A Profile: An Aroma Chemical

Phenethyl Alcohol

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Phenethyl alcohol, or PEA, as it is commonly referred to in the industry, is basically a fragrance raw material, as more than 99% of its volume usage is realized in this area. The usage in flavors is only minor, yet the flavorist will require PEA for defined applications where it cannot be substituted by other materials. Paradoxically, in the area of fragrances, other floral alcohols can be substituted for PEA in the initial creation of a formulation, although the end result will not be an exact match.

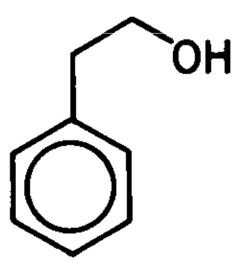
PEA can also be used in place of other floral alcohols when price and availability demand its use. Historically, PEA's price has been lower than that of linalool, its most popular alternative. In global areas where PEA is manufactured locally and linalool is largely imported, the relative volumes of the two materials show far greater amounts of PEA consumed than linalool. Truly, PEA is one of our industry's workhorses and has even been referred to as "the blender supreme".[4]

The secret to PEA's universal popularity clearly lies in the human preference for rose odors, as the fragrance of roses has been shown to be the most desirable odor.[5] Why else would one pay $3,000/kg for natural rose oil.

PEA is found at or near the top of the list for rose raw materials in every published list seen by this author.[6-8]

Prime grade PEA possesses a warm, mild-bland, rose floral impression, shaded with slight honey-green tones. The material falls into a class of synthetic raw materials which display a low impact, bland, almost weak, profile, which makes their organoleptic profiles susceptible to interference from impurities. Similar materials falling in

Phenethyl Alcohol



MW 122 | $C_8H_{10}O$

CAS 60-12-8 | **FEMA-GRAS** 2858

Classification:

A primary saturated, aliphatic alcohol with a phenyl group attached. Found in nature primarily in the extracts of flowers.

Additional Names:[1, 2]

2-Phenyl ethyl alcohol
β-Phenyl ethyl alcohol
Benzyl carbinol
β-hydroxy ethyl benzene
PEA

French: Alcool Phenethylique
German: Phenyl Äthyl Alkohol
Portugese: Alcool feniletilico
Spanish: Alcohol feniletilico

Physical Data:

Appearance:	Clear, colorless, mobile liquid with a slight prismatic sheen.
Specific Gravity at 2°C:	1.0202
Refractive Index at 20°C:	1.5325
Boiling Point (750mm):	219-221°C
Freezing Point:	–27°C
Flash Point TCC:	216°F
Solubility:	H_2O 2 vol% at 20°C, soluble in alcohols, esters, aldehydes, DEP, benzyl benzoate, mineral oil, and chlorinated solvents. Often used to stabilize phenyl acetaldehyde via hemiacetal formation as a 50:50 mixture.

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this class would be linalool, benzyl salicylate and benzyl benzoate, as opposed to high impact products, such as benzyl acetate or cinnamic aldehyde.

Thus, the impurities generated as by-products in the synthesis of PEA by all commonly used processes will impart off-odors which shade PEA's organoleptic profile with green-gassy, metallic-chlorine or earthy chemical tones. Some of the impurities causing these off-odors have been identified[9] as 2-phenethyl chloride, diethylene glycol chlorohydrin 1-phenethyl alcohol, bi-phenyl, bi-benzyl and phenyl propan-3-ol. Thus, manufacturers around the world produce widely varying grades of PEA. The most fastidious of the manufacturers take great pains to purify the product generated from their synthesis units so that the PEA is upgraded to a prime quality.[10] Commercially available PEA can vary widely in organoleptic profile and, hence, quality to such an extent that the various grades can be considered different products and not interchangeable.

Currently, the following grades are offered on the market: phenylethyl alcohol extra, phenylethyl alcohol white extra (IFF), phenylethyl alcohol Coeur FCC, and Phenarose (IFF).

The stability of PEA in even the harshest media makes it one of the industry's most versatile raw materials, as it can survive a wide pH range, exposure to high surface areas and strong oxidants. That is not to say it is indestructible, but it can be used successfully in even the most aggressive media.

Natural Sources

Clearly the most famous natural product containing PEA is rose oil. The concentration of PEA in rose flowers as measured by headspace analysis is from traces for some varieties to about 60% in the Hojune hybrid tea rose.[11] Other observers have reported similar results for extracted rose oil, using solvents, such as petroleum ether. Steam-distilled rose oil shows vastly reduced PEA content (1-8%), as most of the alcohol is dissolved in the condensate water. Extraction of this water phase results in rose water oil which is high in PEA content.

PEA is found in a number of natural products and is thought to arise via the Shikimic acid pathway. This process involves the conversion of 1-phenylalanine to phenylacetaldehyde which is subsequently reduced to PEA. In some systems, such as tea and herbal tea leaves, the PEA arises during the[12] fermentation process, as the appearance of phenylacetaldehyde increases and then decreases as the concentration of end product PEA forms.

Although PEA is frequently found in essential oils, it is invariably present in minor concentrations too small to provide a natural commercial source. It is suspected that PEA is present in many other natural sources in minor concentration, but the methods of isolation of essential oils via steam distillation extracts the PEA out of the organic phase and its presence in the water phase has not yet been noted.

Natural Sources

Apples and apple juice	Lemon balm
Beer	Lilies
Chervil	Mushrooms
Clove	Narcissus
Cocoa	Neroli
Coffe, roasted	Ocimum Basilicum
Cranberries	Orange juice
Daphne	Rum
Geranium oil	Spartium junceum (Genet)
Grapes	Tea leaves
Hyacinths	Whiskey
Iris root	Wine
Jasmin Sambac	

History[13]

PEA was discovered in 1876 by Radzisewski as the reduction product of phenyl acetaldehyde by sodium metal in ethanol solution. Reduction systems using sodium or zinc metal to produce PEA from phenylacetaldehyde or phenyl acetic acid or its esters were probably the first methods used in our industry for inhouse synthesis of PEA. The problem with these systems is that even trace amounts of the acid or the aldehyde (which oxidizes to the acid) impart a honey tone to PEA. Phenyl acetic acid is a stable, persistent and strong aroma chemical.

Thus, in 1905 when Grignard discovered that his now-famous reagent would yield PEA when reacted with ethylene chlorohydrin, a ready commercial market for a prime grade of PEA was waiting. The Friedel-Crafts method of generation of PEA from benzene and ethylene oxide was discovered in 1925 by Schaarschmidt. Despite initially poor yields, the Friedel-Crafts process was rapidly developed for commercial production as the economics were superior to the Grignard route. Most flavor and fragrance firms in the period 1925 to 1950 developed their own inhouse routes to insure an adequate supply of material with a consistent quality. This need is

Table I
PEA Tariff Rates as Percent Ad Valorum
TSUS 2906-29.10

Year	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990
%	37.7	34.7	31.6	28.6	25.5	22.4	19.4	16.3	16.3	16.3	16.3

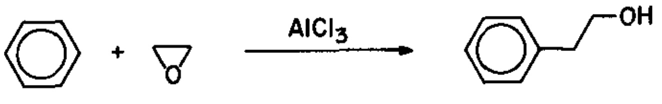
clearly illustrated by IFF's interest in PEA and their current role as a major producer of such a large volume, low margin item.

The search for better routes both economically and organoleptically lead to the development of the production of PEA from styrene oxide via catalytic hydrogenation.

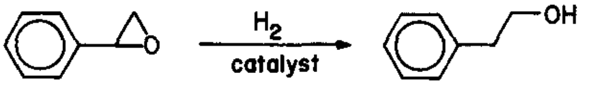
A number of firms produced PEA in the U.S. during the 1950s, but despite favorable tariff barriers (Table I), by 1990 the U.S.'s only manufacturer was IFF. Norda (now Quest) shut down their Orbis production unit in Newark, New Jersey, and started up a new PEA factory in Mexico in the 1970s. IFF's dominant position today is a result of the availability of byproduct PEA from Arco's propylene oxide plant in Texas, which is purified to a usable fragrance grade. However, IFF also produces PEA via the hydrogenation of styrene oxide at their Hazlet, New Jersey facilities. IFF's internal concerns as to using large amounts of benzene at Hazlet and their loss of use of a railroad siding caused them to cease production of PEA via the Friedel Crafts reaction.

Despite the availability of byproduct PEA in the U.S., most of the world production of PEA results from the following processes:

Route I—Friedel Crafts reaction of ethylene oxide with benzene.



Route II—Catalytic reduction of styrene oxide.



The production of F+F grade PEA is not only a synthetic, but also a purification problem. The further cleaning up of crude PEA to prime organoleptic quality has been given probably as much scientific attention as its synthesis. It is reported[10] that two effective methods have been developed to remove the undesirable impurities from PEA streams, i.e., one is continuous vacuum distillation and the other utilizes PEA borate ester formation to remove impurities.

World Consumption

Total world consumption of PEA and its esters by the global flavor and fragrance industry in 1990 is estimated to be 7,000 MTons (15,440,000 lbs.). This consumption is estimated to further break down to specific application usage as follows:

Fragrances	6000 MTons
Flavors	10 MTons
Preparation of Esters, etc.	990 MTons

Regional consumption figures are estimated to be as follows:*

Area	MTons	% World Total
North America	1750	25
Europe (Western)	2250	32
Europe (Eastern)	800	11
Latin America	500	7
China	500	7
Japan	400	6
India	600	9
Others	200	3
World Total	7000	100%

*Consumption as PEA in both alcohol and derivative form.

Pricing

PEA's pricing has increased fairly steadily since the 1950s. In 1960, it sold in the range of $1.10-1.15/lb. and by 1980 had risen to $2.85/lb. Intense competition from imported PEA, which has run as high as 40% of U.S. consumption, forced U.S. pricing to a low of $2.10/lb. by 1985. Much of this competitive pressure resulted from Quest's (Norda) Mexico City plant, which enjoyed GSP status for its product in the U.S. However, Quest ceased production of PEA in October 1988, thus removing 450 MTons of capacity from the world market. Prices immediately moved upward and supplies tightened, but no serious shortages occurred. By March 1989, PEA was selling in the range of $2.80-3.30/lb.

Prices are predicted to remain in the $3.00-4.00 area over the next five years as supply growth keeps pace with, but does not outstrip, demand.

Imports

Since 1980 nearly 450 MTons/year of PEA has been imported into the U.S. In the early 1980s about 400 MTons/year arrived here from Mexico. In 1989, after the shutdown of Quest's Mexico City plant, imports continued at the same 450 MT/year level and broke down as follows as to source:

France		181 MTons
Federal Republic of Germany		140 MTons
China		92 MTons
Japan		20 MTons
U.K.		9 MTons
	Total	442 MTons

Capacity/Supply

The technology to produce PEA either by the Friedel Crafts method or from production of styrene oxide is well known and documented in the scientific literature. Thus, new producers of this material are constantly appearing in the Third World as growing demand there dictates expansion. The world source of PEA versus production routes is estimated as follows:

Friedel Crafts	2700 MTons
Styrene oxide route	2500 MTons
Propylene oxide stream byproducts	1800 MTons

Supply of PEA is expected to grow steadily ahead of demand, especially in Asia and South America, i.e.:

India—The dominant supplier until recently has been Kelkars, but recently five other small units have begun production to meet rising demand.

Brazil—Rhone Poulenc has applied for a license to build a PEA plant in the near future.

Producers

The following are the major world producers of PEA. Most F+F houses today have abandoned inhouse manufacture and purchase PEA from one or more of the following:

IFF—Capacity is estimated at 1850 MTons/year. Their normal grade material is produced at Arco's Channelview, Texas plant as a byproduct and upgraded to fragrance-grade PEA. IFF also offers a white extra and Phenarosa grade of PEA that more resembles PEA produced by the Friedel Crafts system and are equivalent to BASF's grade PEA in the opinion of many perfumers.

BASF—Capacity is estimated at 2000 MTons/year. Their material is produced in Ludwigshafen, Germany via the Friedel Crafts system. This BASF-grade PEA is the best organoleptic profile material available today in the opinion of many perfumers. BASF exports about 150 MTons/year to the U.S. largely because of its fine quality.

Toyotama Japan—Capacity is estimated at 1100 MTons/year of PEA, the bulk of which is produced via catalytic reduction of styrene oxide, while a lesser volume is produced via propylene oxide byproducts. The greater part of Toyotama's production is exported. A large part of these exports are to South America.

Rhone Poulenc France—Capacity is estimated at 900 MTons/year of PEA produced via catalytic reduction of styrene oxide. In 1989, Rhone Poulenc exported 181 MTons of PEA to the U.S.

Quest—Until 1989, Quest produced 450 MTons of PEA via the Friedel Crafts process in Mexico City, Mexico. The plant has been shut down and Quest officials have made statements to the press that production will not be restarted.

Kelkars, Bombay, India—Capacity is estimated at 400 MTons/year of PEA produced via the Friedel Crafts process.

China—The situation in China is unclear, but it is estimated that there are several manufacturers with a collective capacity of 500 MTons, all being produced by reduction of styrene oxide.

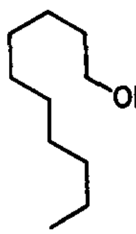
Eastern Europe—It is estimated that this area produces and consumes at least 800 MTons/year of PEA. The bulk of this PEA is thought to be produced via the Friedel Crafts process.

Others—About 300 MTons//year of PEA is estimated to be produced by small manufacturers in the Third World, most likely via the Friedel Crafts process.

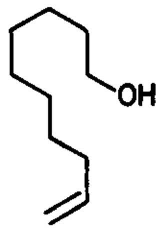
Substitutes

As with many F+F materials, no real substitutes exist for PEA, at least not at the same price levels. In fragrances, floral bases can be built without PEA using substitute materials, such as linalool or some of the materials shown below when the perfumer is creating a fragrance from scratch. In established formulas, substitutes can be devised which mimic PEA, if one is willing to ignore the GLC analysis. In flavors, it is very difficult to substitute PEA in an existing formula. However, its use in flavors is small and the flavorist seldom is faced with the problem.

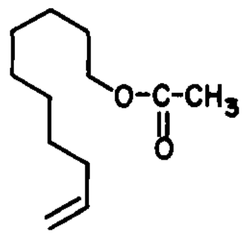
The numbers presented are references to Arctander's work.[3]



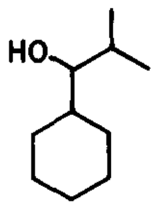
841
sweet-waxy-floral rose



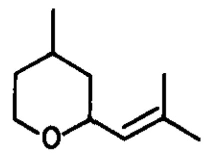
844
fatty-oily-waxy rose



846
oily rose



990
woody-rose



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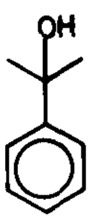
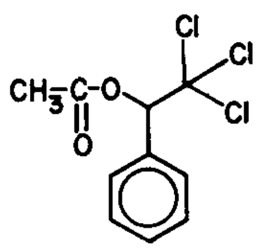


1040
fatty-rose



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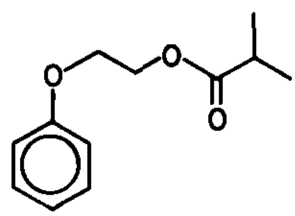

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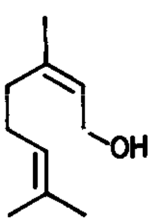
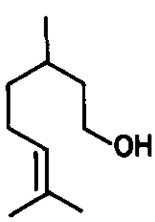
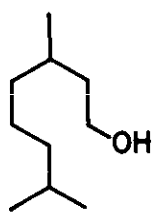


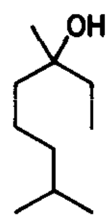
1426
Geraniol



669
Citronellol



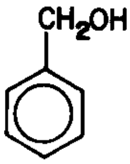
1032
Dimethyl Octanol



2913
Tetrahydro linalool

Analogues

The following materials are structurally related analogues of PEA which offer varying shadings or switches in odor theme from PEA mainly for use in fragrances.



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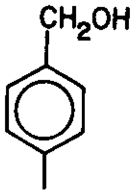

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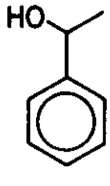

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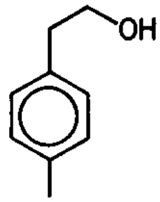

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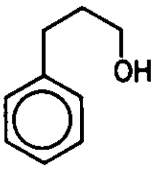
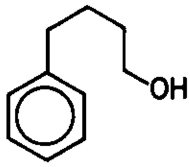
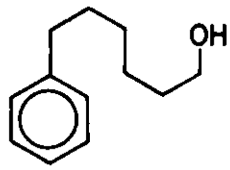


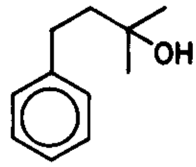
2589
Balsamic floral



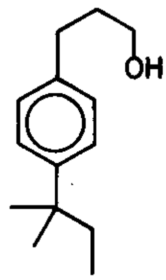
2503
nerbaceaus rose



2576
Lime rose



2541
warm rose



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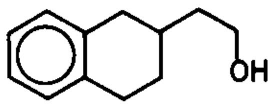

2923
camphor-minty

Derivatives

PEA finds usage in both flavors and fragrances in the form of its esters. About 990 MTons of PEA per year is converted to approximately 1500 MTons of derivatives. Commonly available derivatives are:

	GRAS No.
Phenethyl acetate	2857
Phenethyl anthranilate	2859
Phenethyl benzoate	2860
Phenethyl butyrate	2861
Phenethyl cinnamate	2863
Phenethyl formate	2864
Phenethyl hexanoate	3221
Phenethyl isobutyrate	2862
Phenethyl phenyl acetate	2866
Phenethyl propionate	2867
Phenethyl salicylate	2868
Phenethyl cyclohexyl ether, "Phenafleur" (IFF)	

References

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