

Leaf Alcohol

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Leaf alcohol holds a special position in the field of aroma chemicals. Its importance is due to its unique natural green qualities, although its volume of consumption places it in the area of a specialty material.

Leaf alcohol and its derivatives are a symbol of the "green revolution in flavors and fragrances that developed in our industry during the 1960's". Its commercial introduction changed the nature of flavors and fragrances and resulted in the wide spread use of n-hexenyl based materials. Today, more than 40 structurally related aroma chemicals are being utilized in our industry and all at relatively low formula percentages.

Most intriguing is the nature of the organoleptic impression of these materials, whether the derivative is a simple ester of leaf alcohol or a more intricate de-

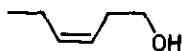
rivative such as the isomeric primary alcohols, aldehydes or related acids and their esters. They all display the same family trait—a distinct green effect when compared to their saturated analogues. The saturated analogues tend to fatty notes, and the acetylenic precursors display a dry, hay-chemical note.

Cis-3-hexen-1-ol—an ethereal like green alcohol impression when smelled neat or in high concentrations. When diluted, the impression is fresh-cut green grass. An almost uncanny refreshing, relaxing natural effect—like the outdoors on a summer's day.

Leaf alcohol, because of its wide distribution in nature and its forefront position as a material imparting a natural note to compounds—is in the minds of most perfumers and flavorists a natural product. However, almost all the commercially available materials is paradoxically a synthetic aroma chemical which is pro-

Leaf Alcohol

(cis-3-hexen-1-ol)



(cis-3-hexen-1-ol)

Mwt 100

C₆H₁₂O

CAS 544-12-7

FEMA-GRAS 2563

Classification:

A straight chain unsaturated aliphatic primary alcohol.

Additional Names:

English: Leaf Alcohol

German: Blaetter-Alkohol

Older literature has caused some confusion as the term leaf alcohol has also been applied to the isomer trans-2-hexen-1-ol, and the name leaf aldehyde is used for trans-2-hexenal.

Physical Data:¹⁻³

Appearance: Fluid, clear, colorless liquid

Specific Gravity: 0.846 (22°C)

Refractive Index: 1.4384 (20°C)

Boiling Point: 156-7°C

Flash Point TCC: 44°C

Solubility: Slightly soluble in water; soluble in ethanol, organic esters, aldehydes, ketones, alcohols and diols.

duced by the selective semi-hydrogenation of 3-hexyn-1-ol. Thus, all producers' material may display secondary notes due to overhydration (hexan-1-ol), underhydrogenation (3-hexyn-1-ol), or prolonged exposure to heat and the catalysts used (cis and trans isomers of 4-hexen-1-ol, 3-hexen-1-ol and 2-hexen-1-ol).

hexan-1-ol—not green, slightly chemical (solvent) with fatty-fruity tones.

3-hexyn-1-ol—dry, hay-chemical with a touch of cardboard.

trans-3-hexen-1-ol—green, but less fresh cut grass, with fatty, vegetable notes.

cis-4-hexen-1-ol—green-fruity, vegetable

trans-4-hexen-1-ol—mildly green and fresh, slightly fatty

cis-2-hexen-1-ol—pungent, green, fruity-vegetable

trans-2-hexen-1-ol—fruity green towards apple, slightly fatty-vegetable

5-hexen-1-ol—acid green-fatty

1-hexen-3-ol—(arises from the isomerization of *trans-2-hexen-1-ol*) chemical with winey, smoky tones, with a touch of garlic.

Commercially available products in the past have

shown tones of impurities from the residues of 3-hexyn-1-ol, amine and other solvent notes. Most of the material offered today is free of these impurities.

In general, leaf alcohol and its derivatives are the most important group of products for green, fresh impressions in flavors. In fragrances, they are important. However, the "green impression" can be constructed by using other non-GRAS materials in perfumery. New IFRA guidelines⁴ have placed limits on the usage of *trans-2-hexenal* and its acetals, but not on leaf alcohols or *cis* or *trans-3-hexenals* in fragrances.

Natural Sources

Cis-3-hexenol and its analogue *trans-2-hexenol* can be found in trace amounts in almost every plant with green foliage. As analytical techniques improve, traces of these alcohols, as well as their aldehydes and esters, are being uncovered in many essential oils. They are also found in many fruits and vegetables, i.e. it is estimated that 10 MTons of *cis-3-hexenol* are consumed by the residents of the U.S. each year via tomatoes alone.⁵

Numerous investigators have explored the presence and source of leaf alcohol in plants. The best picture that can be gleaned to date is that leaf alcohol is derived from *cis-3-hexenal*⁶ by its enzymatic reduction. The *cis-3-hexenal* results from the enzymatic oxidation cleavage of linolenic acid in the presence of oxygen. When a plant is traumatized (crushed or cut), the increased oxygen availability results in rapid cleavage of linolenic acid and the subsequent generation of increased levels of the aldehyde and the alcohol.

The sudden release of leaf alcohol is very apparent when one cuts the lawn, thus bringing to mind fresh-cut grass as a descriptive term for leaf alcohol for most Americans and Europeans. Because this sudden release of leaf alcohol is still at very low absolute levels (but not low organoleptic recognition levels), some observers maintain that leaf alcohol is only present when trauma occurs. This would not explain the presence of leaf alcohol or the aldehydes in living flower essences or the presence of leaf alcohol esters in plants or essential oils. A good guess is that the oxidation cleavage of linolenic acid is taking place continually at a low rate governed by the diffusion rate of oxygen into the plant cells, and that the sudden surge witnessed during maceration of the plant material is due to increased availability of oxygen.

A rough calculation estimates that 1,000,000 MTons of leaf alcohol are available in living plant material sources throughout the globe at any given time (should one wish to crush that many leaves).

Leaf alcohol has been identified in the following sources:

Natural products containing cis-3-hexen-1-ol:

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Achillea Fragrantissima	Laures Leaves
Apples	Lime
Avocado	Melissa Oil
Bergamot Oil	Ocimum Basilicum (Basil)
Black Currant Leaves	Orange Juice
Blueberries	Osmanthus Fragrans, flowers
Citrus Leaf Oils	Parmesan Cheese
Celery Plants	Parsley Leaves
Cruciferous Plants	Passion Fruit, juice
Cow's Milk	Peony
Daphne Flowers	Peppermint
Elderberries	Pimento Oils
Epilobum Angustifolium	Prunus Mume (Ume Plum)
Fragaria Vesca (Strawberries)	Quince Fruit
Filipendula Ulmaria	Raspberries
Meadowsweet)	Sage Leaves
Genet	Sorbus Aucuparia (Mountain Ash)
Geranium	Strawberries
Green Peas	Tea Leaves
Iris Root	Violet Leaves
Jasmin Flowers	Wistaria

To date, the analysis of most commercially available essential oils has not shown the presence of leaf alcohol or its aldehydes. This is most likely due to their method of processing by steam distillation, as most of the lower alcohols are lost in the water fractions due to their high solubility.

The use of leaf alcohol and its derivatives has been paramount to the creation of quality modern flavors. Yet, curiously, in some applications, such as herbal teas, their presence is deemed undesirable.⁷

Only recently has natural leaf alcohol or its derivatives been offered commercially. Current sources of these products are Fleurchem and Robertet. However, the volumes available are small compared to the total market. Yet the growing demand in consumer goods for natural flavors has caused many large firms with in-house requirements to explore natural sources of these green notes.⁸

History

Although leaf alcohol has been a part of the human food chain since time began, it was not until 1895 that its presence was indicated in tea oil⁹ and 1917¹⁰ that its presence in Japanese mint oil was discovered and the structure roughly established. The position of the double bond and cis-trans configuration remained as an academic bone of contention until Stoll and Rouve¹¹ showed that leaf alcohol was cis-3-hexen-1-ol. This controversy was complicated by the fact that the natural product isolated from various sources often was a mixture of alcohols because of the product's precursor's ease of isomerization.

This confusion also led to the isomeric alcohols cis-3-hexen-1-ol and trans-2-hexen-1-ol being referred to as leaf alcohol. As cis-3-hexenol is generated directly from cis-3-hexenal and trans-2-hexen-1-ol is generated indirectly from cis-3-hexenal via its isomerization to trans-2-hexenal, cis-3-hexen-1-ol deserves the name leaf alcohol.

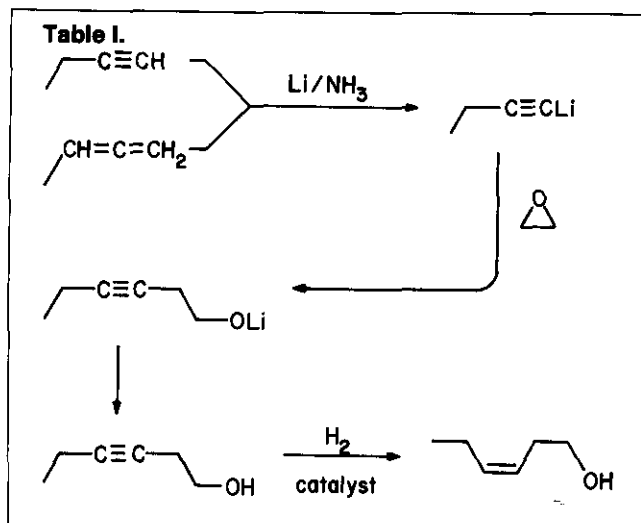
Leaf alcohol was first used by the German firm Schimmel under the trade names "Phyllol" and "Verdalol" before the second world war. It remained a captive specialty of many houses until a fortuitous set of circumstances arose.

In the late 1950's, the market for flavors in the U.S. was beginning to undergo rapid changes. New flavor materials were constantly being introduced which made older flavor formulations obsolete in just a few years.

The demographic changes that occurred in the U.S. since 1914 on resulted in a majority of the population moving from rural to urban environments, contributing to significant changes in the flavor market. Customers became accustomed to buying produce in supermarkets rather than a local farm stalls or growing and picking their own. The fresh pack you picked from your own tree on the farm in 1910 did not taste the same as the supermarket peach available in 1955.

In order to supply the urban markets, farmers were forced to harvest fruit while still not fully ripe to minimize damage in transit. Thus, the flavor of peaches, strawberries, etc. of 1955 were flavors with pronounced unripe green notes. When compared to their counterparts available in beverage and dessert

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flavors, there was a great difference. That difference was mainly in the green note portion of the flavor. It was this phenomena which resulted in the sudden interest in leaf alcohol and the appearance of the green note revolution of the 1960's—which carried over from flavors into fragrance.¹²

The introduction of Diorissimo (1956) was the first successful use of hexenyl esters in fragrances; while the use of hexenyl salicylate in Charlie (1973) created an effect of such magnitude that others soon followed this trend which had placed Charlie in a milestone category of fine fragrances.

It was this need that captured the imagination of a man who would spend his career promoting leaf alcohol and whose names will be historically linked to it—Dr. Paul Z. Bedoukian.¹³ Until the late 1950's, leaf alcohol had been a specialty because there was no commercially available feed stock for its large scale production. In 1958, Air Reduction Chemical Co. began producing 1-butyne (ethyl acetylene) for use as a pharmaceutical intermediate. This material was the key to commercial leaf alcohol production. Dr. Bedoukian approached Air Reduction Chemical Co. to secure a supply for leaf alcohol production.

By 1960, Compagnie Parento, where Dr. Bedoukian was technical director, began offering leaf alcohol based upon 3-hexyn-1-ol made from ethyl acetylene. Dr. Bedoukian introduced a sample of new commercially available leaf alcohol to the flavorists of one of the largest U.S. food companies. Its incorporation into the new fruit flavors of this firm established leaf alcohol as a commercial success.

Other firms, such as Givaudan and IFF, also began producing and offering cis-3-hexen-1-ol, while others produced it for captive use, using the same raw material. By the late 1960's, Oril in France (Fontarome) also started importing ethyl acetylene from the U.S. and producing leaf alcohol and its derivatives. Air Reduction's feed stocks supplied the world needs until 1978, when Japanese firms developed a

route to 3-hexyn-1-ol via low cost 1,2-butadiene found in a byproduct stream of petroleum cracking plants. Ethyl acetylene at \$8.00/lb was dealt a swift death by a byproduct with relatively no value. Air Products Co. (the successor of Air Reduction) ceased production of ethyl acetylene in 1981.

It is ironic that the same byproduct stream was available in the U.S., but U.S. petro-chemical firms could or would not make it available. This change alone resulted in Japan becoming the dominant supplier of leaf alcohol and its derivatives today. A perfect example of a decline in an industry due to lack of cooperation of firms at a national level. If a Japanese petro-chemical firm could open a byproduct stream pipe and make available an intermediate instead of disposing of it by flaring, why could a U.S. producer not do the same?

Over the years many attempts have been made to develop synthetic routes to leaf alcohol. Some of the procedures are quite elegant, but one basic route prevails—the selective semi-hydrogenation of 3-hexyn-1-ol, which is generated from either 1-butyne or 1,2-butadiene by reaction with ethylene oxide.

Industrial routes employed the sodium salt of 1-butyne in liquid ammonia which resulted in over-ethoxylation of 3-hexyn-1-ol to mono- and di-ethylene oxide ethers or incomplete reaction of the 1-butyne and its loss in work-up.

An improved route was developed using the lithium salt which could be reacted with ethylene oxide in liquid ammonia or other solvents such as THF. The use of the lithium derivative leads to more complex reaction of the 1-butyne and little or no further reaction of the resulting 3-hexyn-1-ol lithium salt with ethylene oxide to produce ethers. The use of 1,2-butadiene (an allene) provides the 1-butyne lithium salt in situ and the reaction proceeds just as if one started with 1-butyne (Table I).

The most difficult step in the generation of cis-3-hexen-1-ol is the selective semi-hydrogenation of 3-hexyn-1-ol. Many catalytic systems have been developed and maintained as trade secrets. Most systems employ a palladium catalyst on charcoal modified by "poisons", which prevent the reduction of the cis-3-hexenol to hexan-1-ol. Isomerization of the generated cis-3-hexenol to other isomers occurs easily and is minimized by the catalyst "poison", temperature, time of exposure to the catalyst, and hydrogen pressure in the system.

The production of leaf alcohol is costly due to expensive starting materials, low reactor loadings, multiple steps and its low volume of usage.

World Consumption

Worldwide usage of leaf alcohol in 1990 is estimated to be 250,000 lbs. both as the alcohol and its derivatives. Regional consumption expressed as the

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free alcohol breaks down as follows:

North America	65,000 lbs.
Europe	100,000 lbs.
Japan	40,000 lbs.
Others	15,000 lbs.

Consumption of leaf alcohol is gauged as use in compounds and not as a chemical intermediate. Approximately 30% of consumption is as the alcohol while the remaining 70% is as its esters. Worldwide usage of the esters is as follows:

World consumption of its derivatives is estimated as follows:

cis-3-hexenyl salicylate	100,000 lbs.
cis-3-hexenyl acetate	100,000 lbs.
cis-3-hexenyl benzoate	20,000 lbs.
trans-2-hexen-1-yl acetate	
trans-2-hexenal	10,000 lbs.
cis-3-hexenyl formate	3,000 lbs.

Pricing

Leaf alcohol prices have dropped steadily since the product's introduction in 1960 at \$80.00/lb. Current prices are \$35.00-55.00/lb. depending upon grade and quantity. Prices should slowly rise at about 2% per annum over the next 5 years mainly due to monetary changes and general cost escalation.

Supply

The 250,000 lbs. of leaf alcohol consumed in 1990 will be far below the capacities available from current suppliers. Consumption will be in the form of 65,000 lbs. of alcohol and 260,000 lbs. of esters.

Leaf alcohol consumption in the form of alcohol, esters, and isomeric alcohol esters and aldehyde should grow at a 5% per annum rate over the next decade, reaching a level of 400,000 lbs. by the year 2000.

Some experts feel that a drop in price of leaf alcohol to \$15.00/lb could lead to levels of 2,000,000 lbs. of consumption. However, more conservative estimates project a usage of 800,000 lbs. in 5 years should a price level of \$15.00/lb be obtainable.

Whatever the projected usage level may turn out to be, sufficient capacity is in place in Japan, Europe and the U.S. to supply growing needs.

Synthetic Producers

Nippon Zeon Co. Ltd., Tokyo, Japan: This producer is currently the largest supplier of leaf alcohol and derivatives in the world with an estimated 65% market share and an operating capacity in excess of 200,000 lbs/yr. Some of this capacity is used to produce cis-6-nonenol and cis-jasmone.

Shin-Etsu Chemical Co., Tokyo, Japan: This company is supplying about 30% of the current consump-

tion of leaf alcohol and esters and has an estimated current capacity to produce leaf alcohol of 150,000 lbs/yr. Some of this capacity is used to produce cis-6-nonenol and cis-jasmone.

IFF, U.S. and Holland: IFF both produces and purchases leaf alcohol depending on internal needs. Although currently not producing materials, it is estimated that IFF could produce 100,000 lbs/yr. in current equipment.

Fontarome (Oril), Paris, France: Fontarome has a capacity to produce leaf alcohol estimated at 40,000 lbs/yr. It also produces derivatives such as esters, cis-4-heptenal, cis-6-nonenal and cis-jasmone.

Substitutes

In the area of flavors, there are no near substitutes for leaf alcohol, its esters or its isomeric alcohols and aldehydes. In fragrances, an acceptable green effect may be constructed by use of other materials in conjunction with natural products, for example:

cis-4-hepten-1-al
cis-6-octen-1-al
3,5,5 trimethyl hexanal
2,4-dimethyl-3-cyclohexene aldehyde
cis-3-hexenyl methyl carbonate (Liftarome—IFF)

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5-methyl-3-heptanone oxime (Stemone)
iso-cyclo citral

Analogues

The following are commercially related analogues. These materials are currently available on the market and can be obtained from Bedoukian Research, Inc. and/or Fontarome.

cis derivatives:

	Odor Impression
cis-2-penten-1-ol	ethereal-fruity
cis-2-hexen-1-ol	fresh, green, fruity
cis-4-hexen-1-ol	green, vegetable
cis-4-hepten-1-ol	fruity-green
cis-3-octen-1-ol	fresh, herbaceous-earthly
cis-5-octen-1-ol	fresh watermelon-citrus
cis-2-nonen-1-ol	fresh, waxy melon-green
cis-4-decen-1-ol	wax-fatty

trans derivatives:

trans-2-hexen-1-ol	fresh green, fruity
trans-2-hepten-1-ol	fresh-fatty
trans-2-octen-1-ol	green-citrus
trans-2-nonen-1-ol	sweet, waxy-green
trans-2-decen-1-ol	mild fatty-waxy

related isomers:

1-penten-3-ol	smoky-garlic
1-hexen-3-ol	mild smoky garlic
1-hepten-3-ol	fruity chemical-solvent
1-octen-3-ol	mushroom
1-nonen-3-ol	fresh, sweet, citrus
1-decen-3-ol	fresh citrus

The introduction of a double bond in all these materials imparts a relative fresh-warmth to these materials versus their saturated analogues, while their acetylenic counterparts tend to display a more dry hay-like note. In general, the lower saturated analogues show either tones which shift to fatty tones as the chain lengths increase from 5 up to 10 carbon atoms.

Derivatives

The following derivatives are commercially available through a number of suppliers:

Derivative	GRAS/FEMA #
cis-3-hexenyl acetate	3171
trans-2-hexenyl acetate	2564
cis-3-hexenyl 2-methyl butyrate	3497
cis-3-hexenyl anthranilate	----
cis-3-hexenyl benzoate	3688
cis-3-hexenyl butyrate	3402
cis-3-hexenyl caproate	3403

trans-2-hexenyl caproate	----
cis-3-hexenyl cinnamate	----
cis-3-hexenyl cis-3-hexenoate	3689
hexenyl cyclopentanone	----
cis-3-hexenyl formate	3353
trans-2-hexenyl formate	----
cis-3-hexenyl heptine carbonate	----
cis-3-hexenyl isobutyrate	----
cis-3-hexenyl isovalerate	3498
trans-2-hexenyl isovalerate	----
cis-2-hexenyl lactate	----
cis-2-hexenyl octine carbonate	----
cis-2-hexenyl oxy-acetaldehyde	----
cis-2-hexenyl phenyl acetate	----
trans-2-hexenyl phenyl acetate	----
cis-3-hexenyl propionate	----
cis-3-hexenyl pyruvate	----
trans-2-hexenyl salicylate	----
cis-3-hexenyl salicylate	----
cis-3-hexenyl tiglate	----
cis-3-hexenyl valerate	----
trans-2-hexenyl valerate	----
cis-3-hexenal	2561
cis-2-hexen-1-ol	----
trans-2-hexen-1-ol	----
1-hexen-3-ol	----
trans-3-hexenal	----
trans-2-hexenal	----
cis-3-hexenal diethyl acetal	----
trans-2-hexenal diethyl acetal	----
cis-3-hexenyl 2-methyl-2-pentenoate	----
cis-3-hexenyl methyl carbonate	----

Leaf alcohol is also used as a chemical intermediate for the production of cis-jasmone, trans-2-cis-6-nonadienal and proposed for use in the synthesis of various pheromones.

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