An Aroma Chemical Profile

Benzaldehyde

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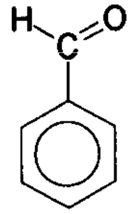
Benzaldehyde's odor and taste are so unique and basic that it, in itself, forms an organoleptic class—benzaldehyde. The odor has a pleasant, sweet, aromatic note and the taste the same, with a slight, sweet, aromatic bite. We recall almonds, marzipan, peach pit meat (what youngster didn't chew a peach pit nut?) and pistachio ice cream.

The industrial cliche for the product is "Bitter Oil of Almonds," a name which has been misleadingly applied to the synthetic product since it emerged from the chemist's flask before the year 1900. Small amounts of synthetic benzaldehyde produced from benzal chloride first appeared on the market as natural oil of bitter almonds about 1890. Since the price ratio between the natural product and the synthetic is significant (currently 100 to 1), the perfumer, flavorist and chemist have been constantly devising methods to differentiate the fraudulent product from the real thing.

The earliest detection methods[6] utilized the precipitation of silver chloride by contacting the aqueous burned residues of benzaldehyde with silver nitrate reagent. Subsequent methods developed for use by both the US Pharmacopeia and the *Food Chemical Codex* employ the visible green-blue color induced in a bunsen burner flame by a copper screen which has been dosed with the product. As industry moved away from the commercial production of benzaldehyde from benzal chloride to direct oxidation of toluene, which yields a product free of chlorine, fraud detection required advanced techniques. At first, carbon-14 isotope analysis was successful in detecting synthetic aldehyde being offered as natural. However, the price differential of $1.00/lb for synthetic versus $100.00/lb for natural benzaldehyde prompted the spiking of the synthetic product with carbon-14 rich material, thus cloaking its nature. Carbon-13/carbon-12 ratios ($^{13}C/^{12}C$) proved ambiguous.[7] The most recent successful method is deuterium/hydrogen isotope ratios.[8] One might say that the

Benzaldehyde



Mwt 106 C_7H_6O
FEMA-GRAS 2127
CAS 100-52-7

Classification:
The first of the series of aromatic aldehydes consisting of a benzene ring substituted with a carbonyl group containing one hydrogen atom. Normally marketed in three grades: Technical, National Formulary (NF), and Food Chemicals Codex (FCC). Both NF and FCC are free from chlorine (FFC). Current production methods usually yield one standard grade which is labeled for the end use.

Additional Names:[1-4]
Benzoic aldehyde
Artificial oil of almonds
Amandol
French: Aldehyde benzoique
German: Benzaldehyd
Portuguese: Aldeido benzoico
Spanish: Benzaldehido

Physical Data:

Appearance:	mobile, colorless liquid
Specific Gravity:	1.041-1.046 at 25°C
Refractive Index:	1.544-1.547 at 20°C
Boiling Point:	179°C
Flash Point:	148°F or 62°C TCC
Odor Threshold:	350-3,500 PPB water[5]
Flavor Threshold:	1,500 PPB water[5]
Solubility:	0.3% in H_2O at 20°C; soluble in ethanol glycerin, propylene glycol, organic esters, ketones, hydrocarbons, chlorinated solvents and essential oils

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crooks are encouraging the advancement of science.

The salient point of the above discussion underscores the true nature of oil of bitter almonds: it is almost pure benzaldehyde, and pure synthetic benzaldehyde is nearly indistinguishable from the natural product. Moreover, during the period 1960 to 1990, almost no natural product was produced and all the "natural" being sold was synthetic, so the question of an organoleptic difference was a moot one.

Natural Sources

As with many desirable aroma chemicals, there is no direct plentiful natural source for benzaldehyde. Currently, the sole noncontroversial commercial source of natural benzaldehyde[9] is the nut meat of apricots, peaches, prunes (plumbs) and bitter almonds. The aldehyde is tied up as a glucoside (amygdalin) and can be released by enzymatic hydrolysis treatment of the meat. The yield based on dry nut meat is about 0.75% by weight. Current production is based on the by-product nuts from fruit processing of peaches, apricots and prunes (plumbs). It is estimated that about 20,000 kg of natural oil of bitter almonds are produced annually from these sources and that this production is of recent development (since 1990). Table I presents an estimate of the sources available should all the nut meat from all the fruit grown be utilized. One should note that all the nuts would not be available due to retail consumption of the fresh fruit.

Table I. Potential sources of bitter almond oil: World total 1994

apricots	1,550,000 kg
peaches	7,309,000 kg
prunes (plumbs)	5,210,000 kg
Total	**14,069,000 kg**

Table II. World flavor usage of benzaldehyde in 1994 by geographical region

North America	230,000 kg
Europe	330,000 kg
Other	245,000 kg
Total usage	**805,000 kg**

Table III. Potential new commercial sources of natural benzaldehyde

Species	Oil yield (%)	Amount (%)	Plant part
Eucalyptus yarrensis Maiden et Cambage	0.1	90	L/T
Prunus laurocerasus L.	<0.1	82	F/L
Zieria compasta Sm.	0.1	90	L/T
Z. cytisoides sens. strict.	0.4	55	L/T
Z. laevigata var. *fraseri*	1.1	80	L/T
Z. smithii Andrews	0.5	50	L/T

L/T = leaves and twigs; F/L = fruit and leaves

The potential available volume of natural benzaldehyde from these sources (Table I) is estimated to be more than 7,000 Mtons, and can satisfy the current world demand for its use in flavors (Table II).

As benzaldehyde usage in flavors is probably growing at a 6% per annum rate, and will possibly continue as such over the next decade, even the potential supplies from the currently used sources will be adequate into the next century.

The issue of potential new plant sources was addressed by Lawrence[10] and is presented in Table III.

The supply of "natural" benzaldehyde obtained from natural cinnamic aldehyde ex-cassia oil is presently a dominant market source and is sold as natural benzaldehyde cassia distillate or roasted cassia oil. A purely thermal cracking of cinnamic aldehyde to benzaldehyde would result in low yields and poor organoleptic quality if no catalysts were employed. The use of inorganic bases as a catalyst would place the "natural" label in question. Thus this source of "natural" benzaldehyde is questionable at least on a theoretic chemical basis.

Benzaldehyde has been noted as a trace constituent in the following materials:

Essential Oils

Acacia farnesiana	trace
cassia	ca 1%
cinnamon leaf	trace-ca 7%
fir needle	trace
Jasminum sambac	trace-ca 1%
mandarin	trace
narcissus	0.05-0.20%
rose - Bulgarian	trace
- Turkish	trace-0.03%
- Ku-Shui	trace
sage	trace-0.20%

Food Stuffs

- almonds
- beer
- bread
- chicken (cooked)
- coffee (roasted)
- HVP volatiles
- mushrooms, Armillaria species
- peaches
- tea
- tomato

History

Benzaldehyde is responsible for the taste and odor of almonds, and this association has overshadowed the fact that benzaldehyde is found as a glycoside in the pit meat of most of the fruits of the Prunus family (i.e., apricots, cherries, nectarines, peaches and plums). Thus, the crude benzaldehyde-containing oils isolated from these "nuts" are commonly referred to as oil of bitter almonds, irrespective of the actual source. Identifying the chemical responsible for this odor proved a "hard nut to crack" for the pioneers in organic chemistry. Investigators as early as 1803 were aware that the extractable organics contained a material with the benzaldehyde odor, but isolation attempts to capture this material led to the discovery of only benzoic acid, due to the facile oxidation of the benzaldehyde during the work-up procedures employed.

Benzaldehyde oxidizes so easily that if a stream of air is bubbled through a container of it, crystals of benzoic acid will appear as a precipitate within 30 minutes. One laboratory wastebasket fire witnessed by this author was due to the spontaneous ignition of paper towels used to clean up a lab benzaldehyde spill. The fire was the result of benzaldehyde's rapid oxidation and its exothermic temperature rise to the flash point.

Early investigations also revealed the presence of hydrogen cyanide (prussic acid) in these nuts and the recognition of its toxicity.

It was the search for the nature of the benzene radical that spurred investigators to explore this area, and in 1832 Wöhler and Liebig, in a mere two-month period, solved the problem with the discovery of benzaldehyde. The discovery was published in a landmark paper which elucidated the structure of the benzoyl radical.[11]

In 1863, Cahours synthesized benzaldehyde via the hydrolysis of benzal chloride, thus unlocking the chemistry for future commercial production. However, the first significant commercial production of benzaldehyde from benzal chloride was not realized until about 1900, as it was dependent on the commercial availability of benzyl chloride. Benzal chloride production via the chlorination of toluene was dependent on the following developments:

- Invention of the dynamo (Siemens, 1866).
- Commercial production of graphite electrodes (1891).
- Commercial production of chlorine (1891).

Thus, after the discovery of the chemical process for the production of benzaldehyde, it took almost 40 years to develop the supporting technology that would allow significant commercial availability.

As in the case of benzyl alcohol, the synthetic dye industry's requirement for benzyl chloride was the impetus for the commercialization of the technology. The production of benzaldehyde was a result of by-product benzal chloride formed in the chlorination of toluene. The first synthetic benzaldehyde seems to have been produced by Schimmel in Leipzig (Germany) and sold as "Bitter Almond Oil" (Bittermandelöl).

Between 1900 and 1910, essential oil houses in Germany and France soon learned to produce synthetic bitter almond oil and market it as natural oil. The purchasers soon learned of the hoax and developed methods of detecting the chlorine residues found in the synthetic product that were not in the natural oil. By 1925, the industry had developed residual organic chloride tests based upon silver nitrate reagents[6] and the copper wire test used today by the *Food Chemical Codex* for FFC grade. The ruse of selling synthetic benzaldehyde as natural continued until the last few years, as the supply of natural was limited or nonexistent and the price differential was great. The FCC test will detect chlorine residue to about .40 ppm. This level was assumed safe until benzal chloride was found to be a carcinogen and subsequently appeared on the proscription list of California's Proposition 65.

Benzaldehyde forms an azeotrope with benzyl chloride (177.9°C) which is so close to the benzaldehyde boiling point (178.9°C) that its separation is difficult. Thus, commercial benzaldehyde produced from chlorinated toluene feed stocks invariably have small amounts of benzyl chloride residues. In the 1950s, Dow Chemical developed a liquid phase, air oxidation route for the production of benzoic acid, with the purpose of producing phenol from the acid. This process produces a benzaldehyde by-product which is totally free of chlorine. The reaction was commercialized by Dow and the production facilities it built were later sold to Kalama Chemical and Chatterton Petrochemical. In Europe, Rhône Poulenc and DSM also began production of benzoic acid and benzaldehyde via similar routes. The availability of chlorine-free benzaldehyde spelled the death of the product made by the chlorination route, although production of benzaldehyde from benzal chloride did not cease until 1993.

Today, no major global manufacturer produces benzaldehyde from chlorinated feed stock.

Synthetic Routes

Chlorination of toluene: The major synthetic process employed from 1900 to about 1970 for the manufacture of benzaldehyde [**3**] was the chlorination of toluene followed by the hydrolysis of the by-product benzal chloride [**2**] (Figure 1).

The benzaldehyde [**3**] thus produced was contaminated with small amounts of organic chlorides, which, if kept below .40 ppm, were never considered a problem for use in flavors or fragrances until benzal chloride [**2**] was found to be a carcinogen. Production of benzaldehyde via this process started to decline in 1960, and ceased in 1993.

Direct oxidation of toluene: In the 1950s, Dow Chemical developed a direct air oxidation of toluene in the liquid phase using cobalt catalysts (Figure 2). The process was designed to provide benzoic acid to be used as a feed stock to produce phenol. The initial step of toluene oxidation produces about 4% by-product benzaldehyde which is marketed at $1.00-1.40/lb versus the selling price of $0.31/lb for phenol; in other words, the by-product is worth more than the product.

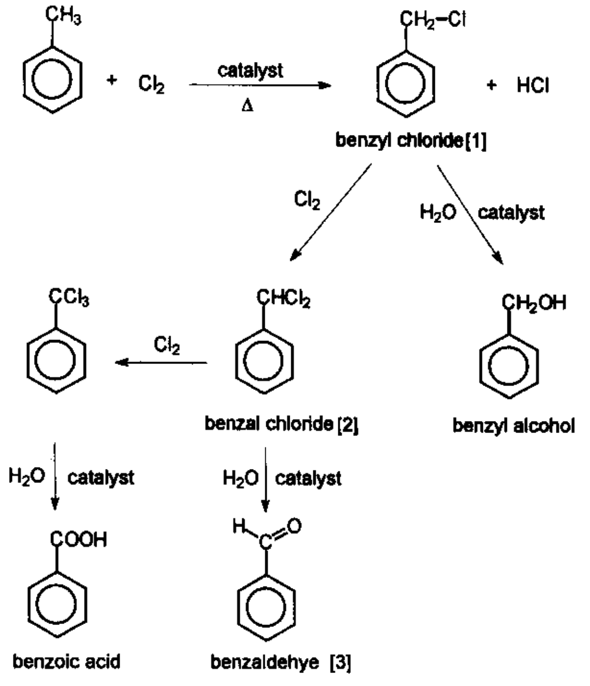

Figure 1. Synthetic benzaldehyde from chlorination of toluene

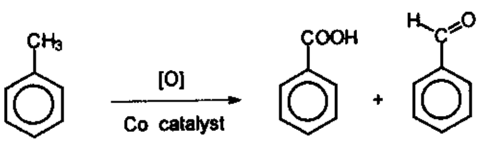

Figure 2. Synthetic benzaldehyde from direct oxidation of toluene

Producers

Synthetic benzaldehyde: It is estimated that world usage of benzaldehyde in 1994 was approximately 13,000 Mtons of which about 6,400 Mtons were consumed directly or indirectly by the world flavor and fragrance industry. The major world producers of synthetic benzaldehyde are presented in Table IV.

Natural benzaldehyde: The natural benzaldehyde market is currently at about 100 Mtons/yr worldwide, and growing at about 5% per year. The major volume sold, about 80 Mtons, is natural benzaldehyde ex cassia oil. The remaining 20 Mtons of product is natural Bitter Oil of Almonds obtained from peach and apricot pit meat. The questionable natural label of benzaldehyde ex cassia oil has been conveniently ignored by the flavor industry as the two products vary so widely in price. For example, natural Bitter Oil of Almonds is selling in the $130-180/lb range while benzaldehyde ex cassia oil is priced at $50-55/lb.

Consumption

World consumption of benzaldehyde for all uses in 1994 is estimated at 13,000 Mtons. Usage in the flavor and

Table IV. Producers of synthetic benzaldehyde

Firm	Capacity	Process
DSM	8,000 Mtons	air oxidation
Kalama	3,600 Mtons	air oxidation
Others	2,000 Mtons	mainly air oxidation
Total	**13,600 Mtons**	

Table V. Producers of natural benzaldehyde

Bell Aromatics	oil of bitter almonds
Kato Worldwide	oil of bitter almonds
Naturalia s.r.l.	oil of bitter almonds
Saofi Bio Industries	natural benzaldehyde
Shanghai Cosfra Ltd. (Florasynth)	natural benzaldehyde

Table VI. Estimated benzaldehyde usage in the flavor and fragrance industry in Mtons 1994

	North America	EEC	Other	Total
flavors	215	380	255	**850**
fragrances	50	100	130	**280**
aroma chemical intermediate	1,000	2,300	2,000	**5,300**
Totals	**1,265**	**2,780**	**2,385**	**6,430**

fragrance industry is broken out in Table VI.

The remaining 6,570 Mtons of benzaldehyde consumed in 1994 was used as a feed stock for benzyl alcohol, benzyl amine, benzylidene acetone, benzyl acetone, dibenzyl amine, pesticides and various other low-volume products. The direct flavor and fragrance industry usage of benzaldehyde is only about 8% of world production; the indirect usage (as amyl cinnamic aldehyde and cinnamic aldehyde) adds another 41% to world consumption. Thus, our industry is responsible for about 49% of the world's usage of this product.

Prices

Benzaldehyde is currently selling in the $0.95-1.20/lb range, depending on grade. It is produced as a by-product by phenol manufacturers, and with phenol currently selling at about $0.31/lb, benzaldehyde is clearly a premium-priced product. The choice of whether to recycle the benzaldehyde to make phenol or sell it "as is" is rather clear. Part of the current tightness in the benzyl alcohol supply is because it sells at $1.10/lb and is largely produced from the benzaldehyde by-product. Thus, manufacturers have chosen to sell benzaldehyde rather than reduce it to the alcohol.

Imports

Benzaldehyde is currently listed under the Harmonized Tariff No. 29121.21.00008 and bears a 9% duty. Imports to

Table VII. Yearly US imports of benzaldehyde 1989-1993

Year	Kg
1989	511,951
1990	776,417
1991	1,028,324
1992	1,041,446
1993	1,363,353

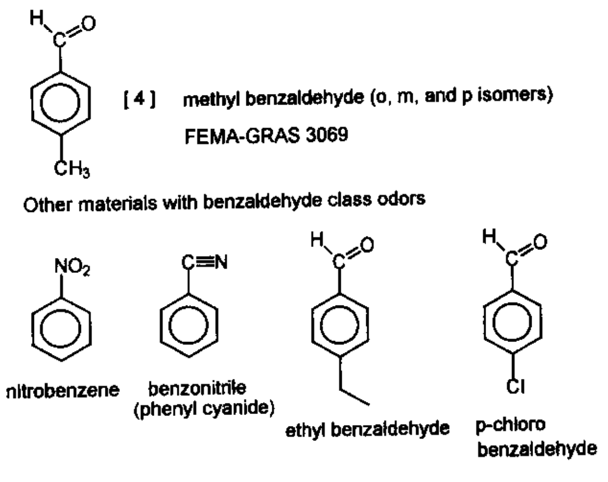

Figure 3. Benzaldehyde substitutes

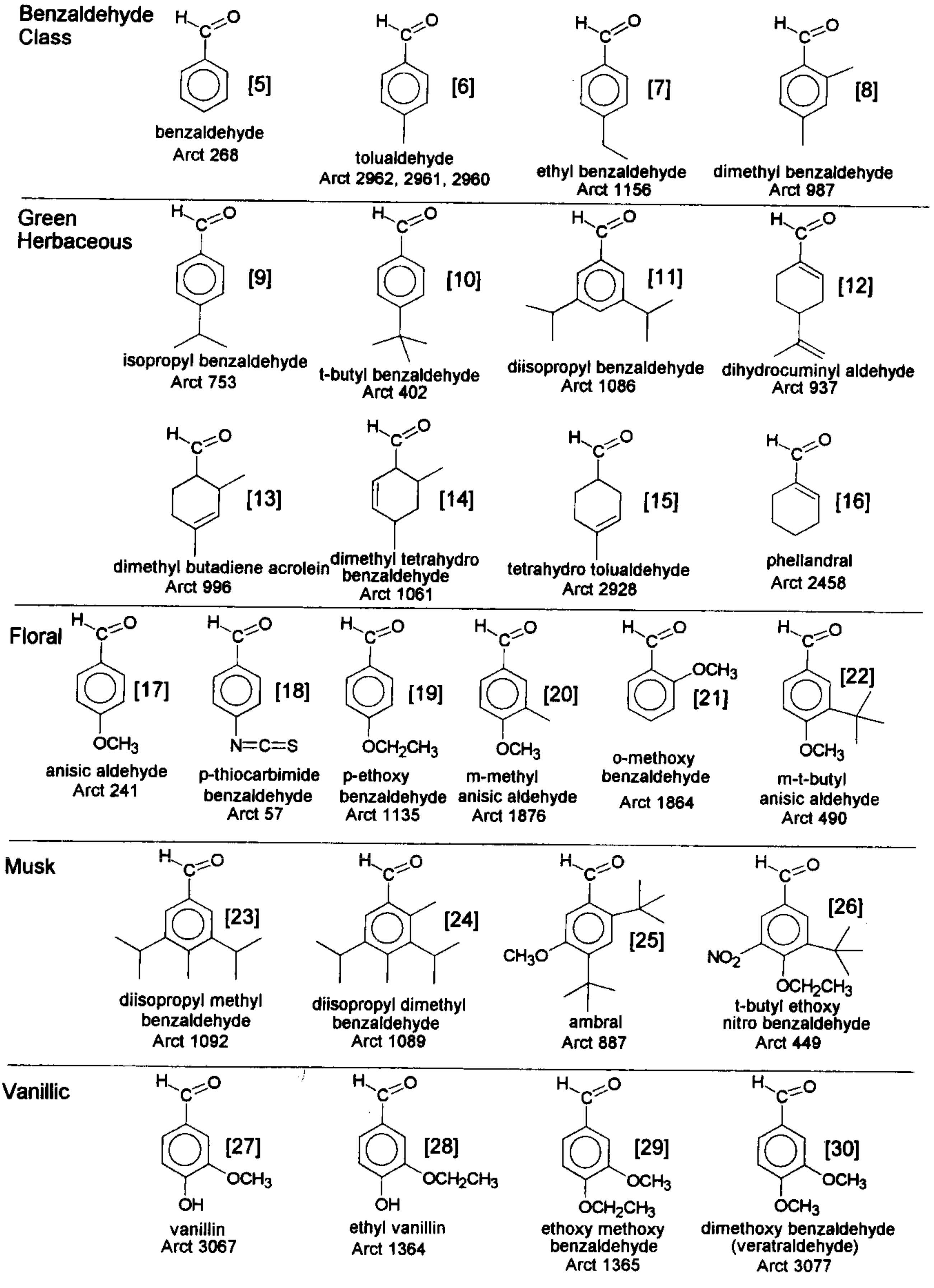

Figure 4. Benzaldehyde analogues

the US have grown recently (Table VII) and now represent about 16% of US current demand.

Substitutes

Numerous materials have odor-taste profiles near benzaldehyde, but few can be used because of product safety considerations. The most successful substitute is methyl benzaldehyde (tolualdehyde [**4**]) (Figure 3).

Approximately 45,000 kg of tolualdehyde are used in flavors worldwide; about 16,000 kg of that volume are used in the US. The major producers of the p-tolualdehyde are BASF and Mitsubishi Gas Chemical Co. Givaudan-Roure offers a mixture of ortho, meta and para isomers.

Analogues

Benzaldehyde's analogues are interesting in their own right and also to illustrate organoleptic shifts (Figure 4).

Small bulky groups, substituted mainly in the para position of the ring of the aldehyde, show benzaldehyde-type odors ([**5**]-[**8**]). However, larger alkyl groupings or destruction of the aromaticity of the ring result in a shift to the green-herbaceous odor class ([**9**]-[**16**]). If more polar substituents are selected, a floral class is created ([**17**]-[**22**]). If the number of polar groupings is increased to excess, a vanillic impression results ([**27**]-[**30**]). If the substitutions of increased bulk are a mixture of polar and nonpolar (alkyl) groups, the odor shifts to the musk class ([**23**]-[**26**]).

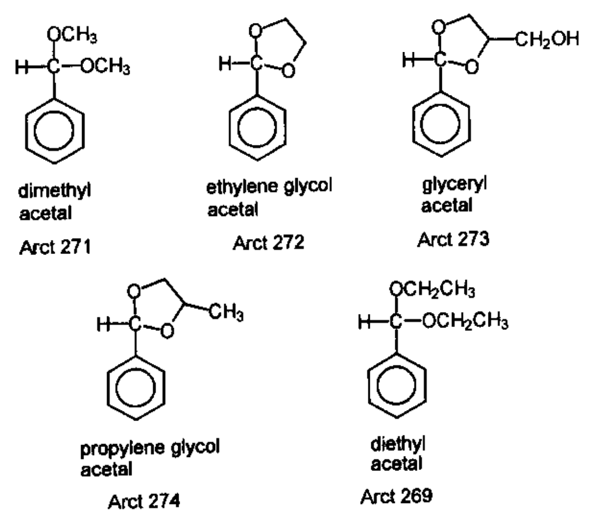

Figure 5. Benzaldehyde derivatives

Derivatives

If derivatives include alcohols or condensation products with other aldehydes (such as the cinnamates), then the benzaldehyde derivatives used in the flavor and fragrance industry are mainly its acetals (Figure 5), which impart a benzaldehyde note for formulations in which benzaldehyde is unstable.

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