THE SATURATED ALIPHATIC ALDEHYDES

Octyl aldehyde	$CH_3(CH_2)_6CHO$	$C_8H_{16}O$	Mol.Wt. 128.22
Nonyl aldehyde	$CH_3(CH_2)_7CHO$	$C_9H_{18}O$	Mol.Wt. 142.24
Decyl aldehyde	$CH_3(CH_2)_8CHO$	$C_{10}H_{20}O$	Mol.Wt. 156.27
[Undecenyl aldehyde	$CH_2{:}CH(CH_2)_8CHO$	$C_{11}H_{20}O$	Mol.Wt. 168.28]
Undecylic aldehyde	$CH_3(CH_2)_9CHO$	$C_{11}H_{22}O$	Mol.Wt. 170.29
Lauric aldehyde	$CH_3(CH_2)_{10}CHO$	$C_{12}H_{24}O$	Mol.Wt. 184.32
Methyl nonyl acetaldehyde	$CH_3(CH_2)_8CH(CH_3)CHO$	$C_{12}H_{24}O$	Mol.Wt. 184.32

At the turn of the century, a number of fatty aldehydes were discovered in various essential oils. Not until twenty years later, however, did perfumers realize the possibility of utilizing small amounts of these highly fragrant substances to give a "lift" to their compositions.

Today, it is almost impossible to find a fragrance which does not possess at least a small quantity of a fatty aldehyde, usually ranging from a trace to as high as one per cent in the so-called aldehydic perfumes.

It is interesting that of the six popular aldehydes having eight to twelve carbon atoms, two do not occur in nature: namely, undecylenic and methyl nonyl acetaldehyde. The former has become popular because of its odor value and low price, and the latter, because of its unusual olfactory characteristics.

Occurrence.–Octyl aldehyde occurs in about eighteen natural oils[1] and plays an important role in the aroma of several citrus oils.

Nonyl aldehyde has been reported in about twenty essential oils[1]. While it is also an important constituent of citrus oils, its discovery in rose oil in 1900[2] drew attention to the usefulness of aldehydes in perfumes.

Decyl aldehyde appears to be the most widely occurring of all the aldehydes—over fifty natural sources have been reported[1]. This aldehyde is most frequently used in citrus type compositions and notable quantities of it are found in a number of citrus oils.

The occurrence of undecylic aldehyde in mandarin and lemon oil has been reported[1].

Lauric aldehyde has been found in at least fourteen sources[1], including lemon and lime oils.

Uses and Olfactory Characteristics of Aldehydes.–Octyl aldehyde, being the lowest and most fugitive of the series, possesses a somewhat pungent odor which on dilution exhibits a citrus character. For this reason, it is widely used in light fragrances such as the old-fashioned but still popular cologne types or where a light top note is required.

Nonyl aldehyde has a pleasant, fatty, rose-type odor which is very desirable in light floral compositions. Because of its relative volatility, only small quantities can be used in formulations.

Decyl aldehyde, in organoleptic characteristics, is perhaps more closely related to octyl than it is to nonyl or undecyl aldehydes. It is softer than octyl aldehyde and can be used more liberally to give both floral and citrus effects. Generally speaking, small quantities of this aldehyde along with the higher aldehydes give the most pleasing results.

Undecylenic and undecylic aldehydes are widely used in many sophisticated types of compositions. They have a green, fatty quality which blends well in woody and mossy formulations. A number of famous perfumes owe their characteristic note to this aldehyde.

Lauric aldehyde has an extremely powerful fatty note, noticeable even in high dilutions. Because of its higher molecular weight, it is long lasting, a property which adds to its value. In general, it is used in conjunction with undecylenic, and to a lesser degree, with decyl aldehyde.

Methyl nonyl acetaldehyde possesses an odor which is surprisingly different from the other aldehydes. It has perhaps the most "animal" note of them all. Its somewhat sweaty odor on high dilution imparts a distinctive quality to perfume compositions.

It is remarkable that octyl, decyl and lauryl aldehydes have odors akin to each other, the differences being largely the result of changes in molecular weight. The aldehydes having odd numbers of carbon atoms in their molecules are quite different in character and are highly valued by the perfumer.

Although aldehydes are prone to oxidation and polymerization, they can be used in most types of perfumes if proper care and attention are given to their behavior. It is a well-known fact that in the presence of alcohols[3], aldehydes form hemi-acetals which are quite stable and possess the olfactory characteristics of the aldehyde.

While aldehydes form highly colored Schiff bases with such amines as indole or anthranilates, it is possible and often necessary to incorporate these amines in a formulation but in very limited quantities to reduce the formation of colored compounds.

Large quantities of aldehydes are used in soap and detergent perfumes. Their stability decreases with alkalinity and with exposure to air. In general, it is best to avoid excessive usage of fatty aldehydes in soaps since gradual polymerization or oxidation will result in a change in the character of the soap fragrance.

It is interesting to note that methyl nonyl acetaldehyde having an alpha methyl group is considerably more stable in soaps than the straight chain aldehydes. Some alpha dimethyl aldehydes are manufactured as "captive" chemicals and exhibit great stability in soaps or in other mildly alkali mediums.

To the perfumer, experience is the best guide on the use of these indispensable compounds in his formulations.

In view of the wide occurrence of most of these aldehydes in nature, it is not surprising that they are used in various flavor formulations and are included in the list of GRAS substances published in 1965.

Preparation of Aliphatic Aldehydes. – Many methods of preparation of aliphatic aldehydes have been reported in the literature, but only a few are used by the perfume industry.

(a) Dehydrogenation of alcohols. This method is employed for the preparation of octyl, decyl and lauryl aldehydes since the corresponding alcohols are available at very low cost by the reduction of natural fatty acid esters. The process is relatively cheap, provided the conditions are standardized for the control and preparation of the catalyst.

The method was developed by Sabatier and Senderens[4] and was later fully discussed by Bouveault[5] who also described suitable apparatus. A practical description of the preparation of a reduced copper catalyst for the dehydrogenation of alcohols for perfumery purposes has been given by Lewinsohn[6]. The difficulty here is to obtain a catalyst which is active yet not easily poisoned. A number of patents describe the addition of various other metals to copper in order to produce a more stable catalyst.

One of the disadvantages of using copper catalysts is that the hydrogen produced in the course of the reaction is capable of reacting with the aldehyde formed, reducing it to the original alcohol. To avoid this, a silver-copper catalyst has been suggested[7]. Davies and Hodgson claimed exceptionally high yields by the use of such a catalyst[8].

The catalyst was prepared by treating 50 g of kieselguhr with boiling nitric acid (*d* 1.42), washing it with boiling water, and impregnating it with 10 per cent aqueous cupric nitrate. Following this, it was immersed in aqueous 2-normal sodium hydroxide in amounts sufficient to give final alkalinity to brilliant yellow paper. The kieselguhr was then removed, washed free from alkali and dried at 100° C. The copper kieselguhr was treated with a stream of hydrogen at 300–360° C to reduce it to elemental copper.

In one experiment, lauric alcohol was oxidized to the aldehyde in very high yields by passing 5 ml of alcohol per minute into the apparatus with an air feed of 250 ml per minute at temperatures of 300–350° C. Either atmospheric or reduced pressures (100 mm) can be applied and the catalyst can be used repeatedly without appreciable reduction in its activity.

Dehydrogenation of alcohols is an exothermic reaction and local overheating may give decomposition products. In large-scale operations, the problem of cooling the dehydrogenation tower presents serious engineering problems.

Nevertheless, the fact that large quantities of octyl, decyl and lauryl aldehydes are produced by this method indicates that these problems have been satisfactorily solved.

(b) Conversion of acids to aldehydes. This method, developed by Sabatier and