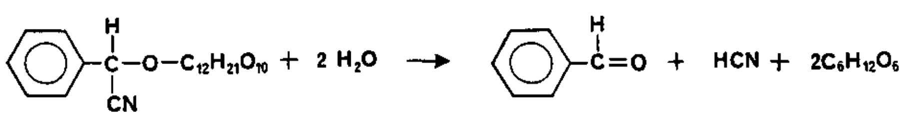
Production

The apricot kernels are first brought to the factory for separating the almonds from the shell (Figure 1). The crushed apricot kernels contain around 20% almonds and 80% shells. The spent shells are used in bakery ovens. The almonds are then crushed in a vise-type press. This yields about 30% fixed fatty oil and 70% of fat-free cake. The oil obtained is equivalent in quality to that of sweet almond oil, which is purified and sold to the cosmetics and pharmaceutical industry. The cakes are then steam-distilled (Figure 2) to yield about 1% of the unrefined essential oil of bitter almonds and 80% of a dried cake which is used as a cattle feed.

The unrefined essential oil of bitter almonds is treated with hydrous ferrous and calcium hydroxide in order to remove the hydrocyanic acid which separates in the form of ferric ferrous cyanide (Prussian blue).

A subsequent steam distillation, followed by filtering and drying, yields about 75% of prussic acid-free essential oil of bitter almond (FFPA). The weight breakdown during production is shown in Figure 3.

The oil produced is tested for hydrocyanic acid (HCN) by reacting an aliquot with 0.1N ferrous sulfate, 0.1N NaOH (green precipitate) and 0.1N HC1. If HCN is present, a blue precipitate is formed. If HCN is absent, the green hydroxide precipitate is dissolved. This is an extremely sensitive test and can detect any traces of HCN present in the oil.[6]



Reaction I

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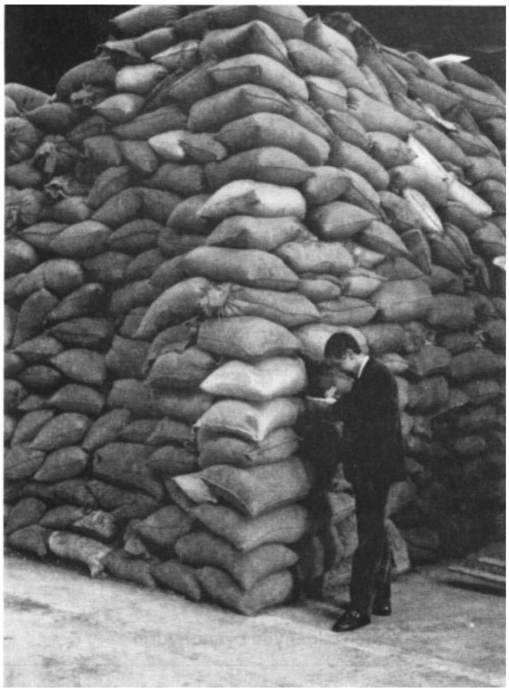


Figure 1 (a and b). The "tons" of apricot kernels (left) and the almonds after removal from their shells (above).

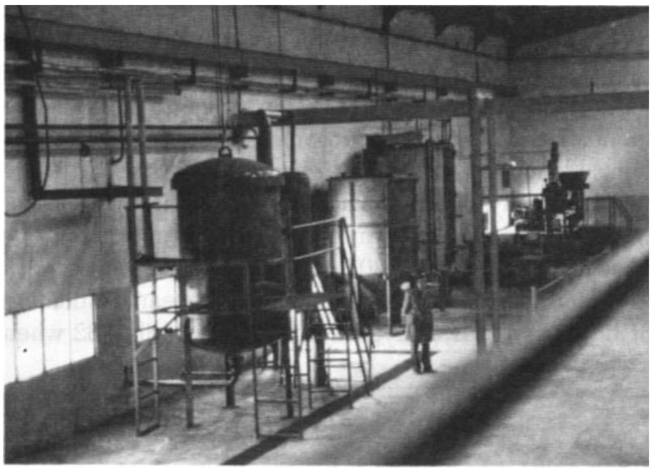


Figure 2. Steam distillation facility for oil of bitter almond

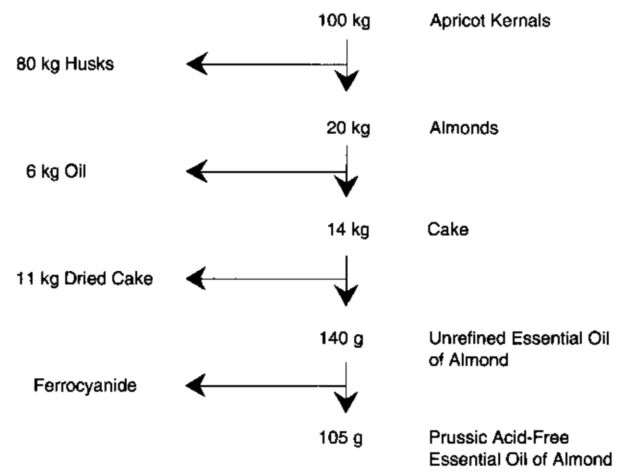


Figure 3. Weight breakdown during production of oil of bitter almond

Besides the liberation of hydrocyanic acid as a by-product from the production of natural oil of bitter almond, a number of chemical problems may be encountered which require knowledge and expertise to control. Among them are:

Air Oxidation of Benzaldehyde—This is encountered during and after the production of oil of bitter almond as shown in Reaction II.

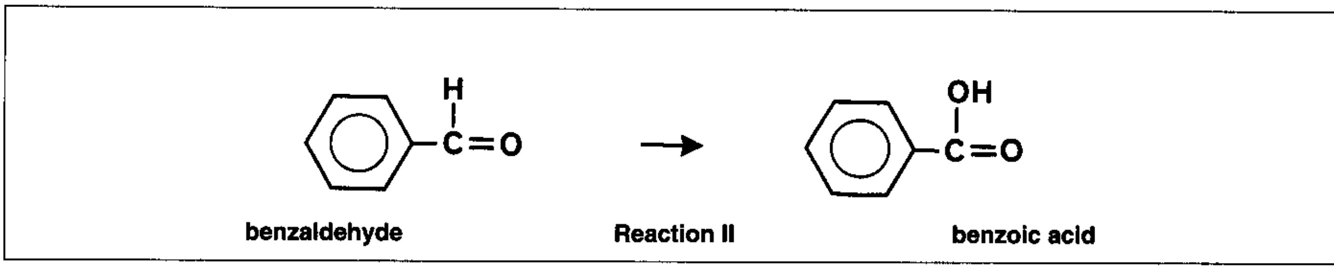
Polymerization of Benzaldehyde—In the presence of HCN, present during the chemical wash and fixed distillation of the final product, two molecules of benzaldehyde condense to form benzoin, which considerably reduces the yield of the oil of bitter almond, as shown in Reaction III.

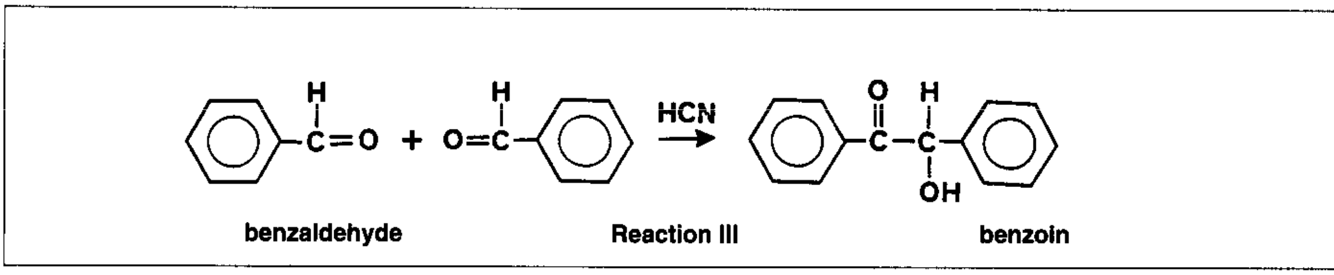
Addition Reactions—Another reaction between HCN and benzaldehyde produces an intermediate compound, benzaldehyde cyanohydrin (Reaction IV).

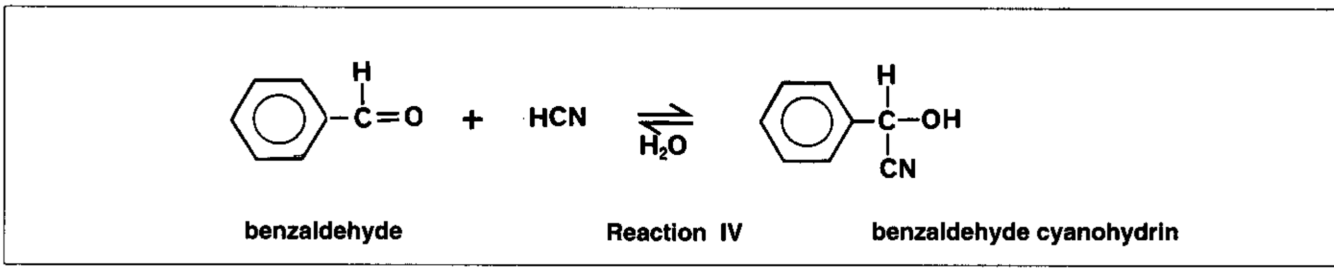
Fortunately, this acid catalyzed reaction is reversible in aqueous medium and, with the appropriate conditions, the yield of benzaldehyde is maximized.

Benzaldehyde

Any discussion on the topic of oil of bitter almond should focus on the active principle, benzaldehyde. This chemical



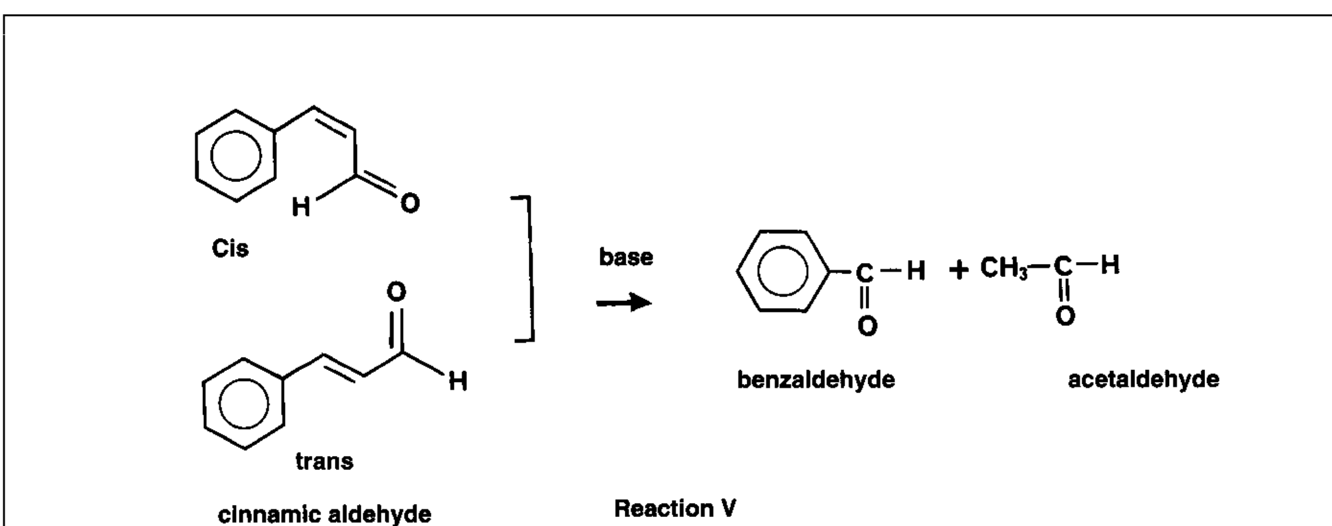


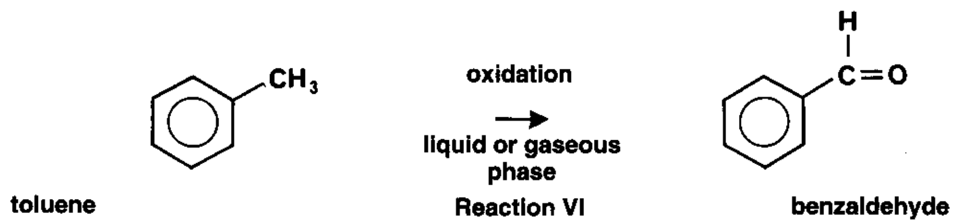


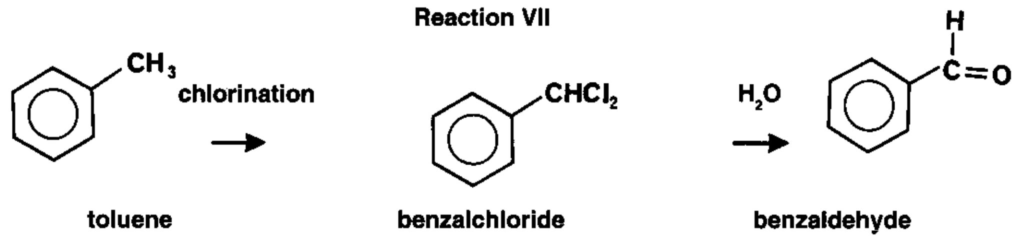
can be obtained synthetically from petrochemical feedstocks at a fraction of the cost of the oil of bitter almond which, if left unchecked, allows for misbranding and adulteration of the natural oil. To further complicate this matter, there exists in commerce two other forms of benzaldehyde. The first is natural benzaldehyde which is obtained via the enzymic or microbial oxidation of natural feed stocks and the other is so-called natural benzaldehyde which is obtained through base catalyzed oxidation of natural feed stocks such as cinnamon bark, cassia oil, cinnamon leaf oil, etc.[7] containing cinnamic aldehyde as shown in Reaction V.

Distinguishing synthetically derived benzaldehyde from those naturally derived benzaldehyde or oil of bitter almond requires a battery of sophisticated analytical tests. This topic will be addressed later in this paper. To lay down the foundation, however, it is appropriate to discuss the chemical, benzaldehyde.

Historically, benzaldehyde (FEMA #2127) was one of the first aromatic compounds to be isolated and chemically characterized.[8] In 1802, Schrader and Vauquelin misidentified the oil generated from the steam distillation of bitter almonds as hydrocyanic acid,[9] until 1832 when







Wohler and Liebig[10] showed that the kernel of bitter almonds contained the glucoside amygdalin, which when enzymatically hydrolyzed, yielded an oil consisting almost exclusively of benzaldehyde with traces of hydrocyanic acid. Since this work was done prior to Kekule's discovery of the molecular structure of benzene, benzaldehyde's structure was not elucidated until 1876 when Lippman and Hawliczek[11] successfully synthesized benzaldehyde by oxidizing toluene.

Benzaldehyde is currently synthesized via one of two general procedures.[9] The first proceeds and involves the direct oxidation of toluene with fewer detectable impurities as shown in Reaction VI.

The second involves the chlorination of toluene to benzalchloride which is readily hydrolyzed to benzaldehyde as shown in Reaction VII.

This reaction, however, has several detectable impurities other than unreacted toluene which is possible in both reactions; namely, benzyl chloride, benzal chloride and benzotrichloride. The presence of oxidized benzoic acid is also possible from both reactions mentioned above.

Thus, the presence of any minute quantities (in parts per million) of toluene, benzyl chloride, benzal chloride or benzo trichloride in either natural benzaldehyde or oil of bitter almond, is a telltale that synthetic benzaldehyde has been added to misbrand and adulterate the natural products.

Other sophisticated techniques for the detection or misbranding of adulteration of oil of bitter almond are currently available.

Detection of Adulteration and Misbranding

Throughout history, the lure of windfall profits has attracted a few in the food industry to "sophisticate," "adjust," "modify," "misbrand" or "adulterate" expensive raw materials with lower-priced additives or substitutes. A number of sophisticated analytical techniques involving the use of both radiogenic isotopes (e.g., ^{14}C) and stable isotopes (e.g., ^{13}C and ^{2}H) has been used to ensure proper labeling and deter the fraudulent use of synthetic compounds to adulterate expensive natural products.

A number of techniques currently exists for the control of authenticity of orange juice by isotopic analysis,[12] vanillin in vanilla beans,[13-17] benzaldehyde in oil of bitter almond,[18-20] citral in lemon grass,[21] menthol[21] and anethole.[22] Other products have also been successfully monitored such as maple syrup, honey, apple and grape juice through the use of stable isotope ratio analysis (SIRA) and radiogenic techniques.[23]

Radiogenic and SIRA techniques, as they apply to the detection of the addition of synthetic benzaldehyde to natural oil of bitter almond, have been adequately addressed and reported in the literature. The reader is encouraged to read the review articles by Krueger and Reisman[23] as well as one by Bricout and Koziet.[21] For the techniques dealing with benzaldehyde and oil of bitter almond, the articles by Culp & Noakes,[18] Schmidt et al.[19] and Krueger[20] should be consulted for the interpretation of the data.

Analytical Controls

Oil of bitter almond FFPA, CAS #8013-76-1, should conform to FCC (1972 or 1981) and EOA (No. 215) specifications.[24,25] These specifications are included in the following analytical controls of this product.[26]

Organoleptic Properties—A colorless to pale yellow clear oily liquid with a characteristic flavor and aroma of almond oil. Odor and color should be compared to a standard that is stored in a refrigerator in a dark-filled bottle. The taste evaluation is made on a diluted sample as follows: Add 1 ml of oil to 100 ml of 95% ethyl alcohol. Then use 0.5 ml of this mixture in 500 ml of sucrose solution.

Physical Properties—Specific gravity at 25°C:1.025-1.065; Refractive index at 20°C:1.535-1.555; Angular rotation:Optically inactive; Boiling point at 760 mm/Hg:177-181°C; Melting point:-26°C +/- 3°C; Flash point, open cup:165°F +/- 5°F; Flash point, closed cup:148°F +/- 5°F; Solubility, water 20°C:3 grams/liter; Solubility, alcohol 50%:1 volume in 5 to 6 volume; Solubility, alcohol 90%:1 volume in 1 volume.

Chemical Properties—Benzaldehyde assay: 98% min. by GC method AOAC 19.098; Hydrocyanic acid assay: <0.01% by AOAC method 19.105; Benzoic acid assay: Below 1% by AOAC method 19.104; Acid value: Not more than 8.0 (FCC 1981); Chlorinated compounds: Passes FCC 1981 test; Heavy metals (as Pb): Passes FCC 1981 test.

Isotopic Properties—Oil of bitter almond FFPA should pass the University of Georgia's Center for Applied Isotope Studies[28] or equivalent. Typical data[26] are as follows:

i. Value of $\delta\ ^{13}C$ is -29.50 to -27.50 (parts per mil 0/00 relative to PDB)
ii. Value of ^{14}C is 15.5 to 17.5 (dpm/gC)
iii. Value of δD is -87 to -95 (parts per mil 0/00) relative to V-SMOW)

The sample has a ^{14}C activity of 107% natural relative to the 1987 reference activity of 15.5 dpm/g Carbon indicating no fossil fuel derived material.

Biological Properties[29]—Based on our experiments, following biological properties were found.

- *Acute toxicity:* The acute oral LD_{50} in rats was reported as 1.49 ml/kg and the acute dermal LD_{50} in rabbits exceeded 3 ml/kg.[30]
- *Irritation:* Undiluted almond oil bitter FFPA applied to the backs of hairless mice and swine produced hyperkeratosis and dry desquamation.[31] Tested at 4% in petrolatum it produced no irritation after a 48-hour closed-patch test on human subjects.[32]
- *Sensitization:* A maximization test[33] was carried out on 25 volunteers. The material (RIFM No. 76-13) was tested at a concentration of 4% in petrolatum and produced no sensitization reactions.[32]
- *Phototoxicity:* No phototoxic effects were reported for undiluted almond oil bitter FFPA on hairless mice and swine.[31]

Storage—Oil of bitter almond should be packed, stored and shipped in containers purged with nitrogen, in a cool area away from sunlight. The material rapidly oxidizes to benzoic acid (white crystals around caps) if not stored properly. Shelf-life, when stored in glass or food-grade approved, epoxy-lined metal containers and under the above conditions, should be about one year. All opened containers should be transferred to smaller containers allowing minimal headspace and purged with nitrogen prior to storage. When alcohol will be used with oil of bitter almond, as in alcoholic beverage applications, it is highly recommended that 10% solution of ethanol be added. It has been demonstrated that a minimum of 10% ethanol has a stabilizing effect on the benzaldehyde content. This is probably due to the reversible acetal formation of benzaldehyde.

Applications of Natural Oil of Bitter Almond FFPA

According to the Research Institute for Fragrance Materials, Inc. (RIFM),[35] oil of bitter almond FFPA has been in public use before 1890 and was used extensively in fragrances in the USA.[35] As the "natural" trend continues in the USA, increased usage of oil of bitter almond is envisioned.

In flavors, no volume estimates are available. It is used extensively, however, in the following applications:

- *Household extracts:* Natural almond extract used for home or institutional cooking purposes has a standard of identity and may only be produced using oil of bitter almond FFPA. Natural benzaldehyde is not allowed in this category.
- *Carbonated beverage industry:* Used extensively in the production of "cherry" flavored soft drinks.
- *Alcoholic beverage industry:* BATF clearly states that alcoholic beverages that are labeled as "natural cherry" flavored, such as brandies, cordials or schnapps can only be flavored with oil of bitter almond. In cases such as Amaretto or other invented name products, it is permissible to use natural benzaldehyde in the

flavor, however, it is not permissible to show a picture of almond or other fruit kernel on the product label.

- *Baking industry:* Used extensively in baked goods and other speciality items with oil of bitter almond taste such as Marzipan, Persipan, Macaroon pastes, etc.
- *Other food and pharmaceutical industries:* Used in confections, chocolates, ice cream, pharmaceutical preparations and other products requiring a natural "cherry" or "bitter almond" taste.
- *Flavor and fragrance industry:* Used in the creation of "natural" flavors and fragrances for use in the baking, beverage, confections and pharmaceutical industries.

Legal Status

Natural oil of bitter almond FFPA, was given GRAS status by FEMA in 1965. It is approved by the FDA for food use (GRAS). In 1974, the Council of Europe included oil of bitter almond in the list of substances, spices and seasonings deemed admissible for use with a possible limitation of the active principle in the final product. *The Food Chemicals Codes* (1981) has a monograph on almond oil bitter FFPA.

The subject of natural vs. synthetic and the legality of labeling a product or a flavor as "natural" has been clearly addressed in the code of Federal Regulations.[36] The Title 21 of the CFR, Section 101.22 clearly states that the term "natural flavor" or "natural flavoring" means the "essential oil, oleoresin, essence or extractive...which contains the flavoring constituents derived from a spice, fruit...whose significant function in food is flavoring rather than nutrition." In response to a letter from a flavor and fragrance company to the FDA dated April 18, 1991, inquiring if benzaldehyde can be called natural if it is derived from cassia oil or cinnamic aldehyde, Manjeet Singh, Assistant Director of the Division of Regulatory Guidance at the FDA, responded by quoting the above paragraph in the CFR and adding:[37]

> "Accordingly, benzaldehyde derived from Cassia oil or cinnamic aldehyde which do not contain benzaldehyde in nature cannot be called a 'natural flavor'."

Earlier, in a letter dated December 31, 1989 also from the same flavor and fragrance company to L. Robert Lake, the director of the Office of Compliance at the FDA, requesting his opinion regarding the use of the term "natural" to describe benzaldehyde from cassia oil or any other source unless such flavoring is obtained by fermentation, extraction or enzymolysis. The Director, Mr. Lake, responded by again quoting the 21 CFR 101.22 and concluding:[37]

"Therefore, a product cannot be called "natural benzaldehyde" if it is obtained by use of chemical reactions such as ozonolysis which was a topic of previous discussion, or such as acid or base catalysts or by means other than those listed in the above regulation."

Thus, to the best of our knowledge and until further clarification from the FDA, it is our opinion, that the so-called natural benzaldehyde which is derived through acid or base catalysis of cassia oil, and of course the synthetically-derived benzaldehyde are unacceptable substitutes for oil of bitter almond or for the purposes of labeling products as containing "natural flavors."

Acknowledgment: *The authors would like to acknowledge the assistance, both technical and commercial, that was generously provided by our staff at Kato Worldwide, Ltd. in New York, and specifically the efforts of Richard Peterson, Nehla Azzo, Gideon Andemicael, Tom Smith and Tom Buell.*

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