An Aroma Chemical Profile: Nonadienols

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In search of green notes. The green phenomena in aroma chemicals begins in the C_6 group in a number of examples. The green effect extends thru C_7 and C_8 to end at the C_9 level with the nonadienols. The green effect slowly fades into a floral tone and then disappears into the oily-fatty area in the higher aliphatic molecules above C_9. The nonadienols are truly representative of the term, "specialty aroma chemical," because their singular and collective volume is small by any standard. The 3,6-Nonadienol used above in Figure 1 as the structural illustration for this group represents the latest product introduced, and the dedication aroma-chemical manufacturers have invested in their markets. It is forecast that the R&D expenditure needed to develop this latest specialty will most likely never be recouped, based upon the projected sales volume and its present price level.

3,6-NONADIEN-1-OL

Mwt 140 HNr. 2905.29 CAS 76649-25-7
$C_9H_{16}O$ FEMA-GRAS

Classification: Unsaturated primary aliphatic alcohols

Additional Names[a] (1,2,3)

3,6-Nonadien-1-ol, (Z, Z)-3,6-Nonadien-1-ol, (cis, cis)-3,6-Nonadien-1-ol, Cucumber Alcohol, Melon Alcohol, Violet Leaf Alcohol

Physical Data:
- Appearance: clear, colorless to pale yellow liquid
- Specific Gravity: 0.863-0.871 at 25°C
- Boiling Point: ~70°C at 2 Torr
- Refractive Index: 1.462-1.469 at 20°C
- Flash Point: 104°C TOC
- Odor Threshold-Air: ~ 50 ppb (estimated)

Solubility: Only very slightly soluble in water (~0.001% at 20°C), soluble in ethanol, esters, most liquid aroma chemicals, aliphatic, aromatic and chlorinated hydrocarbons.

[a]Many of these common names were or are still used interchangeably for many of the Nonadien-1-ol isomers, as their organoleptic properties area form a continuum one to the other.

Organoleptically, the nonadienols are an interesting group of medium-volatility range alcohols because they possess unique green-vegetable-cucumber-melon properties. These organoleptic attributes cannot be readily found in any other materials, save their related aldehydes. Table 1 presents their organoleptic profiles along with those of the corresponding aldehydes.

Natural Sources

There are a number of nonadienols found in nature; 2,4-nonadien-1-ol, 2,6- nonadien-1-ol and 3,6- nonadien-1-ol. Their structures are complicated by their existence in cis and trans forms for each double bond, leading to a number of possibilities. Their exact identification has sometimes been tenuous, thus the reports of finding one isomer are sometimes in error and the entity found is in reality another isomer or a mixture of isomers.

Nonadienols have been identified in the following natural products; champaca absolute, cucumbers, melons, muskcadine grapes, salmon, squid, violet flowers and leaves, and yeraishan. All natural sources of these alcohols that have been found to date, contain such small concentrations of these products that a commercial natural source is unavailable.

The series C_9 -dien aldehydes and alcohols arise from the cleavage of linolenic acid by lipoxygenase catalysts, followed by various further dehydrogenations, reductions and isomerizations. Because there is usually a dynamic equilibrium present in living tissue between the aldehyde-alcohol and acid forms of aliphatic chemicals, one can assume that the nonadien-1-ols could be found in living

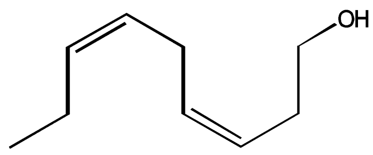

Figure 1. 3,6 Nonadien-1-ol

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Table 1. The Organoleptic Impression of the C_9 Series

Material	Price $/kg	Impression
Nonanal	20.00	fatty-floral
Nonan-1-ol	28.00	oily-floral
cis-2-Nonen-1-ol	650.00	waxy-melon
trans-2-Nonenal	200.00	fatty-waxy-orris
trans-2-Nonen-1-ol	400.00	waxy-green
cis-3-Nonen-1-ol	330.00	waxy-green-melon
cis-6-Nonenal	1500.00	fresh-melon
cis-6-Nonen-1-ol	800.00	powerful-melon
tran,trans-2,4-Nonadienal	600.00	powerful-fatty-green
trans,trans-2,4-Nonadien-1-ol	1,600.00	mild-fatty
trans,cis-2,6-Nonadienal	1,800.00	green-vegetable-cucumber
trans,cis-2,6-Nonadien-1-ol	2,300.00	green-cucumber
trans,trans-2,6-Nonadienal	2,300.00	green-citrus
trans,cis-3,6-Nonadien-1-ol	2,300.00	melon-cucumber
cis,cis-3,6-Nonadien-1-ol	3,500.00	melon-cucumber

matter where the corresponding aldehydes have also been identified. In most systems where both have been found, the levels of the alcohols are orders of magnitude less than the aldehydes, thus challenging their identification. However, the occurrence of C_9 aldehydes in cooked meat and fish is largely a result of thermal splitting of fatty lipids, which does not involve a set of equilibria with the alcohol.

History

The first nonadienol to be discovered in nature was 2E, 6Z-nonadien-1-ol, uncovered by Ruzicka in 1935 as a constituent of violet leaves.[4] Takei isolated 2E, 6Z-nonadien-1-ol from violet leaves and synthesized it from leaf alcohol in 1938, eventually isolating it from cucumbers in 1939.[5]

The exact structure was explored and determined by Seidel in 1944.[6] The problems of determining the structure of these alcohols is complicated by the ease of their isomerization, which results in not only cis-trans shifts, but also movement of the double bonds up and down the aliphatic chain. This problem has perplexed chemists during attempts to synthesize these molecules, especially in the development of commercial processes. Ruzicka developed a laboratory process for the nonadienols in the period 1926-1929,[3] which was scaled up by Firmenich which furnished relatively small amounts of nonadienol for captive use in fragrances and flavors in the late 1930's.[7] The first commercially available product was 2E, 6Z-nonadien-1-ol, offered in the early 1960s by Compagne Parento as a result of the research of Paul Bedoukian, their technical director, at that time. In 1979, Bedoukian Research began production of the isomer 2Z, 6Z-nonadien-1-ol, and in that same year, introduced 2, 4-nonadien-1-ol. The 2E, 6E-nonadien-1-ol isomer was introduced in 1980 by Fontarôme. The next isomer to be produced was 3Z, 6Z-nonadien-1-ol, which was commercialized by Bedoukian Research in 1984. The most recent product, 3Z, 6Z-nonadien-1-ol, was introduced by Nippon Zeon in 1996 and marketed in the US by Bedoukian Research.

Consumption[8]

The consumption of natural nonadienols by humans worldwide from all food sources is estimated at about 2,000kg/year for 1998. About 90% of this consumption is via fruits and vegetables and the remaining 10% via fish. Current consumption of all types of synthetic nonadienols in both flavors and fragrances is estimated at 900kg/year. About 80% of the usage for the synthetic nonadien-1-ols is currently in the fragrance area, while only 20% is used in flavors. This may seem surprising due to the high price of the items.

Applications

The occurrence of either the aldehyde or alcohol in a natural product would indicate the potential use of either in flavor of fragrance creations using that theme. Because the corresponding aliphatic alcohol usually has a similar organoleptic impression as the aldehyde, only when muted (see Table 1) the alcohol can be used in flavor systems naturally incorporating the aldehyde to extend its impression and reinforce the effect. The use of the alcohol in place of the aldehyde in fragrance applications is sometimes necessitated where aldehydes do not stand up well, such as in high surface areas or pH extremes. Even then, the nonadien-1-ols have been reported to be unstable to extremes of pH in aqueous systems, undergoing a retro-aldol condensation to heptanal.

Nevertheless, those natural products containing the aldehyde give a clue as to where to use the alcohol in new formula creations. The nonadienals have been reported in the following materials; cooked alligator meat, avocados, warmed-over flavor in beef, cherries, cooked chicken fat, roasted chicory, cornmint oil, boiled crayfish, cucumbers, daphne odora flowers, fresh and cooked duck, fermented fish paste, iris roots, kiwi fruit, mangos, skim milk, muskcadine grapes, muskmelons, mutton, narcissus poeticus, oysters, peas, pepper, popcorn, potato chips, rice, salmon, tea, tomatoes, and woodruff.

The types of consumer products which lend themselves to the use of the nonadienols are:

- Beverages: In new-age tea drinks as a modifier of basic citrus types (lemon, orange, grapefruit) to create a melon-vegetable-cucumber twist; in vegetable-flavored salad dressings, mushroom gravies for a new fresh effect; and as a modifier of standard liqueur types, to create a twist which brings a slight natural vegetable effect to traditional flavors such as -anisette, caraway, vermouths, apéritifs, etc.
- Fragrances: Fine fragrances for the introduction of cucumber-melon notes, and a fair volume of usage is foreseen in the area of cosmetic products, where natural, unperfumed and vegetable-health themes are popular, big sellers.

Future Potential Growth

Aroma chemicals are a complex group of products when it comes to defining them in a marketing sense. The price sensitivity relationships for each aroma chemical are not the same and the potential sales volume is difficult to predict. The economic forces that effect them roughly divide aroma chemicals into four groups:

- Bulk commodity chemicals where the main use is outside the flavor and fragrance industry, where the economics are dictated by another industry. Here the pricing is set very low due to the commodity nature of the industrial chemical business with products like acetophenone, benzyl alcohol, butyl acetate, ionone and methyl benzoate.
- Bulk chemicals where the technology is fairly open to all and the use is mainly within the flavor and fragrance industry. The economics in this group are depressed and profits minimal, with products like phenethanol, linalool, and galaxolide.
- Low-volume specialties without patent protection used mainly in the flavor and fragance industry. Generally moderate profit margins with products like allyl isothiocyanate, aldehyde C-12 MNA, indol, octyl acetate and the nonadienols.
- Low-volume specialties with patent protection used mainly in the flavor and fragrance industry. Generally high profits margins in this group, including products like bacdanol, brahmanol, hédione, isosuper E and timberol.

Pricing Issues and Their Impact on the Flavor and Fragrance Industry

The nonadienols fall into the third group, where profit margins are fair, but sales volumes are low, at 100-10,000 kg/year. A general rule of thumb for this group is that the higher the price of these materials, the lower the sales volume (this rule does not hold for the products in group 4).

An exclusion graph plot of aroma chemical prices/kg versus volume in kgs for some 152 aroma chemicals shows that almost no aroma chemical priced at over US$60/kg will attain a sales volume of over 1000kg/year.[9] At prices of US$1600-2,300/kg, any individual nonadienol will not attain a sales volume over the 1000kg/year level. Moreover, the use of synthetic nonadienols in flavors is limited by the current market stress on natural flavors.

At the current price levels of the synthetic products, there is a great incentive for natural aroma-chemical producers with biotechnology production systems to develop a route to manufacture natural nonadienols. At the same time, the flavorist working in the beverage area can often use the available natural aqueous-based melon or pumpkin essences on the market to build the same effect.

The most advantageous application area for the synthetic nonadienols would be the fragrance market, where the stability advantages of these alcohols over their aldehydes could open up new formula volumes in new consumer products. The introduction of lower-priced nonadienols would receive the same attention afforded new materials, perhaps setting off a new fragrance-market trend; natural-green-vegetable-melon. If the price could be brought down to the US$40-50/kg level, then their use in fragrances would most likely increase greatly. At those price levels an annual volume of 25,000-100,000kg/year could be realized. Nonadienols have a better volume potential for use in fragrances than leaf alcohol which is now priced in the US$60-75/kg area. Conversely, leaf alcohol has a wider need in flavors than the nonadienols.

Substitutes

Cucumber-melon-type materials are rare. The old practice to evoke the flavor, before the advent of nonadien-1-ols, was to use a mixture of fruit esters and other peripheral contributors, which yielded a poor rendition. The corresponding aldehyde of each nonadien-1-ol will often work as a substitute for the alcohol in some applications. The use of the aldehyde alone may provide a shallow effect. For an economical melon-cucumber effect in flavors and fragrances, melonal (2,6-Dimethyl-5-heptenal; FEMA-GRAS 2389) will provide a note in the general organoleptic area as the nonadien-1-ols at a price of about US$173.00/kg.

The isomeric alcohol analog of melonol, α-melonol (2,6-Dimethyl-6-hepten-1-ol; FEMA-GRAS 3663), is also available on the market. In the past, cyclamen aldehyde (p-isopropyl; α-methyl hydrocinnamic aldehyde; FEMA-GRAS 2743) was used to help attain a cucumber-melon effect in both flavors and fragrances.

Derivatives

The main derivatives of these materials are their corresponding aldehydes, all of which became commercially available before the alcohols. No source has yet been seen for the corresponding nitriles. The market offers the acetate esters of both 2E, 6Z-nonadien-1-ol and 3E, 6Z-Nonadien-1-ol, which have recently attained FEMA-GRAS status. The only acetal of this group that is offered is the diethyl acetal of trans, cis-2, 6-Nonadienal, which possesses a smooth violet-melon odor.

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