An Aroma Chemical Profile

Aldehyde C-11

By George Stuart Clark IV, Cameron & Stuart, Inc., Easton, Maryland

The terms *aldehyde* and *aldehydic* have become an intregal part of the vocabulary of the fragrance and flavor industry. The term *aldehyde* was coined in 1835 by von Liebig from the term *dehydrogenated alcohol* (alcohol dehydrogenatus).

Chemically, the term *aldehyde* represents a class of organic chemicals, lying structurally between alcohols and carboxylic acids. Practically, *aldehyde* or *aldehydic* also represents a class of fragrances looked upon as classic by some and modern by others. Yet, *aldehyde* in each case entails a different meaning. The chemist uses it to denote any molecule with an aldehydic grouping, while the flavor and fragrance industry usually uses the term to denote the aliphatic aldehydes. The perfumer thinks of aliphatic aldehydes as materials in the C-8 to C-12 range, while the flavorist uses the term to mean aliphatic aldehydes in the C-2 to C-7 range.

The first aldehydes used in our industry were mainly aromatic aldehydes. They were discovered as follows:

- Benzaldehyde, Liebig (1837)
- Cinnamic Aldehyde, Chiozza (1856)
- Phenylacetaldehyde, Cannizzaro (1861)
- Heliotropin, Fittig (1869)
- Vanillin, Tiemann and Haarmann (1874)
- Anisaldehyde, Tiemann (1877)

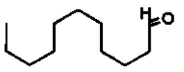
All these materials quickly became available commercially as synthetic aroma chemicals and were sold in "volume."

Natural aliphatic aldehydes: The aliphatic and acylic aldehydes known from the period 1850 to 1900 were all isolates of the natural essential oils citral and citronellal or they were laboratory curiosities. A popular chemistry textbook from 1899 states that 24 aldehydes were known at the time (Table I).[5] The straight-chain aliphatic aldehydes did not become known beyond academic circles until after 1900. (See **Nineteenth Century Perfumers Turn Noses Up at Aliphatic Aldehydes**)

As synthetic aroma chemicals slowly displaced natural products in formulas, the need for top notes and lift became more of a concern.

Aldehyde C-11

ALDEHYDE C-11



	Mwt 170 $C_{11}H_{22}O$
	CAS 112-44-7
	FEMA 3092
Classification:	saturated aliphatic aldehyde
Additional Names:[1-3]	1-undecanal; n-undecyl aldehyde; hendecanal; α-oxo-undecane; undecanal
French:	aldèhyde n-undècylique
German:	N-undecylaldehyd
Portuguese:	aldèido n-undecilico
Spanish:	aldehido n-undecilico
Physical Data:	
Appearance:	clear, colorless liquid
Specific Gravity 25/25°C:	0.825-0.833
Melting Point:	25°C
Boiling Point:	170-172°C at 760 Torr
Refractive Index at 20°C:	1.430-1.434
Flash Point:	79°C (175°F)
Odor Threshold-Air:[4]	0.004 mg/m³

In 1900, essential oil researchers discovered aliphatic aldehydes in natural essential oils, setting the tone for the innovations employing aliphatic aldehydes to come. Table II shows the major essential oils used at that time and their aldehyde content. The citrus essential oil concentration levels employed in colognes were in the 50-70% range and, thus, provided a total aldehyde content 0.1-0.3% in the final formula. From 1900 to 1920, the application dosage of aldehydes mimicked nature and was based upon the relative amounts found in the fragrance formulas as would be provided by the alternate use of essential oils. All of that changed with the introduction the synthetic C-11 aldehydes.

Synthetic aliphatic aldehydes: The first aliphatic

Table I. The 24 aldehydes reported as "known" in 1899[5]

Chemical name	Formula	Source	Boiling point	Melting point
formic aldehyde	$H{\cdot}CHO$	*oxidation of methyl alcohol*	21°	
acetic aldehyde	$CH_3{\cdot}CHO$	oxidation of ethyl alcohol	21°	
propionic aldehyde	$C_2H_5{\cdot}CHO$	oxidation of propyl alcohol	49°	
butyric aldehyde	$C_3H_7{\cdot}CHO$	oxidation of butyl alcohol	74°	
valeric aldehyde	$C_4H_9{\cdot}CHO$	oxidation of amyl alcohol	102°	
caproic aldehyde	$C_5H_{11}{\cdot}CHO$	distillation of calcium formate *with calcium caproate*	*128°*	
oenanthic aldehyde	$C_6H_{13}{\cdot}CHO$	distillation of castor oil	155°	
caprylic aldehyde	$C_3H_{15}{\cdot}CHO$	distillation of castor oil	160°	
rutic aldehyde	$C_9H_{19}{\cdot}CHO$	oil of rue		
lauric aldehyde	$C_{11}H_{23}{\cdot}CHO$	oil of rue		44.5°
myristic aldehyde	$C_{13}H_{27}{\cdot}CHO$			52.5°
palmitic aldehyde	$C_{15}H_{31}{\cdot}CHO$			*58.5°*
stearic aldehyde	$C_{17}H_{35}{\cdot}CHO$			63.5°
glyoxal aldehyde	$CHO{\cdot}CHO$	oxidation of glycol		
glyceric aldehyde	$C_2H_5O{\cdot}CHO$	oxidation of glycerol		
acrylic aldehyde	$C_2H_3{\cdot}CHO$	oxidation of allyl alcohol	52.5°	
crotonic aldehyde	$C_3H_5{\cdot}CHO$			104°
benzoic aldehyde	$C_6H_5{\cdot}CHO$	*bitter almond oil*	*179°*	
cinnamic aldehyde	$C_8H_7{\cdot}CHO$	oil of cinnamon	246°	
salicylic aldehyde	$C_6H_5{\cdot}CHO$	oil of meadowsweet	196°	
cuminic aldehyde	$C_9H_{11}{\cdot}CHO$	oil of cumin	235°	
anisic aldehyde	$C_7H_7O{\cdot}CHO$	oil of anise	248°	
vanillic aldehyde	$C_7H_7O_2{\cdot}CHO$	vanilla pods		80°
pyromucic aldehyde	$C_4H_2O{\cdot}CHO$	*distillation of bran with dilute* sulfuric acid		162°

Table II. Citrus oils and their aldehyde content

Essential oil	C-7	C-8	C-9	C-10	C-11	C-12
bergamot	-	0.06	0.05	0.6	0.20	-
lemon, CP	0.004	0.12	0.20	0.07	-	0.03
lime, CP	-	0.8	-	0.09	-	0.006
orange	-	-	0.05	0.4	0.02	0.06
petitgrain	-	-	-	*trace*	-	-
tangerine	-	0.3	0.07	0.2	-	0.05

aldehyde used in a fragrance was not found in nature; it was a synthetic aliphatic aldehyde called aldehyde C-12 MNA, introduced by Darzens in 1904, and used in the fragrance Floramye by Piver in1905. Aldehyde C-12 MNA was used again by Piver in 1907 in the fragrance Pompeia, but this time it was used in conjunction with other synthetic aldehydes. By 1908, Roure-Bertrand was using aldehydes C-9 *and C-10 as in-house specialties and by 1910, aldehyde C-8* was generally available.[6] Other fine fragrances containing aliphatic aldehydes began to appear during this period, but World War I soon interfered and also set the stage for a new post-war aldehyde era in the industry.

Three factors converged after World War I to allow the development of what we now refer to as the modern era in perfumery. One was the social upheaval after the war and the rebellion of the Jazz generation. Another was Rosenmund's discovery of the conversion of organic acid into aldehydes via their acid chlorides. A third factor was the increased acceptance and use of synthetic aroma chemicals by the perfume industry.

This was the reality of the period that allowed Ernest Beaux to exercise his creative talents and produce the "overdose" of aldehydes that marks Chanel No. 5 as a milestone in the fine fragrance world. The use level of aldehydes in Chanel No. 5 can be viewed as an overdose, because the aldehyde levels in fragrances at the time, achieved through essential oils, normally were around 0.3%, and their use in Chanel No. 5 reached the 1% level.

Undecanal: One can group aldehydes, especially of this post-war period, in two categories: those with mid and dry-out notes and those with top to mid notes. The known and used aldehydes prior to 1900 all fall into the first category of materials with mid and dry-out notes. The aliphatic aldehydes commercially developed during the 1900 to 1925 period all fell into the second category: materials with top to mid notes.

Undecanal, a prime example of materials of the second category, is at the upper limits of a group of frequently used aliphatic aldehydes in the range C-6 to C-14, all with top to mid notes. It still incorporates the fresh citrus notes of the lower aldehydes, but it also contains the floral effects of the higher aldehydes.

Undecanal can be described as a powerful, waxy, citrus, rose floral odor with a fatty, waxy, citrus-like taste. This product's odor is so strong and waxy that minute traces of it will strongly color the profile of both perfumes and flavors in which it is incorporated. Moreover, Mookherjee and Trenkle have shown that minute amounts of C-6 through C-15 aliphatic aldehydes are generated in the sun light on cotton fabrics from fatty acids and are responsible for the fresh clean odor we associate with clean laundry.[7] Only sparingly soluble in water, undecanal displays an odor threshold of approximately 5 ppb in water.

Usage levels: Initially the concentrations of aldehydes and their relative amounts paralleled nature, but as time progressed, the ratios of the various aldehydes changed with the fashions and as new materials became available. Table III presents an overview of these changes.

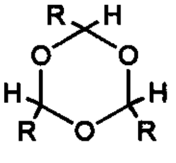
Table III. Aldehyde ratios used in fragrances

Aldehyde	Classic colognes via citrus oils 1900 (%)	Aldehyde blend circa 1930 (%)	Aldehyde blend circa 1970 (%)	Soaper's use 1990 (%)
C-8	6.3	4.1	12	23.1
C-9	10.5	11.1	5	1.0
C-10	27.5	15	20	40
C-11	1	0	30	2
C-11, unsaturated	0	43	10	23
C-11, MOA	0	0	0	4
C-12, lauric	55	21	15	0
C-12, MNA	0	6	8	0

Problems

The initial experiences of perfumers and flavorists with synthetic aliphatic aldehydes began to explain some of the problems that occured in fragrance applications, such as the discoloration of fragrances in high and low pH media in the presence of amines. This problem now could be attributed to the presence of aldehydes. Moreover, the aliphatic aldehydes introduced new unforeseen problems with stability, polymerization, oxidation, discoloration and other reactions.

Stability: Undecanal is stable for as long as one year if stored in an airtight aluminum container at approximately 16-25°C under an inert gas atmosphere, but is very prone to trimerization [**1**] in the presence of air and traces of acid. Undecanal also will oxidize to undecylic acid in the presence of air, which further encourages the trimerization reaction. The addition of an antioxidant will help stabilize this aldehyde. The addition of an alcohol to the aldehyde will help prevent trimer formation and air oxidation to the acid, because the alcohol forms a hemi-acetal with the aldehyde, which is far more resistant to oxidation than the aldehyde [**2**].



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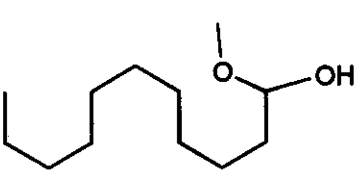
Aldehyde trioxane



2

Undecanal-methanol hemi-acetal

Polymerization: In most cases, the polymerization is actually a trimerization. The trioxane derivative [**1**] is formed by most straight chain aliphatic aldehydes. This trioxane formation has been blamed for the reduction of the aldehydic effect noted in bar soaps in which aliphatic aldehydes were part of the fragrance formula. Steric hinderance by an alkyl group at the a or b position of the aldehyde will eliminate or at least minimize the trioxane formation.

Among those aliphatic aldehydes used in perfumery and flavors, the most obvious example of a trimer former is aldehyde C-12, lauric, which will trimerize to the trioxane even when stored at cool temperatures in the absence of air. Aldehyde C-12 is hydrophobic and readily trimerizes to a solid trioxane, as the reaction is driven to completion by the physical elimination of the water produced by phase separation and evaporation. The trioxanes of the aliphatic aldehydes C-5 through C-11 tend to be viscous liquids or semi-solids miscible with the aldehyde; hence polymerization in these cases is observed as the formation of viscous raw material.

The trioxane reaction is reversible. Trioxanes will generate aldehydes if they are heated in the presence of acid catalysts and water. In the case of formaldehyde, the free aldehyde is almost impossible to isolate and is obtained as either the trimer, a chain polymer or the hydrate in water solution.

Oxidation: Compounding and storage of aliphatic aldehydes revealed a serious problem: their facile oxidation in contact with air. Oxidation resulted in the formation of the corresponding organic acid, which catalyzed the polymerization reaction and also imparted an undesirable off-odor to the aldehyde raw material.

Table IV lists the common aliphatic aldehydes used in flavors and fragrances, their corresponding acids and the odors of each. In particular, the acids generated by the C-5 to C-10 aldehydes are considered most undesirable. Moncreiff[8] lists butyric acid (122nd) below sour milk (110th) in his list of 132 common materials ranked by odor preference. The C-6 to C-8 acids are even more replusive than butyric or valeric acids to all noses except that of a goat.

Discoloration: It was soon discovered that the aldehydes reacted with amines in the formulas to form colored products, just as they had in the laboratory under more controlled conditions. This reaction had been reported by Hugo Schiff,[9] a professor at the University of Turin, who spent most of his life studying the condensation products of aldehydes and amines. These colored materials have been named Schiff bases in his honor.

The properties of the Schiff bases were explored with the purpose of both using these products and preventing their formation. The Schiff bases are defined chemical entities and can be obtained as pure crystalline solids. However, on a practical scale, the products offered in the flavor and fragrance industry soon evolved into a series of undefined mixtures produced from aldehydes and usually an excess of methyl anthranilate. The most common Schiff base is formed from hydroxycitronellal and methyl anthranilate.

When the Schiff base is formed from an aldehyde and an aromatic amine (such as methyl anthranilate or indol), a very potent dye system results due to the formation of chromophors generated in resonance with the benzene ring. Schiff base mixtures still are used partly for their own odor value, but more so for their tinting value to color fine fragrances.

Other reactions: The laboratory chemist recognized the reactivity of the aldehydes early on in the form of the aldol condensation, which results in the polymerization and dehyration of the resulting polymer of self-condensation of aldehydes in high pH media. This reaction limits the pH environment of aldehyde applications to a pH below 8 or 9. The reaction of aldehydes with sodium bisulfite to form a solid addition product became a method to isolate and purify aliphatic aldehydes from the crude reaction mixtures produced by the early manufacturing processes.

When used in alcoholic fragrances and flavors, the aliphatic aldehydes are unexpectedly stable. This stability was found to be the result of hemi-acetal formation [**2**]. Investigation of this phenomenon uncovered the aldehyde acetal derivatives. The acetals were found to be very stable in high-pH media and to have odors similar (in many cases) to the corresponding aldehyde, especially the dimethyl acetal derivatives (Figure 3). Conversely, the acetals are not very stable in low-pH aqueous media and thus have found little use in most liquid flavor systems.

Table IV. The odors of aliphatic aldehydes and their acids

Aldehyde	Odor	Acid	Odor
acetaldehyde	pungent-winey	acetic	sour-vinegar
propional	pungent-winey	propionic	sour-vinegar
n-butyraldehyde	pungent-fruity	butyric	repulsive-rancid-butter
isobutyraldehyde	pungent-fruity	isobutyric	repulsive-rancid-butter
n-valeraldehyde	pungent-apple	valeric	replusive-rancid-sweat
hexanal	fatty-green	caproic	sour-rancid-goat
hexenal	green-leafy	hexenoic	pleasant-fatty-green
heptanal	harsh-nauseating-fatty	heptanoic	sour-sweat-goat
octanal	sweet-orange-fatty	caprylic	rancid-sweat-goat
nonanal	sweet-rosey-orange	nonanoic	fatty-goat
decanal	sweet-orange-rose	capric	sour-fatty-rancid
undecanal	pleasant-fatty-floral	undecanoic	fatty-waxy
dodecanal	sweet-waxy	lauric	fatty-waxy

Natural Sources

The aliphatic aldehydes arise in natural systems as a result of the enzymatic oxidation of unsaturated aliphatic acids. Octanal, nonanal, decanal and undecanal are thought to arise from the oxidation of oleic acid in plant systems.

Undecanal is found in nature in a variety of sources. It can't be considered as ubiquitous, but it also is not rare, and

Table V. Estimated human consumption (in kg) of aliphatic aldehydes in the U.S. in 1997

Aldehyde	In food chain	In added flavors
acetaldehyde	860,000	200,000
propional	170,000	400
butyraldehyde	210,000	600
isobutyraldehyde	48,000	500
n-valeraldehyde	500,000	8,000
2-methylbutanal	4,000	200
3-methylbutanal	65,000	900
hexanal	140,000	2,500
trans-2-hexenal	220,000	3,000
cis-3-hexenal	2,500	500
aldehyde C-7	26,000	80
aldehyde C-8	11,000	1,200
aldehyde C-9	275,000	150
aldehyde C-10	15,000	1,400
aldehyde C-11	750	100
aldehyde C-12	90,000	500

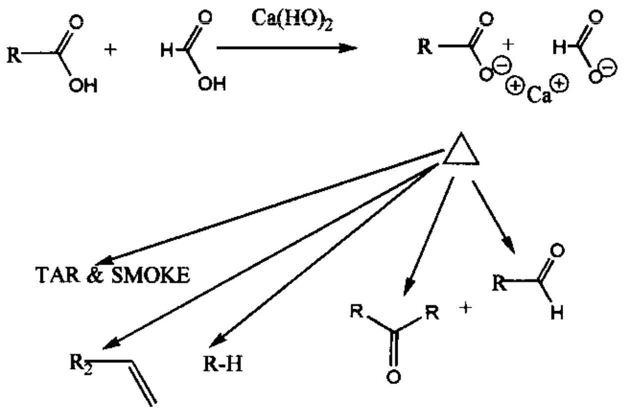


Figure 1.

is found in many common foods including bergamot oil, butter, calamus oil, carrots, chicken, cistus oil, coriander leaf and seed oil, grapefruit oil, lemon oil, lime oil, kesom oil, key lime, mandarin oil, milk, narcissus flowers, narcissus absolute, orange oil, bitter orange, peanuts, plums and potato chips. No commercial source of natural undecanal has yet been found, because no natural product has been uncovered that contains an economically attractive concentration. Table V presents estimates of human consumption of the aliphatic aldehydes in the U.S.

Synthesis of Aliphatic Aldehydes

All the aliphatic aldehydes were late in coming to applications in the area of perfumes and flavors. Most aliphatic aldehydes, C-6 to C-12, could be made available by 1880, but no commercial interest appeared. Until 1890, few aldehydes were widely known, but in 1900 the presence of C-8 to C-10 aldehydes was noted in natural essential oils.

Undecanal was one of the aliphatic aldehydes discovered around 1853 by Bertagnini and Piria, but regular supplies of good quality material did not appear on the market until after 1910 as a by-product of the castor oil industry.

Pyrolysis: The aldehydes first were synthesized by Piria in 1856 via the pyrolysis of the calcium salt of the corresponding aliphatic acid.[10] This method seems to have evolved from the alchemist era when anything and everthing was subjected to fire.

The pyrolysis method was initially used to synthesize ketones and later was improved upon for the synthesis of aldehydes by the use of a mixture of the organic acid calcium salt and calcium formate. This is the reaction used by Cannizarro[11] for his discovery of phenylacetaldehyde in 1861. If the pyrolysis was carried out using an excess of calcium formate in the mixture, a preponderance of the corresponding aldehyde could be obtained (Figure 1). The reaction mixture obtained was a complex elixer of many products, leading the early chemists to call such a product "a dog's breakfast."

This pyrolysis of the metal salts of fatty acids over an open flame to generate a volatile, flammable product was an invitation to disaster. It was also one of the biggest inhibiting factors to development of the use of aliphatic aldehydes in perfumery and flavors from a manufacturer's point of view. During the process, the difficulty of controlling a reaction temperature in an open fire resulted in the production of all kinds of by-products. The products yielded from this reaction were many, in varying quantity and organic chemical class. If even small amounts of sulfate were present, the products would contain organic sulfides and the introduction of other impurities in the raw materials would impart a smoked note to the aliphatic aldehyde. In order to clean up the product, the bisulfite addition product was employed. This salt precipitated, was filtered off, washed with volatile, flammable organic solvents, dried and then added to water, the pH adjusted and the aldehyde regenerated. The isolated aldehyde was dried and distilled to yield a product that only then could be used. This production method was the major route to aliphatic aldehydes until the use of chromic salts in the presence of sulfuric acid became available.

Oxidation of alcohols: By 1900, new general methods for the synthesis of aliphatic aldehydes had been developed, such as the oxidation of aliphatic alcohols using chromium salts and sulfuric acid, but these routes proved only marginally better in yield and economics. This method for the oxidation of alcohols worked well for secondary alcohols and their conversion to ketones, but gave much lower yields with primary alcohols and their conversion to aldehydes. Until 1918, aliphatic aldehydes were of quite variable organoleptic quality. They also were expensive and not commonly available.

Rosenmund: After World War I, new technology became available for the more economical production of improved organoleptic grades of aldehydes. By 1925,[12] all the common aliphatic aldehydes we use today were available to the flavor and fragrance industry.

The best of these new methods was the Rosenmund reaction. It was a very powerful tool for the organic chemist, because it converts the acid into the corresponding aliphatic, acyclic or aromatic aldehyde without altering the other sections of the molecule or generating organic by-products. It also allowed the commercial production of aliphatic aldehydes of superior organoleptic quality. However, it is not without fault, especially in an era of environmental concern; it produces noxious gases (SO_2 and HCl). However, newer and more efficient synthetic methods were soon to follow.

Nineteenth Century Perfumers Turn Noses Up at Aliphatic Aldehydes

Considering that aliphatic aldehydes were known as early as the 1850s, one might ask why the flavor and fragrance industry showed no interest in the organoleptic properties of aliphatic aldehydes prior to 1900? The answer seems to be found in the art of perfumery in the 1800s. The gradual transition from fragrances made solely of essential oils to fragrances comprised in the main of synthetic aroma chemicals during the period 1870 to 1950 was the reason for the initial complacency toward the aliphatic aldehydes. In 1870, there was no perceived need for these materials because essential oils provided the natural aldehydes for the lift in fragrances. Moreover, the perfumes of the period tended toward the heavy floral-spicy themes, except for the colognes with their pronounced refreshing citrus effect. The use of citrus oils provided the dose of aliphatic aldehydes required for this era's fashion needs.

Modified Sabatier synthesis: The pyrolysis of the vapors of the selected organic acid and formic acid over a solid catalyst in a hot tube reactor is the modified Sabatier synthesis. It was developed in the late 1920s and is still used in further modified form. In the 1930s methods for the vapor phase oxidation of aliphatic alcohols over solid catalysts was developed and is used today for the commercial production of aliphatic aldehydes.

Catalytic hydrogenation: In the late 1930s, the reduction of aliphatic acid esters by catalytic hydrogenation was developed and optimized. It continues today as a major route to higher aliphatic alcohols, especially those from the fatty acids found in palm and coconut oils. This reduction method furnishes some of the raw material for the catalytic oxidation of alcohols to aldehydes.

Oxo-synthesis: In 1938, the oxo-synthesis was developed in Germany for the conversion of olefins to aldehydes and, via their catalytic reduction, to aliphatic alcohols. This method was extensively commercialized after World War II, and now has become the world's largest source of aliphatic alcohols and aldehydes. More than 4 million metric tons of oxo-process alcohols are produced each year. The organoleptic quality of the raw materials produced by the oxo-synthesis is sometimes too poor to allow these materials to be used in fragrances or flavors. Recent developments by Exxon have made available an oxo-process undecanol suitable for the commercial production of flavor and fragrance-grade undecanal.

Castor oil derivatives: Pyrolysis of castor oil or its derivative ester, methyl ricinolate, yields aldehyde C-7 and undecylenic acid or methyl undecylenate. Hydrogenation of either material furnishes the saturated undecanoic acid, which is reduced to undecanal via the modified Sabatier process.

World Production of Undecanal

The C-11 aldehydes are somewhat unusual in their raw material source. They can be produced from petroleum feed stocks via the oxo-process, however the more economical route is usually from castor oil derivatives. The economies of the oxo-process or castor oil route will vary with the feed stock market, but are not so different as to cause severe fluctuations in the pricing of this specialty chemical. Once a producer has selected a production route, the system then is locked in and the alternate route excluded.

Table VI. Estimated 1997 regional consumption of undecanal as a direct additive to flavors and fragrances

Region	Kg
North America	5,000
Europe	10,000
Japan	1,000
Rest of the world	4,000
	20,000

Since the volumes of production in the flavor and fragrance industry are so small, the production units resemble the pilot plant units of the chemical industry and the investment in capital is relatively small. This allows the dual production methods used by some producers. The changing relative economics of the various production methods has resulted in two major routes being used for the manufacture of undecanal today. One is the oxo-process, which is employed by three of the world producers. The other is the modified Sabatier method using undecanoic acid and formic acid.

The world usage of undecanal is too small to allow a large number of producers to operate economically. But for 1997, one could mention four world producers of undecanal: Firmenich, Givaudan, IFF and Kao. Producers using the oxo-process can produce undecanal by the changing feed stock in their multipurpose equipment. Producers using the castor oil derivative route are locked in to that method for their production. The low volume of usage of undecanal causes all the manufacturers to use a "make or buy" policy for the material they need. Although all four producers mentioned can make the material, on any given day some of them may not actually do so.

World Consumption

The global flavor and fragrance industry annually consumes approximately 70,000 kg of undecanal, of which approximately 50,000 kg are used as feed stock for the production of aldehyde C-12 MNA. The remaining 20,000 kg are added directly to flavors and fragrances; Table VI breaks out this component by region. Presently, all of the undecanal used in industrial perfumery is synthetic. Approximately 100 kg of undecanal are used each year in flavor formulations.

Global aldehyde C-11 consumption should grow at the rate of 4% per year over the next decade in the flavor and fragrance industry. All of this growth will be for synthetic undecanal.

World Trade in Undecanal

Imports: Annual imports of undecanal into the United States are estimated at 5,000 kg. Undecanal is dutied under Harmonized Tariff No. 2912.19.20 and enjoys GSP status; therefore it is duty-free for many nations, such as China, Brazil, India and Mexico. The producers in other countries, such as those in Europe, will have their product dutied at 4.8% ad valorum.

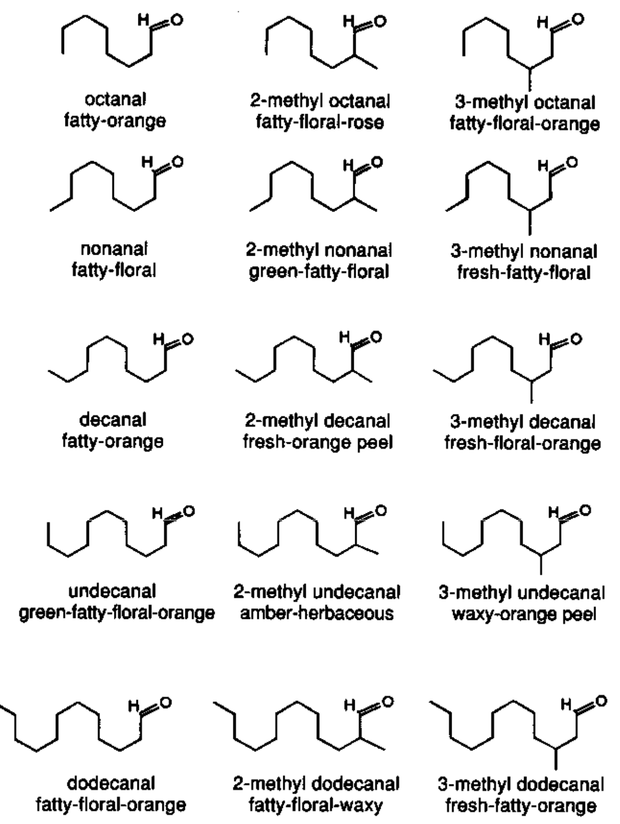
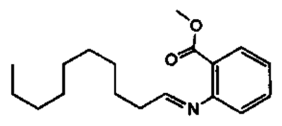


Figure 2. Saturated aliphatic aldehydes: Substitutes and analogs of undecanal

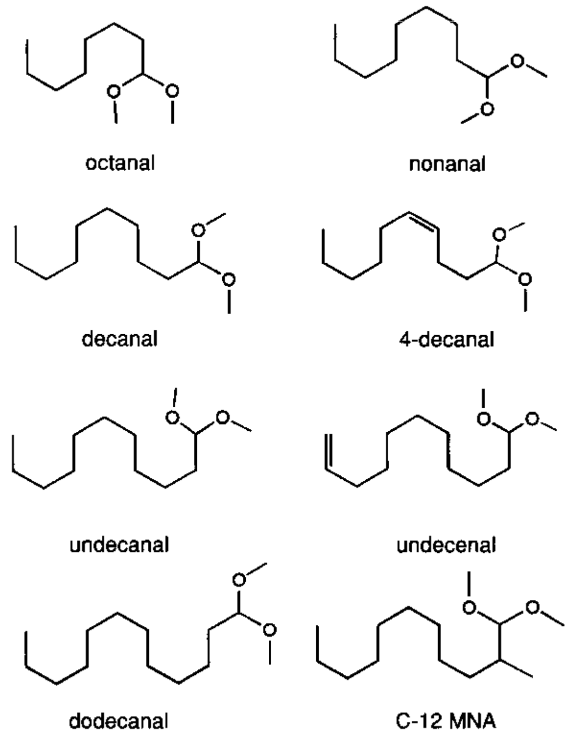


Acetal derivatives of common aldehydes

Structure 3.

Pricing: Prices have stagnated for synthetic flavor and fragrance-grade aldehyde C-11. It was priced at $9/lb in 1987, and today can be purchased at $9–10/lb.

Substitutes and analogs: The aliphatic aldehydes are seldom used alone. The usual application technique is to add a blend of aliphatic aldehydes to a new fragrance creation. The fashions in odor preference change periodically and there seems to be a swing in popularity every ten to twenty years from undecanal to undecenal and then back again. This swing involves the substitution of undecanal or undecenal, one for the other, in the favored aldehyde mixes currently in vogue to develop fragrances. These aldehyde blends have an odor profile that can be approximated by the use of varying amounts of all or only some of the aldehydes presented in Figure 2.[4,13]



octanal

nonanal

decanal

4-decanal

undecanal

undecenal

dodecanal

C-12 MNA

Figure 3. Dimethyl acetal derivatives of common aldehydes

Derivatives

There are only two groups of direct derivatives of the aldehydes: the Schiff bases and the acetals. One could view acids, alcohols or nitriles as the derivatives of aldehydes, but that would be stretching a point.

Schiff bases: This group of aldehyde derivatives, discovered by Schiff in 1864, was extensively explored by him, to such an extent that this class of chemicals bears his name. Over the years every conceivable aldehyde and amine have been mixed together and reacted to yield their corresponding azomethine or Schiff base.

The Schiff base is a defined, stable chemical and can be isolated as a pure crystalline solid. The commercially offered materials on the market today are all derivatives of methyl anthranilate and as such have their azomethine group in conjugation with a benzene ring, which gives them a powerful yellow-orange color.

Schiff bases are used for their odor value in fragrances, but also for their ability to tint fine fragrances. However, the items of commerce are inexact mixtures made from an excess of methyl anthranilate. The excess of methyl anthranilate is used to drive the reaction equilibrium to completion and hence eliminate almost all traces of the free aldehyde. Even small amounts of the free aldehyde will overwhelm the odor of the Schiff base. Thus, the Schiff bases that are offered commercially are ill-defined mixtures that resemble compounds rather than aroma chemicals.

The most popular Schiff base is the hydroxycitronellal-methyl anthranilate mixture. Of the aliphatic aldehydes, only the Schiff bases of decanal [3] and octanal are commercially offered. The Schiff bases of amylcinnamic, cinnamic, cuminic aldehydes and Lyral[a] and Triplal[a] also are commercially available.

Acetals: As with the Schiff bases, every combination of alcohols and aldehydes has been reacted to create their acetal derivatives, either as single reactants or as alcohol mixtures. The number of acetals found in the chemical literature is too large to estimate. On a practical scale, only those acetals with a molecular weight under 300 seem to have achieved any real use, because those of higher molecular weight are not volatile enough to make their presence known efficiently in a fragrance formula. The most common acetals of the C-8 to C-12 aliphatic aldehyde group are presented in Figure 3.

Aldehyde C-12 MNA: This old standby aldehyde was originally made by the Darzens reaction using methyl nonyl ketone as the starting material. In the 1970s, Blumenthal at IFF developed a new technology using undecanal as the feed stock (Figure 4).[14,15] It replaced the older, more costly route.

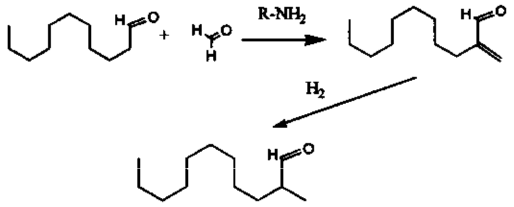


Figure 4. IFF route to aldehyde C-12 MNA

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[a] International Flavors & Fragrances, New York, NY, USA

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Address correspondence to George S. Clark, Cameron & Stuart, Inc., 6304 Waterloo Drive, Easton, MD 21601, USA, or e-mail: GeoSClark@aol.com

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