Unsaturated Aliphatic C9-Aldehydes as Natural Flavorants

(E,Z)-2,6-Nonadienal

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Unsaturated aliphatic aldehydes are known to play a major role in odors of plants, foods and insects. They are believed to originate from unsaturated fatty acids in several nonenzymatic and enzymatic processes, such as autoxidation, photosensitized oxidation, lipoxygenaze, peroxydaze, and microsomal enzymes, which have been suggested as initiators of lipid oxidation.

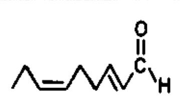
Many papers have shown the potency and significance of C9-aldehydes for the aroma of numerous volatiles. They are able to contribute to the flavor by themselves, but in addition, used in concentrations below the flavor threshold value, they can mask an undesirable odor or enhance a desirable one.

(E,Z)-2,6-Nonadienal, called sometimes violet leaf aldehyde, has a green, fresh cucumber-like odor.[1] Its structure has been well established on the basis of physicochemical studies and confirmed by syntheses[1-3] and spectral data.[4] The physicochemical and spectral data of the aldehyde are given in Table I.

Occurrence

The presence of (E,Z)-2,6-nonadienal in violet leaf essential oil was first reported in the 1930s.[5-7] This aldehyde is an important contributor to the fruit aroma of cucumbers.[8-10] More recent analytical studies reported finding 2,6-nonadienal in tea,[11] kiwi,[12] mango,[13] cherries,[14,15] rice,[16]

Table I. Physicochemical and spectral data of (E,Z)-2,6-nonadienal



$C_9H_{14}O$ **MW 138.21**

Boiling Point (°C/Torr)	Refractive Index (n_D)	Density (d) (g/mL)	Infrared (cm^{-1})	^{1}H-NMR (δ)	Reference
88-88.5/11	$1.4732^{18.5}$				1
89-90/12	1.4700^{24}	0.866			2
88/10	1.4710^{21}				3
			2940,2850, 2710,1700, 1640,980, 780,710	0.95, 1.85-2.3 5.23-5.50, 9.5	4

NMR = Nuclear Magnetic Resonance

This is the first of three articles by Kula and Sadowska on the unsaturated aliphatic C9-aldehydes as natural flavorants.

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green pea[17] and pepper.[18] It was also identified in steam-distilled products of fresh edible algae.[19] The aldehyde occurs in animal products, such as fish,[20-23] oyster,[24] beef and mutton.[25]

Chemical and Biological Properties

(E,Z)-2,6-Nonadienal is a compound relatively sensitive to water, pH and temperature. A study reported on retro-aldol degradation of unsaturated aldehydes.[26] The results indicated that 3-hydroxy-(Z)-6-nonenal was formed first by the addition of water to the alpha-beta double bond; this was followed by a retro-aldol degradation of the 3-hydroxy compound to yield (Z)-4-heptenal and acetaldehyde (Figure 1).

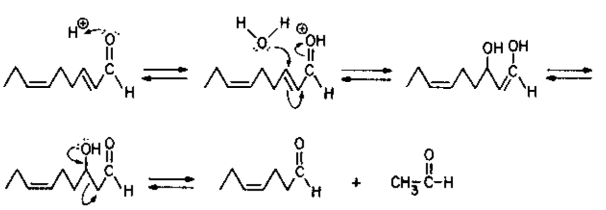

Figure 1. Mechanism for the (E,Z)-2,6-nonadienal degradation to (Z)-4-heptenal via retro-aldol condensation[26]

The formation of (Z)-4-heptanal was enhanced substantially at alkaline pH, but was greatly diminished at acidic medium. Heating (to 90°C) of aqueous solution of (E,Z)-2,6-nonadienal held at neutral pH also enhanced the rate of formation of cis-4-heptanal. These observations are of great importance, because during processing and storage of fish and other seafood the concentrations of 4-heptanal sometimes accumulate to the extent that the product becomes unacceptable for consumption.[27]

Similar alterations of green tone in the aroma of fish oil were noticed; the flavor turned to burnt after exposure to light.[28] (E,Z)-2,6-Nonadienal is reported to demonstrate some biological activity. It was shown to be a repellent to the cockroach Periplaneta americana,[29] and (as a component in a mixture) an attractant between cockroach and cricket.[30]

Synthesis

Presently, no rich natural source of (E,Z)-2,6-nonadienal is known and therefore a number of syntheses have been developed. However, the position of the double bonds and the cis configuration of one of them cause many problems in construction of such a system. Consequently, all the published methods for synthesis of this double unsaturated aldehyde are multi-stage or require expensive chemicals. We will review a few syntheses of 2,6-nonadienal which illustrate, to some extent, the complexity of the issue.

First partial preparations of (E,Z)-2,6-nonadienal were possible due to discovery of a suitable starting material, which was leaf alcohol, in the Japanese mint oil. The first total synthesis of this compound reported by Sondheimer in 1951[3] was based on 1,5-hexadiyne as the key intermediate.

A convenient method for the synthesis of 2,6-nonadienal was described by Jutz (Figure 2).[1] cis-3-Hexenol was converted to chloride which in the next step reacted with magnesium and this was followed by reaction with 1-(N-methyl-anilino)-1-propenal to give the aldehyde.

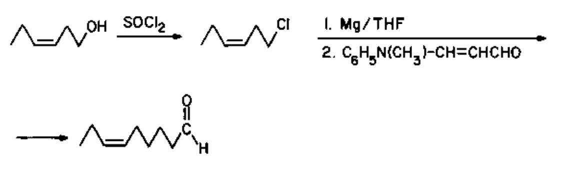

Figure 2. Synthesis of 2,6-nonadienal according to Jutz[1]

Another procedure given by American authors[31] starts from cis-4-heptenal (Figure 3). A malonic acid condensation with (Z)-4-heptenal gave (E,Z)-2,6-nonadienoic acid. Methylation of the acid, subsequent lithium aluminum hydride reduction to the alcohol, and MnO_2 oxidation of the alcohol furnished (E,Z)-2,6-nonadienal.

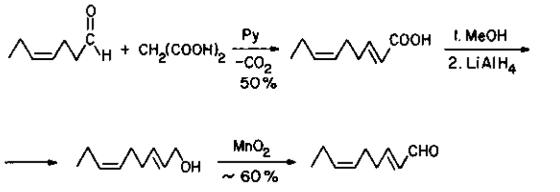

Figure 3. Synthesis of 2,6-nonadienal from 4-heptenal[31]

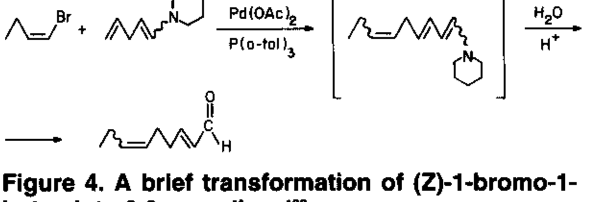

Figure 4. A brief transformation of (Z)-1-bromo-1-buten into 2,6-nonadienal[32]

According to Bender[32] a mixture of stereoisomers of 2,6-nonadienals is obtained when (Z)-1-bromo-1-buten is condensed with N-(1,4-pentadienyl)piperidine in the presence of 3% of palladium acetate and 6% of tri-o-tolilophosphine, followed by oxalic acid catalyzed hydrolysis (Figure 4). The product (total yield 28%) consisted of a mixture of 80% (E,Z)-isomer and 20% (E,E)-isomer.

Vig et al.[4] reported a multi-step synthesis of (E,Z)-2,6-nonadienal from 2-pentyne-1-ol (Figure 5).

Besides its direct use as a component of flavors and fragrances, (E,Z)-2,6-nonadienal can also be applied to the preparation of other compounds of practical potential. For example, the aldehyde with cysteine gives an adduct that is applied to margarine,[33] and (E,Z)-2,6-nonadienenitrile is

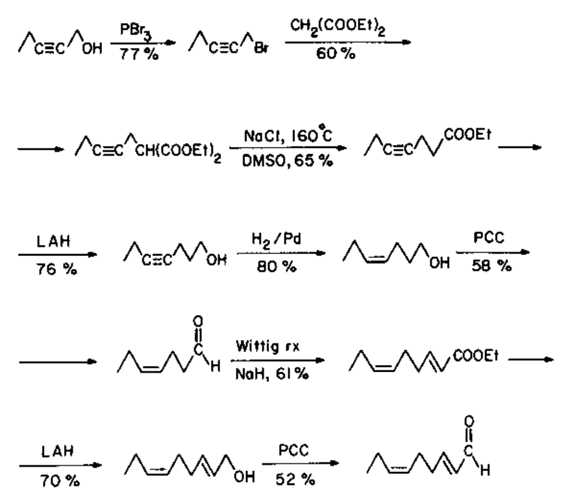

Figure 5. A total synthesis of (E,Z)-2,6-nonadienal according to Vig[4]

useful as a strong odorous perfume or as fixative and fragrance material for cosmetics, detergents and disinfectants.

Summary

Because of its odor properties and low odor threshold (0.01 ppb[34]), (E,Z)-2,6-nonadienal is a powerful flavorant. It is also shown to be a compound of biological activity. However, the published syntheses of the aldehyde are multi-stage processes and that contributes to its relatively high price.

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