An Aroma Chemical Profile

Aldehyde C-11 Undecylenic

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The use of aliphatic aldehydes in fragrances is part of the mystique of our industry. Did not Ernest Beaux find a few bottles of aliphatic aldehydes on the lab shelf, smell them for the first time any perfumer had smelled them and suddenly realize that they would make the perfect theme for Chanel No. 5?

Sorry, but no. Beaux was a man of his times and made by his times. His "overdose" use of fatty aldehydes in Chanel No. 5 was more a result of the natural developments in organic chemistry and perfumery. If Beaux had not used these products as he did, some other perfumer would have done so—and in a very short time. His creative use of these aldehydes was a result of their commercial availability at reasonable price levels, due to Rosenmund's discovery of the reaction that bears his name (Figure 1).[4]

The Rosenmund reaction reduces aliphatic fatty acids to aldehydes via their acid chlorides. The Rosenmund reaction also is typical of its time: it generates a great deal of chemical waste—including gaseous HCl, SO_2 and tar—and is not environmentally friendly by today's standards.

Prior to 1918, when Rosenmund reported his work, aliphatic aldehydes were available, but in limited quantities and at fairly inhibiting prices. It is difficult to understand today, in an age of abundant information, but the chemists, perfumers and flavorists of a century ago literally were operating in the dark. In 1897, only about 24 aldehydes were known (Table I).[5] The only effective route to aliphatic aldehydes was via the pyrolysis of the calcium salts of their corresponding aliphatic acids. Thus these new aroma chemicals were expensive and of variable and poor quality.

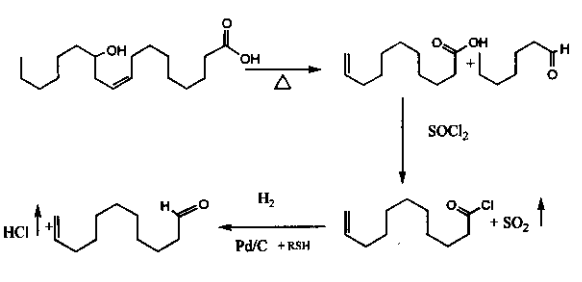
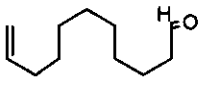


Figure 1. The synthesis of undecenal from ricinoleic acid via the Rosenmund reaction

Undecenal was first offered commercially around 1920 and immediately began competing with undecanal to see which C–11 aldehyde would be more often used in fragrances. Undecenal is the more powerful of the two, usually being dosed at approximately 30% of the undecanal levels. Organoleptically, undecenal can be described as a powerful, waxy, citrus, rose floral odor material with a fatty, waxy, citrus-like taste. Undecenal's odor is so strong and waxy that minute traces of it will strongly color the profile of flavors or perfumes in which it is incorporated. Soluble

Aldehyde C–11 Undecylenic



Mwt 168 C_{11} $H_{20}O$
CAS 112–45–8
FEMA 3095

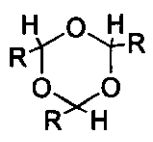
Classification: Unsaturated aliphatic aldehyde, not found in nature

Additional Names:[1] 10-undecen-1-ol; n-undecenoic aldehyde; Ambrolione (Firmenich); Pekleol (de Laire)

French: aldéhyde 10-undécylénique
German: 10-undecylenaldehyde
Portuguese: aldéido undecilenico
Spanish: aldehido 10-undecilènico

Physical Data:[2,3]

Appearance: clear, colorless liquid
Specific Gravity 25/25°C: 0.840-0.848
Melting Point: 7°C
Boiling Point: 110-116°C at 5 Torr
Refractive Index at 20°C: 1.440–1.445
Flash Point: 100°C (212°F)
Stability: Undecenal is stable for as much as one year if stored in an air-tight aluminum container at 16–25°C under an inert gas atmosphere. This aldehyde polymerizes in the presence of air and reacts with free amino groups in fragrance compounds to form colored Schiff bases. Undecenal also oxidizes in the presence of air to form undecenic acid, the presence of which encourages the trimerization reaction in which most straight chain aliphatic aldehydes will form the trioxane derivative shown as **[1]**. The addition of an oxidation inhibitor will help stabilize the aldehyde.



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only sparingly in water, undecenal displays an odor threshold of approximately 5 ppb in water.

Undecenal is a minor active additive, used in flavors at levels of 0.05-0.2 ppm in the final formula. The higher levels of application, such as 0.2 ppm in ice cream and candies, are rarely seen today because artificial flavors are experiencing declining popularity. Today this aldehyde finds limited use, mainly in imitation citrus flavors.

Undecenal's largest use is in fragrances, where it has been used at up to 1% levels. Undecenal has been found in a large number of fragranced products on the market ever since its development in the 1920s during the "New Aldehyde" craze. It is used fine perfumery, and also in soap and detergent products, because it is slightly more stable at higher pH levels than some of the lower aliphatic aldehydes.

Natural Sources

10–Undecenal is not found in nature.

History

The term aldehyde was coined in 1835 by von Liebig from the term dehydrogenated alcohol (*alcohol dehydrogenatus*). The aliphatic aldehydes were first synthesized by Bertagnini and Piria in 1853 via the pyrolysis of the calcium salt of the corresponding aliphatic acid. This method was later improved on by using a mixture of the aliphatic calcium salt and calcium formate.

The pyrolysis reaction was not very efficient, giving low yields. It also created a fire hazard in the production area because an open flame was used and a very flammable, volatile vapor (the aldehyde) was generated. The price of aliphatic aldehydes was high and the availability limited.

All of the aldehydes found late application in the area of perfumes and flavors. Most aliphatic aldehydes, C–6 to C–12, were available by 1880, but no commercial interest appeared. Up until 1900, only anisaldehyde and cinnamic aldehyde were widely known and used, but in 1900 the presence of C–8 to C–10 aldehydes was noted in natural essential oils. By 1905, aliphatic aldehydes—mainly octanal, nonanal, decanal and Aldehyde C–12 MNA—were used in a very limited way in fine fragrances and *Taschentuchparfümen*.[6] The aldehydes were most often used as inhouse secret specialties.

The first fine fragrance to include fatty aliphatic aldehydes in its formula was Pompeia (Piver, 1907). By 1908, Roure-Bertand Freres was using aldehydes C–9 and C–10 and had devised analytical assay methods, which were published in bulletin form.

Undecenal was one of the aliphatic aldehydes discovered around 1915 by French aroma chemical researchers exploring the possibilities of using products and by-products of castor oil. However, no economical synthesis existed until Rosenmund published his work in 1918.

After World War I, Aldehyde C–11 undecylenic was produced from undecylenic acid via the Rosenmund process and was, therefore, available during the Chanel No. 5 aldehydic era. Its effects were explored in the flavor and fragrance industry. The Rosenmund reaction then became the standard method for the production of aliphatic aldehydes until after 1938, when the catalytic reduction of aliphatic esters, catalytic oxidation of aliphatic alcohols and oxo-synthesis were developed.

Another complication to the growth of undecenal was the emergence of Aldehyde C–11 (undecanal). Both aldehydes had redeeming properties. Since 1920, the relative use of each has swung back and forth as the fads of the market and perfumer changed. Today it has found its place, but it is still not what you'd call a "multi-tankcar" chemical.

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

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

World Consumption

The global fragrance and flavor industry consumes approximately 70,000 kg/year of

undecenal. Most of this is used in fragrances; only about 100 kg presently is used in flavor formulations. Flavor formulation use of undecenal is limited to reconstructed citrus flavors where the product can bear a "Nat. & Art." (natural and artificial) label. Presently, all of the industrial flavor use of synthetic materials is decreasing due to consumer demand for natural flavors. Thus, undecenal does not have a very bright future in that area. The regional consumption breakdown is presented in Table II.

Undecenal's consumption in flavors and fragrances in the United States should grow at the rate of 2% per year over the next decade and reach approximately 25,000 kg/year by the year 2007. Growth will occur solely in the fragrance area.

Table II. World consumption of undecenal by region (in kgs)

Europe	33,000
North America	21,000
Latin America	4,000
Asia	10,000
Other	2,000
Total	70,000

Trade

Imports: Annual imports of undecenal into the United States are estimated at less than 2,000 kg. Undecenal is dutied under Harmonized Tariff Number 2912.19.20 and enjoys GSP (General Status Preferred) status; that is, 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.

Pricing: Prices for synthetic undecenal of flavor and fragrance grade rose from $16.75/lb in 1986 to $20.00/lb in 1996.

Synthesis

The usual synthesis employed for the manufacture of the saturated aliphatic aldehydes fails in the case of undecenal due to the complications from side reactions caused by the double bond. The Bertagnini and Piria pyrolysis of calcium salts generates an unusable mess of by-products. Thus, soon after its discovery was announced, the Rosenmund reaction (Figure 1) was adopted for the production of aldehyde C–11 undecylenic and other aldehydes.

The Rosenmund reaction remained the favored process for synthesis until around 1960. Today, the favored synthetic route is the modified Sabatier reaction in which undecenic acid and formic acid are heated in the presence of TiO_2 to yield undecenal and CO_2.

Current producers of synthetic undecenal of flavor and fragrance grade include Firmenich, Givaudan, IFF, Kao and Rhône-Poulenc.

Substitutes

The question of substitutes in the case of aliphatic aldehydes is a little more complex than with other aroma chemicals such as citral or geraniol. Aliphatic aldehydes normally are employed as a mixture or blend of three or four, not as a single material. Since aliphatic aldehydes with overlapping organoleptic profiles are fairly numerous,[7] a blend with the desired impact and profile may often be obtained via the use of a number of aldehydes. Thus, a substitute for undecenal may be a mixture of two or three other aldehydes and not just another aroma chemical. Figure 2 shows other aliphatic aldehydes with organoleptic profiles similar to undecenal. Figure 3 shows undecenal's analogs, which also may be considered as potential substitutes.

Figure 4 shows derivatives of undecenal that are used when aggressive media is encountered. In this figure, the organoleptic description of undecanonitrile is that of Sell and Cairns,[8] and it is at odds with that found in Arctander (Number 839).[9] It is most likely that Arctander's sample was impure and contaminated with lower aliphatic nitriles or other materials.

Derivatives

The first aldehyde derivatives to be explored were the acetals, which proved to be much more stable in high pH media than the aldehydes themselves. However, the acetals also proved to be unstable in low pH media, reverting to the aldehyde and the alcohol.

Acetals initially were considered to have similar but weaker odors than the corresponding aldehyde. This may or may not be true, depending on the acetal. The weak performance of acetals in acidic media encouraged investigators to find another aldehyde derivative that would be stable at all pH levels and also have the exact organoleptic profile of the corresponding aldehyde. This quest for the

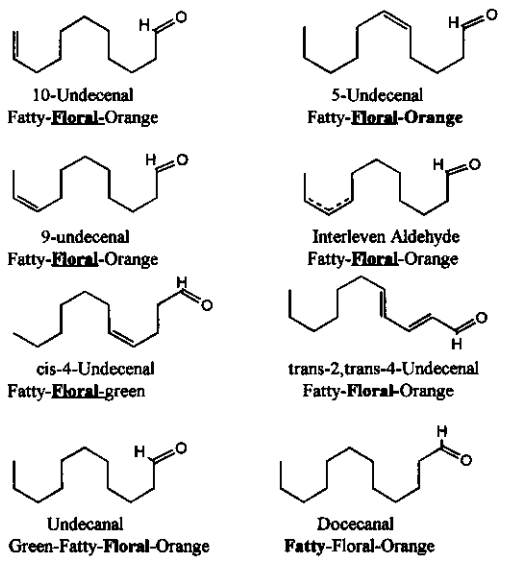

Figure 2. Substitutes for 10-undecenal (bold and underline indicates the predominant organoleptic impression)

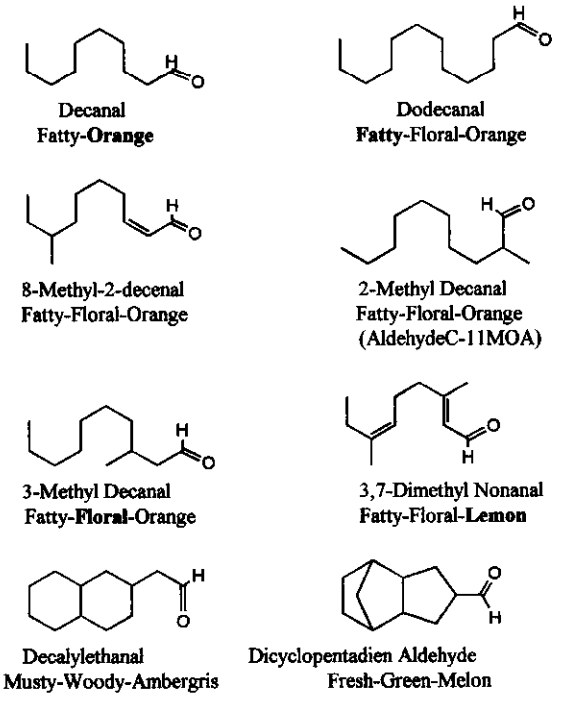

Figure 3. Analogs of 10–undecenal

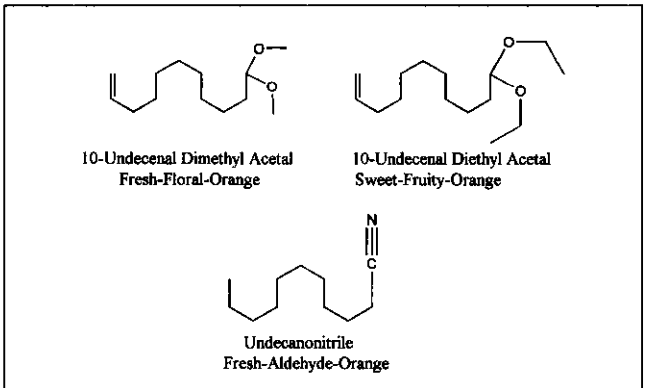

Figure 4. Derivatives of 10-undecenal

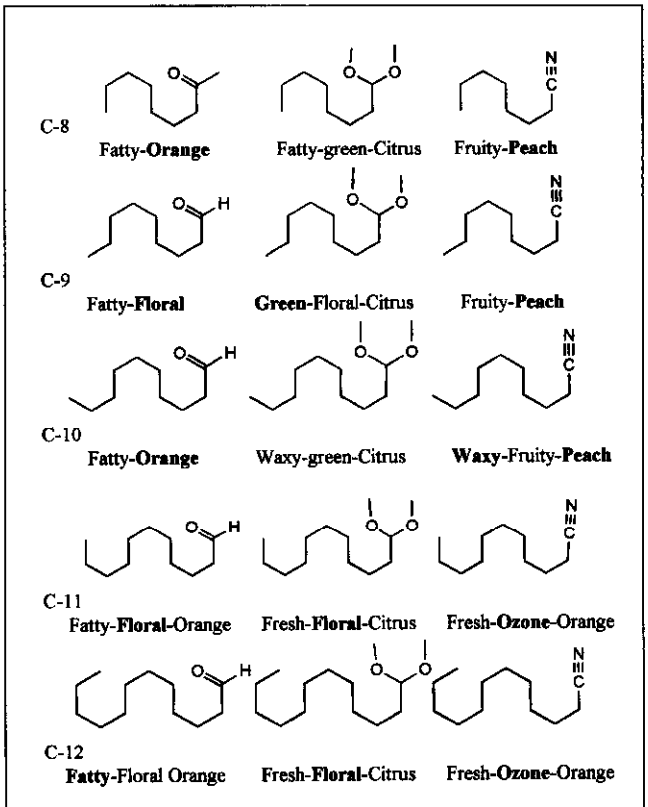

Figure 5. Organoleptic profiles of aliphatic aldehydes, acetals and nitriles

perfect aldehyde replacement was almost found in the nitrile derivatives.

The first active use of nitrile derivatives was by Igolen and Igolen[10] at Antoine Chiris & Co. in 1940. However, their efforts were not reported until 1979. The 1970s saw an explosion in the research efforts to discover new nitriles with valuable organoleptic properties. Among the many commercial successes were geranonitrile[a] and cinnamyl nitrile.[b]

Figure 5 compares the organoleptic profiles of the corresponding aliphatic aldehyde, acetal and nitrile. As can be seen in Figure 5, the profiles are often different from one another. The aldehydes will tend to have floral-orange profiles. The acetals will tend toward a floral-citrus (lemon) and the nitriles will fall into a fresh-ozone area with a main body tone of peach transcending to orange.

The answer to the age-old question as to the closeness of the aldehydes' organoleptic profile to that of the acetal or nitrile derivative is clear: sometimes it is close and sometimes it isn't. All aliphatic aldehydes and their corresponding nitrile are closest in organoleptic profile at the C–11 molecule.

[a] Citralva, IFF, New York
[b] Cinnamalva, IFF, New York

References

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