

A Profile: An aroma Chemical

Linalool

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Pure linalool possesses a fresh, clean, mild, light floral odor with a slight citrus impression. The products produced by each synthetic process display slight odor variations, inherent to that process. For most purposes, the prime grades from each source are interchangeable. Less pure grades may show enough variation from the true note to render them usable only in specific applications. Because of the concentrations employed, the variations in odor usually are more critical in fragrances than in flavors.

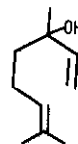
The small amount of natural linalool available is produced from Bois de Rose oils of Brazil and Paraguay and Ho-leaf oil from Taiwan and China, (see Tables I and II). Natural linalool is now considered a specialty.

History of Linalool

Linalool and its esters are distributed in a vast number of essential oils from trace up to major amounts. Its early production was accomplished in 1875 by isolation from Cayenne Bois de Rose oil from French Guiana. A Frenchman by the name of Licare was so involved with the oil's production that linalool was initially called Licareol. Subsequent production shifted to Brazil (Bois de Rose oil) and Mexico (Linaloe oil) and more recently from Ho-leaf and Ho-wood oil (Taiwan, China and Japan). Availability of natural linalool has remained fairly constant since 1925.⁶ The volume of supply of natural product, however, has been dwarfed by the supply of synthetic product. The demand for linalool cannot be met by the production of natural oils.

Growing world demand for aroma chemicals just after the second world war led to intense research programs to synthesize products and discover new substitutes for others. Coincidentally with that activity, the chemical developments in synthetic vitamin production made by BASF and

Linalool



MW 154

CAS 78-70-6
126-90-9

$C_{10}H_{18}O$

FEMA-GRAS 2635

Classification

An acyclic, unsaturated, monoterpenoid tertiary, allylic alcohol found widely in nature as a constituent of essential oils.

Additional Names

A number of common names for this alcohol will be found in the literature. The most common linalool refers to its early isolation from linaloe oil.¹⁻³

3,7-Dimethyl-1,6-Octadien-3-ol
2,6-Dimethyl-2,7-Octadien-6-ol (incorrect numbering)
Linalool
Linalyl alcohol
Licareol
Coriandrol

French = Linalol
Portugese = Linalol
German = Linalool
Spanish = Linalol

Physical Data

Appearance: Mobile, clear, colorless liquid
Specific Gravity: 0.865 (15°C) 0.8622 (20°C)
Refractive Index: 1.4615 (20°C)
Boiling Point: 198-199°C
Flash Point TCC: 76°C (approximate)
Solubility: H₂O (20°C) <1%. Soluble in ethanol, DEP, benzyl benzoate, most aliphatic and aromatic esters, mineral oil and chlorinated solvents.

Table I. Linalool Content of Essential Oils^(5,6)High %

bois-de-rose	65-90
ho leaf	80-90
coriander	60-80
linaloe	30-70
sweet basil	30-50
lavender	20-50
mentha citrate	20-50
lavandin	30-40
spike lavender	20-40
petit grain	20-30
bergamot	10-30
clary sage	10-25
ylang ylang	10-15
geranium	8-15

The above oils contrast with most spice oils and citrus oils, i.e.:

Low %

marjoram, sweet	3.0
anise	0.2
chamomile	0.3
laurel leaf	2.0
lime0.5*	
rosemary	2.0

Trace

acacia	T
cassis	T
clove	T
cumin	T
nutmeg	T

*Adjusted mathematically to exclude limonene content

Hoffmann La Roche provided raw material product streams which allowed the production of synthetic linalool and its derivatives.

Initially pure, clean, synthetic linalool met with great resistance by perfumers. It lacked the fine, intricate shading of organoleptic impression that the natural products displayed due to the presence of its trace amounts of impurities. Moreover, the synthetic linalool contained impurities that shaded the impression in a new way. In most cases, these impurities are not a direct result of the primary feed stock used to begin the production, but arise from the co-generation of by-products in the steps just prior to the creation of the linalool.

As the impurities are present in small amounts and of similar boiling points, their removal is prohibited by economics, if not technology. Nevertheless, the availability and price eventually won out and synthetic linalool became the dominant product.

World Consumption and Production

Consumption in 1988 of synthetic linalool and its esters in the flavor and fragrance industry is estimated at 13 million pounds (5900 M tons) worldwide.

Regional consumption figures are estimated on Table III.

Linalool prices have remained relatively flat since 1960 until mid-1986 with the breakdown of price in US dollars per pound as follows: (1960 (2.70), 1980 (1.94), 1986 (2.40), 1987 (3.50) and 1988 (3.90-4.25).

Because synthetic linalool is a by-product of vitamin production, manufacturers of vitamins A and E convert intermediate feed stocks into linalool and other products in order to maintain their plants at optimum capacity.

The major sources of synthetic linalool are Fritzsche D&O (BASF), Givaudan (Hoffmann-LaRoche), Glidco (SCM), and Kuraray, and these manufacturers of synthetic linalool can be divided into two groups:

1. Producers with in-house capacity to convert intermediates into vitamins, such as BASF and Hoffmann-LaRoche (Givaudan)
2. Producers who sell linalool or downstream products to the flavor and fragrance industry and to vitamin producers, such as Glidco (SCM) and Kuraray

In the past the dedication of plants to manufacture vitamins as the prime item of commerce has led to the decision to cease or terminate supply-

Table II. Natural Sources and Estimated Production⁽⁶⁾

Year	Production in Metric Tons/Year			
	Bois de Rose <u>Cayenne</u>	Bois de Rose <u>Brazil</u>	<u>Linaloe</u>	Ho-Leaf <u>China, Taiwan</u>
1920-25	95	-	2.5 (Mex)	NA
1932-37	10	60	NA	NA
1944-60	2	100	NA	60
1970-80	NA	120	3.0 (India)	10
1984	NA	140	NA	10 est.

ing linalool whenever vitamin demand requires the intermediate production. This dual outlet system for the intermediates was the major cause of the severe shortage of linalool and other aroma chemicals during the 1974 chemicals dislocation, when insufficient raw materials such as caustic soda and acetone forced vitamin producers to cut back intermediate production.

The linalool suppliers in the second group produce linalool for sale to both the flavor and fragrance and vitamin industries. Thus, their decision as to where to sell product is based upon pure economics rather than an internal policy of strategy and economics. The flavor and fragrance industrial concern of supply of linalool and related products free from the threat of supply curtailment has resulted in Glidco (SCM) becoming the world's largest supplier of linalool/geraniol.

Production capacity for linalool has been fairly constant over the last twenty years except for the capacities added by Glidco and Kuraray. These

new sources resulted in a continuation of over-capacity existing from the 1960s until recently. Linalool usage has only grown by about 4% per year, over the last twenty years. The recent semi-shortage of supply resulted from Givaudan's plant problems in Switzerland last year. Now that Givaudan's production has been resumed, the supply situation should return to normal with capacity for linalool again in slight excess of demand. The future growth in demand should increase by the historic 4% per year factor which projects linalool to need new production capacity by the mid 1990s.

Although world fragrance sales have lagged in some areas in recent years, the growing trend to liquid versus solid detergents will contribute significantly to the steady growth for linalool. In 1984 the ratio of solid to liquid detergent was 4:1, and it is projected to reach 1:1 by 1990. As liquid detergents contain twice the amount of fragrance, they will be important outlets for aroma chemicals. In anticipation of this growth, Glidco has announced an increase in production capacity of 1000 metric tons over the next two years.

Producers

Fritzsche D&O (BASF) has displayed a linalool capacity estimated at 500 M tons. This term, "displaced capacity," refers to the excess vitamin intermediate capacity the firm has used to supply linalool and not to the amount of linalool that could be made available if all intermediate capacity was converted to the product. Initially, BASF began production of vitamins via the acetylene-acetone route to methylheptenone via methylbutynol, which generates the intermediate dehydrolinalool.⁷ Dehydrolinalool is subse-

Table III. Regional Consumption Figures

Area	<u>Linalool</u>	<u>Esters</u>
North America	2,200,000	1,600,000
Europe	3,200,000	2,200,000
Japan	1,000,000	450,000
Other	1,600,000	700,000

Linalool

quently semi-hydrogenated to linalool. However, this route never completely removes all the dehydrolinalool unless the hydrogenation is incomplete and the remaining dehydrolinalool is destroyed by reversing the ethynylation process, leading to yield losses. Attempts to remove the dehydrolinalool by over hydrogenation result in production of tetrahydrolinalool. The presence of traces of dehydrolinalool and/or tetrahydrolinalool is one means of detecting a reconstituted essential oils compound with product from this process.

BASF's most recent process uses methyl heptenone generated by the condensation of isobutylene, formaldehyde and acetone. The methylheptenone is then converted to linalool via a vinyl Grignard reagent, producing a clean, synthetic product, which is difficult to detect in reconstituted essential oils.

Givaudan (Hoffmann-LaRoche) has an estimated displayed capacity of 1400 M tons per year and it is produced in Europe only. Hoffmann-LaRoche's technology continues to be based on the classical acetone-acetylenic route through methyl butyl via Tedeschi catalytic ethynylation. Methyl butynol is converted to methyl heptenone which is then catalytically ethynylated to dehydrolinalool, which is semi-hydrogenated to linalool.

As in the original BASF process, linalool produced via this process contains trace amounts of dehydrolinalool, thus marking it as synthetic. The advantage of the Hoffmann-LaRoche technology is that it allows variations in ketone feed structures to produce substituted linalools, i.e., ethyl linalool.

Glidco (SCM) has an estimated capacity of 8000 M tons of linalool/geraniol and is the only one to produce the material in the United States. Its process begins with α -pinene obtained from turpentine.⁸ The α -pinene is converted to 2-pinanol via the hydroperoxide, which is pyrolysed to linalool. Linalool can then be isomerised to geraniol. Glidco's process is thus capable of adjusting the ratio of linalool or geraniol to suit the demand of the market.

Through foresight in investment in new innovative technology and construction of a modern plant at Colonel's Island in Georgia at a time when worldwide linalool capacity was in great excess, its capacity today has made Glidco the largest producer of linalool/geraniol in the world and greatly helped in easing the recent tightness of supply.

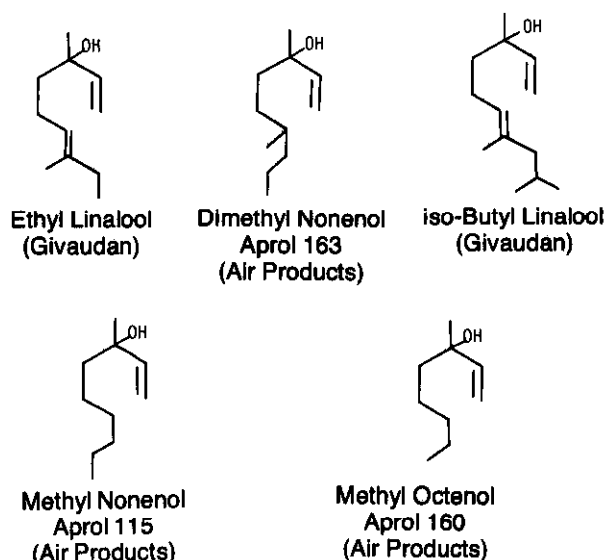
Kuraray's linalool capacity has never been

stated, but is estimated at 3000 M tons per year if all efforts were used for linalool. However, significant capacity is used to produce isophytol and squalene as well as linalool.

Kuraray has licensed the old Rhodia process utilizing isoprene to generate prenyl chloride which is subsequently converted to methyl heptenone. Catalytic ethynylation of methyl heptenone in liquid ammonia then yields dehydrolinalool which is semi-hydrogenated to linalool.

Analogs

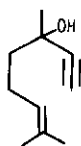
Of the analogs offered over the years, only ethyl linalool is currently being offered.



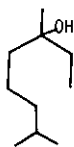
Substitutes

The following materials have an odor profile which would allow their use as a substitute for linalool in fragrances. Only one tetrahydrolinalool is allowed in flavors.

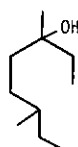
Linalool



dehydrolinalool
(BASF, Hoffmann-La Roche)



3,7-dimethyl
octan-3-ol
tetrahydrolinalool
GRAS 3060
(Givaudan)



3,6-dimethyl
octan-3-ol
(AR-1, Aprol 100)
(Fritzsche D&O)
(Air Products)

Derivatives

Linalool is used both in flavors and fragrances in the form of its esters

Acetate	GRAS 2636
Anthranilate	GRAS 2637
Benzoate	GRAS 2639
130-Butyrate	GRAS 2640
Caproate (C)	GRAS 2643
Caprylate (C ₈)	GRAS 2644
Cinnamate	GRAS 2641
Citronellate	
Formate	GRAS 2642
Heptanoate	
Methyl Anthranilate	
Methyl Tiglate	
Phenyl Acetate	GRAS 3501
Propionate	GRAS 2645
Tiglate	
Isovalerate	GRAS 2646

In addition, the following derivatives find use in fragrances: linalool oxide (Givaudan) and linalyl methyl ether.

References

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