Cinnamic Aldehyde

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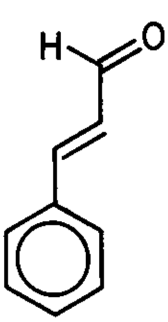
Cinnamic aldehyde's odor is as familiar to all of us as grandmother's cookies. Its smell invokes childhood memories of home baking and a warm kitchen on a cold winter's day. In our organoleptic world of terminology, cinnamic aldehyde falls into the class of "spice" and by itself defines a subclass "cinnamon." The high levels of cinnamic aldehyde present in cassia and cinnamon spice, their oils and oleoresins have so colored their impressions as to have created a blur both organoleptically and practically in our industry. In the U.S., no distinction is made between cassia (Cinnamonum Cassia Blume) and cinnamon (Cinnamomum zeylanicum Nees in Wall); while in other regions of the world, the two spices are recognized as separate entities.[4] In addition, the historic practice of stretching cassia oil by adding synthetic cinnamic aldehyde, one of the worst kept secrets of the industry, has further confused the products. Thus, a review of cinnamic aldehyde inescapably involves these spice oils and related products.

Cinnamic aldehyde possess a pleasing, spicy unique odor and a sweet spicy taste, which can only be described using the term "cinnamon." Its positive impression upon humans goes back to the dawn of history and was recorded by Moncrieff[5] as ranking 33 (Cinnamon bark oil) in preference out of 132 materials.

Cinnamic Aldehyde



Mwt 132 C_9H O

CAS 104-55-2 **FEMA-GRAS** 2286

Classification:

A conjugated unsaturated aromatic aldehyde found in nature as the trans isomer, mainly in plants of the Cinnamomum species.

Additional Names:[1,2]

Cinnamyl aldehyde
Cinnamaldehyde
Cinnamal
Cassia aldehyde
3-Phenyl-2-propenal
γ-Phenylacrolein

French:	Aldéhyde Cinnamique
German:	Zimt aldehyd
Portuguese:	Aldéido Cinamico
Spanish:	Aldehido Cinamico

Physical Data:[3]

Appearance:	clear, slightly yellow liquid
Specific Gravity:	1.050 at 25°C
Refractive Index:	1,6219 at 20°C
Boiling Point:	246°C
Freezing Point:	-7.5°C
Flash Point:	71°C
Solubility:	H_2O sol. at 0.014% at 20°C, soluble in alcohols, aldehydes, ketones, esters, DEP mineral oil chlorinated solvents and hydrocarbons and terpenes.

 0272-2666/91/0004-2501$4.00/00

Commercially available cinnamic aldehyde is mainly a synthetic product, produced by all manufacturers by the Claisen-Schmidt condensation reaction of benaldehyde with acetaldehyde. This reaction results in some further reaction of acetaldehyde with the cinnamic aldehyde generated in the process, yielding small amounts of 5-phenyl penta-2,4-dienal. The dienal is almost impossible to remove completely from the cinnamic aldehyde finished product; thus, allowing the identification of synthetic cinnamic aldehyde in essential oils by the presence of trace amounts of this dienal.

All the commercially available synthetic cinnamic aldehydes are similar in organoleptic profile. They generally are clean, pure products free of burned notes or other undesirable tones. Only old material stored poorly and exposed to air will show off odors due to oxidation (cinnamic acid) and resinification.

Cinnamic aldehydes is mainly a flavor material with about 95% of its consumption found in that area. The material has been used in the past in fragrances but cinnamic aldehyde, cassia oil and cinnamon bark oil were flagged by RIFM as potential sensitizers and their use was limited in perfumes for skin contact at 1% formula levels. The small amount of cinnamic aldehyde still used in fragrances are now added as a mixture with limonene which seems to quench the sensitizing effect. Current consumption of cinnamic aldehyde in fragrances is about 5% of F&F direct usage, i.e., not included is use as a chemical intermediate for the production of derivatives, and is mostly confined to use in air fresheners and other odor masking applications where the product does not normally come in contact with human skin.

Year	MTons
1985	251
1986	59
1987	221
1988	308
1989	196
1990	333
Average	**228**

Figure 1. U.S. Cassia Oil Imports

Natural cinnamic aldehyde has been isolated from cassia and cinnamon oils in low volumes for many years. The demand was never very great, as cassia oil is just as desirable for use in flavors. However, the industry's concerns as to real and bogus essential oils and chemicals derived from them, became acute in the 1980s. Various analytical techniques (including use of Carbon 14 isotope analysis) showed that much of the natural benzaldehyde or "natural" oil of bitter almonds being sold in the world market was actually relabeled synthetic benzaldehyde, originating from petroleum feed stocks.[6-9] Once this practice was uncovered, suppliers began manufacturing "natural" benzaldehyde by the retro-aldol condensation reaction using natural cinnamic aldehyde isolated from cassia oil. The type of catalyst employed in these processes was next to be questioned. These questions were raised as a result of a letter of complaint from Champon Flavors & Fragrances Inc. sent to the U.S. Food & Drug Administration (FDA): To date, the FDA has not clearly defined just what constitutes a natural aroma chemical or what catalyst produces a natural product.

Natural Sources[10]

Cinnamic aldehyde should be found in almost every species of plant, as it is generated as part of the Shikinic acid pathway which starts from sedoheptulose, which is converted to cinnamic aldehyde via *l*-phenylalanine, and eventually ends up as lignin; one of the major structural materials of plant cells. However, this mechanistic pathway involves very low levels of steady state concentrations of intermediate reactants in most of the plant kingdom. Thus the concentration of cinnamic aldehyde present are in minute to trace amounts. Cinnamic aldehyde has been reported in trace quantities in the following essential oils:

Bulgarian Rose
Hyacinth
Indian celery seed oil
Myrrh
Patchouli
Ylang-ylang

The large concentrations of cinnamic aldehyde found in the cinnamonum species are explained as the result of a kinetic bottleneck in the mechanistic pathway, which results in the accumulation of large quantities (60-95%) of this aldehyde. Botanist place the Lauraceae family, to which the cinnamonum group belongs, on the bottom of the evolutionary ladder. Thus an anomaly in its mechanistic behavior would not be unexpected.

The cinnamonum group comprises more than 100 species, all native to Southeast Asia and growing in a tropical rain forest environment. The species commercially harvested for their spice or essential oil content are as follows:

C. Zeylanicum Nees
C. Cassia Blume
C. Laurcirii Nees
C. Burmanni Blume

Natural cinnamic aldehyde is consumed as the spice, the oleoresin and the distilled oils. Some 30,000 MTons/year of cinnamon spice is produced each year of which the U.S. consumes about 41%.[11] This amount of spice is capable of generating about 725 MTons of cinnamon-cassia oil per year. However, only 202 MTons of cassia oil[12] and about 20,000 lbs. of oleoresin are actually currently being produced. In 1984, the estimated production of cassia oil was 160 MTons.[13] These two figures are perplexing in the light of reported U.S. importation figures for Cassia oil (Figure 1).

These U.S. importation figures indicated that either the United States is consuming the total world's production of cassia oil or that some of the cassia oil imported is synthetic or at least only partially natural.

History

Cinnamic aldehyde was first identified in 1853 by Bertagnini[12] and synthesized in 1855 by Civozza via the condensation of benzaldehyde with acetaldehyde. Little has changed since then in the process scheme. The aldehyde is fairly easily prepared in general plant equipment, thus, many firms have produced it over the years. However, the very competitive nature of the market has reduced the number of suppliers of this product over the last 30 years. In 1960, it is estimated that the global market had thirteen producers of cinnamic aldehyde. Today, no more than three major producers can be identified.

In 1950, The U.S. saw FDO, Trubek (UOP), Norda and Chem Fleur producing this product. By 1990, the U.S. had no producer of cinnamic aldehyde and all demand was satisfied by imports mainly from Dutch State Mines (DSM) in Holland. In the 1980s, both FDO and Quest (Norda Mexico) had ceased manufacturing cinnamic aldehyde;

although Quest has constructed a new plant in Mexico which should begin producing in 1991.

Current Producers

DSM: Is clearly the dominant manufacturer of cinnamic aldehyde in the world with a demonstrated capacity of over 3,000 MTons per year with a probably real capacity in excess of 4,000 MTons.

Quest-Mexico: A new modern production facility has been built with an estimated capacity of more than 1,000 MTons per year.

Haarmann & Reimer (Germany): This automated facility at Holzminden is capable of producing 400 MTons of cinnamic aldehyde per year. However, the unfavorable $/DM exchange rates have caused this source to appear inactive.

In addition to the above three manufacturers, capacity for production exists in Japan, China, Italy, France and recently India. Little, if any, quantities of cinnamic aldehyde from these sources has been seen on the world market in recent years.

Imports

Since the demise of the ASP system of tariff duties in 1979, the duty of cinnamic aldehyde has been set at a nominal 11.9% ad valorum, a level which is normal for benzenoid materials. Thus, U.S. industry has not been sheltered from foreign competition. Moreover, since Mexico enjoys GSP status, future imports of cinnamic aldehyde from Quest, Mexico will arrive duty free, giving Quest a decided advantage in the U.S. market.

World Consumption

The world usage of cinnamic aldehyde from all sources, including its consumption directly via spices, is estimated to be about 3820 MTons per year. In 1991, this figure breaks down as follows:

World Consumption as Cinnamic Aldehyde:

	MTons
Spices	500
Essential Oils	300
Oleoresins	20
Synthetic Flavors	2200
Intermediate Usage	800
Total	3820

The worldwide usage of cinnamic aldehyde in the form of essential oils, synthetic and partially synthetic oils and flavors and as an intermediate for derivatives is estimated to be 3320 MTons in 1991. End use areas are estimated as follows:

Cinnamic Aldehyde Usage Areas (1991)

Area	%	MTons
Beverages	23.0	770
Confectionary	12.7	422
Culinary-Savory	8.0	266
Oral Hygiene	16.9	567
Bakery Goods	11.0	365
Intermediate	25.0	830
Other	3.0	100
Total	99.6	3320

Percentages add to 99.6% due to rounding.

Regional consumption figures are estimated to be as follows (consumption excludes the use of the spice directly but includes usage as a chemical intermediate):

Area	%	MTons
North America	36.0	1200
Europe	42.0	1400
Japan	5.0	160
Latin America	6.0	200
Others	11.0	360
Total	100.0	3320

Pricing

Cinnamic aldehyde prices have been depressed until recently due to competitive factors stemming from excess capacity in the period between 1970 to 1989. US average prices for cinnamic aldehyde for the period 1970 to 1991 are (in US$):

1970 - $1.20/lb	1982 - $1.60	1988 - $1.50
1975 - $1.30/lb	1984 - $1.60	1990 - $1.56
1980 - $1.80/lb	1986 - $1.50	1990 (4th Quarter) $1.90
		1991 - $2.05

The market has seen very intense competition from many sources, i.e., FDO, Quest (Mexico), DSM, H&R, ASAP Italy, and China over the years. By 1985, ASAP, H&R and China were no longer serious factors in the market and a slight upward adjustment occurred. In 1989 FDO ceased production and Quest shut down their older plant in Mexico, leaving the market open to DSM and prices rose accordingly to their present levels.

Prices are forecasted to remain in the lower $2.00/lb. area until Quest's new plant begins production, which should bring prices down to more historically normal levels, i.e., $1.60-1.80/lb. Cinnamic aldehyde usage should grow by about 3% per annum over the next five years, thus the market will face overcapacity and renewed competition by the end of 1991.

Table I. List of items with cinnamic-type organoleptic profiles

FEMA GRAS	Substitutes	Arctander Reference Number
	cinnamic aldehyde-2, 4-dihydroxy-4-methyl pentane acetal (use in alkali media)	621
	cinnamic aldehyde dimethyl acetal	622
2287	cinnamic aldehyde ethylene glycol acetal	623
	cinnamyl nitrile	641
2495	furfural acetone	1414
2494	furyl acrolein	1421
2697	α-methyl cinnamic aldehyde	1951
2704	α-methyl-β-furyl acrolein	2034
3640	p-methyl cinnamic aldehyde	

Table II. List of materials directly structurally related to cinnamic aldehydes

FEMA GRAS	Derivatives	Arctander Reference Number
2288	cinnamic acid	617
2294	cinnamic alcohol	618
	cinnamic aldehyde diethyl acetal	620
	cinnamic aldehyde-2, 4-dihydroxy-4-methyl pentane acetal	621
	cinnamic aldehyde dimethyl acetal	622
2287	cinnamic aldehyde ethylene glycol acetal	623
	cinnamyl nitrile	641
2887	3-phenyl propionic aldehyde	2580
2885	3-phenyl propyl alcohol	2589
	Tetrahydro cinnamic aldehyde	2896

Substitutes

A review of the literature reveals that most substitutes for cinnamic aldehyde are derivatives of that structure. The few items possessing cinnamic-type organoleptic profiles which are not derivatives disclose an interesting insight into just what chemical structure is required for the cinnamon impression (Table I).

All the items listed in Table I have one common structure theme, i.e., a polar unsaturated group (sometimes in the form of the acetal) connected via a single double bond to a planar aromatic ring of five or six atoms. Aromatic is defined in this sense as have resonance, i.e., being stabilized by reduced internal resonance energy. The furan ring is estimated to have an internal energy of ca 20Kcal versus its non-aromatic linear isomer. Thus, the key determined of the cinnamon effect can be viewed as:

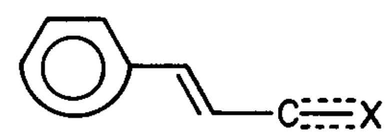


Table III. Materials containing basic cinnamic structure, with additional alkyl groupings

FEMA GRAS	Analogs	Arctander Reference Number
2061	α-amyl cinnamic aldehyde	149
2191	α-butyl cinnamic aldehyde	425
	α-methyl-para-tert-butylhydrocinnamic aldehyde (Lilial) (Bamca)	496
	3,4-dimethoxy cinnamic aldehyde	980
	α-ethyl cinnamic aldehye	1189
2569	α-hexyl cinnamic aldehyde	1653
	para methoxy-α-amylcinnamic aldehyde	1863
	para methoxy cinnamic aldehyde	1869
2697	α-methyl cinnamic aldehyde	1951
	α-propyl cinnamic aldehyde	2688

Derivatives

The materials directly structurally related to cinnamic aldehyde which are normally available to the perfumer or flavorist are listed in Table II.

Analogs

Table III desribes the materials that contain the basic cinnamic structure but generally have additional alkyl groupings attached which modify the odor impression. Note that the addition of an α-alkyl group, next to the aldehyde group, destroys the cinnamon effect and creates a new group with a green floral impression. A simple alkyl addition on the phenyl ring only results in a slight change in the cinnamon note.

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