Unsaturated Aliphatic C9-Aldehydes as Natural Flavorants

(E,E)-2,4-Nonadienal

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Unsaturated aliphatic aldehydes are microcomponents of a great many plants and animal products. They are believed to be secondary products originated from fatty acids. (E,E)-2,4-Nonadienal is one of a few unsaturated C9-aldehydes which are produced industrially. The physicochemical and spectral data of the aldehyde are given in Table I.

The compound has a fatty, waxy odor and is applied both in flavors and in fragrances. Its biogenesis, as with (E,Z)-2,6-nonadienal, can be rationalized by invoking a reasonably small number of metabolic pathways in which nonvolatile polyunsaturated fatty acids serve as the most important precursors in biogeneration of aromas.

(E,E)-2,4-Nonadienal is also a product of oxidative degradation of methyl and ethyl esters of linoleic acid.[1,2] Although this aldehyde occurs in several plants and animal products, there are no known rich natural sources of this flavor compound.

Occurrence

The nonenzymatic and enzymatic oxidation of fats and oils gives rise to a myriad of flavor compounds among which carbonyl compounds are prominent. As the oxidative processes occurring in nature are slow and the carbonyls are volatile, the concentration of degradative products is not large (on the order of ppm). However, (E,E)-2,4-nonadienal, owing to its low odor threshold (0.09 ppb),[3] contributes significantly to the total flavor of the parent source of smell. Thus, this aldehyde participates in the flavor creation of roasted popcorn,[4] potato chips,[5] roasted filberts[6] and black tea.[7] It is present in the volatiles of bitter melon,[8] chicory[9] and sweet woodruff.[10] 2,4-Nonadienal has also been identified in some processed animal products like pork,[11] beef[12] and chicken.[13]

Synthesis

It would not be cost effective to separate (E,E)-2,4-nonadienal as a natural isolate; therefore this commercially available aldehyde is of synthetic derivation. A few chemical syntheses of 2,4-nonadienal have been developed from more abundant raw materials, including petrochemical feedstocks.

One of the substrates for the preparation of this diunsaturated aldehyde is 2-heptenal which is also synthetically manufactured. The method described by Forss[14] consisted in condensation of 2-heptenal with malonic acid according to Figure 1.

Another approach to the synthesis of α, β-γ, δ-diunsat-

Table I. Physicochemical and spectral data of (E,E)-2,4-nonadienal

$C_9H_{14}O$ MW 138.21

Boiling Point (°C/Torr)	Refractive Index (n_D)	Density (d) (g/mL)	Ultraviolet (nm)	Reference
72-74/3	1.5184^{27}	0.862^{25}	274	16
98-99/10	1.5174^{20}	-	262	15

This is the second of three articles by Kula and Sadowska on the unsaturated aliphatic C9-aldehydes as natural flavorants. (E,Z)-2,6-Nonadienal was discussed in the September/October 1993 issue.

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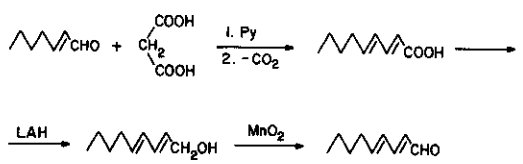

Figure 1. Preparation of (E,E)-2,4-nonadienal according to Forss et al[14]

urated aldehydes from α-unsaturated aldehydes has been reported by Makin et al (Figure 2).[15]

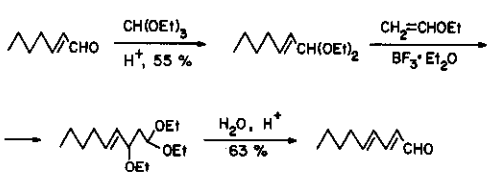

Figure 2. Synthesis of 2,4-nonadienal from 2-heptenal and ethyl vinyl ether[15]

It has been found that unsaturated bromides can be useful as raw materials for 2,4-nonadienal synthesis. Figure 3 shows the use of a Grignard reaction for this purpose.[16]

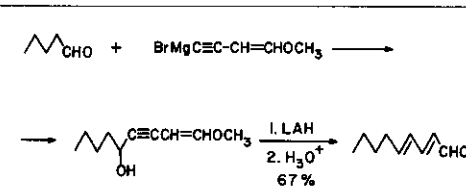

Figure 3. Synthesis of 2,4-nonadienal by Grignard reaction[16]

An interesting method of synthesis of 2,4-dienals from vinyl halides was published in 1981.[17] 2,4-Nonadienal was obtained in 76% of the total yield (Figure 4). The reaction was carried out in piperidine and the final product is a mixture of stereoisomers with the E,E-form predominating.

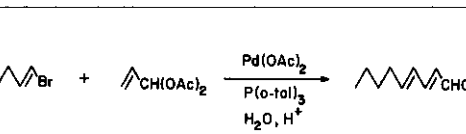

Figure 4. A brief synthesis of 2,4-nonadienal from vinyl halide[17]

The use of fumaraldehyde monodimethyl acetal[18] looks promising as a building block for polyunsaturated aldehydes. (E,E)-2,4-Nonadienal of high purity was synthesized with good yield by this method (Figure 5).[19]

This aldehyde is utilized in a food flavoring composition and in fragrances. According to a French patent,[20] its addition in the amount of 0.5-40 mg/kg to animal fats, soybean oil, margarine and bakery products reduces the aroma losses of the food products during their storage. At 0.1-100 ppm, 2,4-nonadienal in the form of alkyl thioacetals is recommended as an additive to some food products to

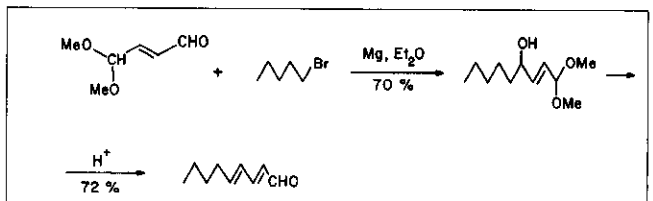

Figure 5. Fumaraldehyde dimethyl acetal as a block building in manufacture of 2,4-nonadienal[18]

impart or enhance meaty, chicken-like, fatty and pork-like flavors and aromas.[21]

However, an investigation of the lethal effects of a linoleic acid hydroperoxide and its autoxidation products, unsaturated aliphatic aldehydes, on human diploid fibroblasts revealed that (E,E)-2,4-nonadienal was among the most toxic toward the cells.[22]

The aldehyde is also a useful intermediate in the syntheses of many chemicals.[16,23]

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