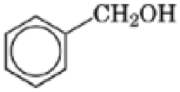
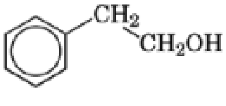
Kirk-Othmer Encyclopedia of Chemical Technology.

BENZYL ALCOHOL AND *β*-PHENETHYL ALCOHOL

Benzyl alcohol (**1**) and *β*-phenethyl alcohol (**2**) (2-phenylethanol) are the simplest of the aromatic alcohols, and, as such, are chemically similar. Their physical properties are given in Table 1.



(1)



(2)

1. Benzyl Alcohol

Benzyl alcohol (**1**) occurs widely in essential oils both as the free alcohol, and, more importantly from a fragrance standpoint, in the form of various esters. Although benzyl alcohol itself is rather bland in odor, combined with its much more fragrant esters it is an important part of the odor of jasmine, ylang-ylang, gardenia, some rose varieties, narcissus and peony, as well as castoreum, balsams of peru and tolu, and propolis. Benzyl alcohol occurs primarily in flower oils and tree exudates, whereas a large number of essential oils obtained from other parts of a wide variety of plants contain no benzyl alcohol or its esters (1).

Benzyl alcohol readily undergoes the reactions characteristic of a primary alcohol, such as esterification and etherification, as well as halide formation. In addition, it undergoes ring substitution. In the presence of acid, polymerization is observed, and the alcohol can be thermally dehydrated to toluene [108-88-3]. Catalytic oxidation over copper oxide yields benzaldehyde; benzoic acid is obtained by oxidation with chromic acid or potassium permanganate. Catalytic hydrogenation of the ring gives cyclohexylmethanol [100-49-2].

1.1. Manufacture

Today benzyl alcohol is almost universally manufactured from toluene which is first chlorinated to give benzyl chloride [100-44-7]. This is then hydrolyzed to benzyl alcohol by treatment with aqueous sodium carbonate.

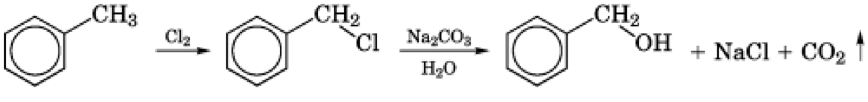
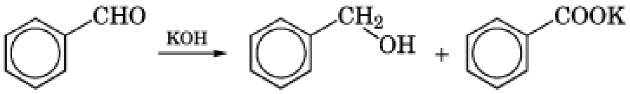


Table 1. Physical Properties of Benzyl Alcohol and β-Phenethyl Alcohol

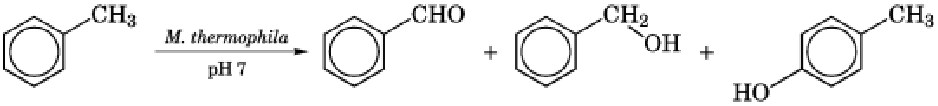
Property	Benzyl alcohol	β-Phenethyl alcohol
molecular formula	C_7H_8O	$C_8H_{10}O$
CAS Registry Number	[100-51-6]	[60-12-8]
mp, °C	−15	−25.8
bp at 101.3 kPa[a], °C	205.4–205.7	219.5–220
bp at 1.33 kPa[a], °C	89.0–89.5	99–100
d_{15}^{15}		1.0242
d_{25}^{25}	1.0441	1.017
n_D^{20}	1.53955	1.5323
flash point, closed cup, °C	100.4	
open cup, °C	104.4	
autoignition temp, °C	436	
vapor density (air = 1)	3.7	
vapor pressure at 58°C, kPa[a]	0.133	0.133
100°C, kPa[a]	2.02	1.33
surface tension at 20°C, mN/m (=dyn/cm)	39	
80°C, mN/m (=dyn/cm)	33	
viscosity at 25°C, mPa·s(=cP)	5.05	7.58
50°C, mPa·s(=cP)		3.19
solubility at 25°C, water	1 g/25 mL	1 g/51 mL
30% ethanol		1 g/12 mL
50% ethanol	1 g/1.5 mL	1 g/1.7 mL

[a] To convert kPa to mm Hg, multiply by 7.5.

Prior to the commercial development of this process benzyl alcohol was obtained from benzaldehyde [100-52-7] which undergoes the Cannizzaro reaction (2) upon treatment with potassium hydroxide. High yields of benzyl alcohol and potassium benzoate are obtained by this route which cannot compete with the present day process because of the high cost of benzaldehyde (qv).



In the future it may be possible to oxidize toluene microbially to produce benzyl alcohol. Treatment of toluene in the presence of air with a culture of *M. thermophila* in a phosphate buffer is reported to yield a mixture of benzaldehyde, benzyl alcohol, and *p*-cresol [106-44-5] (3).



1.2. World Consumption and Uses

Eleven companies in the United States, Western Europe, and Japan have a total annual capacity for benzyl chloride of over 154,000 t. In 1988, total production for these three regions was 97,000 t. Overall, 1988 consumption exceeded 91,000 t, of which benzyl alcohol accounted for 23% or approximately 21,000 t (4).

In the soap, perfume, and flavor industries benzyl alcohol is primarily used in the form of its aliphatic esters. Benzyl benzoate [120-51-4] finds widespread use as a fragrance diluent. Benzyl alcohol is frequently

Table 2. Specifications of Benzyl Alcohol[a]

	Grade				
Determination	Technical	NF	Reagent	Photo[b]	Textile
assay (OH determination)	98% min	99% min	99.0% min	99% min	99% min
solubility in water at 25°C	1 g/30 mL	1 g/30 mL	1 g/25 mL	1 g/25 mL	1 g/25 mL (at 50°C)
benzaldehyde content (uv determination)	0.3% max	0.2% max	0.03% max	0.04% max	0.2% max
halogen (Beilstein)	0.1% max	neg	neg	neg	neg

[a] Benzyl alcohol is sold in fractional and 3.5-kg glass bottles, and steel drums containing 22, 113, and 208 kg. The photo and textile grades are available in tankwagon and tankcar quantities. Freight classification: chemicals, NOIBN; ICC regulations, none.
[b] Photo grade contains 0.01–0.02% of a hydroquinone monomethyl or benzyl ether to prevent the oxidation of the alcohol to benzaldehyde.

employed in bar soap fragrances at 30–40 wt % of the fragrance. Benzyl alcohol is commercially available in five grades (Table 2).

The largest proportion of benzyl alcohol is for use in the photographic and textile industries although the latter use has been declining. The photo grade is used in a developing bath for color motion pictures (5), for the development of color transparencies (6), as a dispersing reagent for silver halide grains in mixed packet emulsions (7), as a stop bath for production of lithographic plates (8–10), as a dispersing agent and film softener in an antistatic treating compound (11), and as an activator in a print-out image method (12). The textile grade is used as a dyeing assistant for wool (13–15) and nylon (16).

The NF and reagent grades are employed in the pharmaceutical industry which makes use of benzyl alcohol's local anesthetic, antiseptic, and solvent properties (17–20). It also finds use in cough syrups and drops; ophthalmic solutions; burn, dental (21), and insect repellant solutions and ointments; and dermatological aerosol sprays. It is used in nail lacquers and as a color developer in hair dyes by the cosmetics industry (22), and in acne treatment preparations (23).

Because of its strong polarity and limited water solubility, the technical grade of benzyl alcohol is used in rug cleaners as a degreasing agent (24), in leather dyeing (25), in ballpoint inks (26), as a cleaner for soldering (27), and as an extractive distillation solvent for xylenes and cresols (28, 29). It is used as a stabilizer in insecticidal formulations by the agriculture industry (30) and in treating fruits and vegetables (31). In addition, benzyl alcohol is used extensively in the polymer industry (32–37) and in the manufacture of automobile tires (38).

1.3. Health and Safety

Benzyl alcohol is listed on the U.S. *Toxic Substances Control Act* (TSCA) *Chemical Substances Inventory*, the *European Inventory of Existing Commercial Chemical Substances* (EINECS), *Australian Cone Inventory of Chemical Substances*, and the *Canadian Domestic Substances List* (DSL) (39–42). This material has a Generally Recognized As Safe (GRAS) status indicated by the Flavor and Extract Manufacturers' Association for use in flavors and by the Council of Europe for use as a flavor (43–45). Benzyl alcohol satisfies the most current guidelines published by the International Fragrance Association (IFRA) which governs the use of fragrance materials (46).

Human sensitization studies were negative at 10% solution (47). Undiluted benzyl alcohol produces moderate dermal irritation in guinea pigs and mild dermal irritation in rabbits (48, 49). Severe eye irritation was noted in a rabbit study (50). Acute oral rat LD_{50} values were reported between 1.23 and 3.10 g/kg (50–52). A dermal rabbit LD_{50} value of 2.0 g/kg has been reported (49). Rats died after 2 h when exposed to a 200-ppm vapor concentration (53). Benzyl alcohol is readily oxidized in animals and humans to benzoic acid [65-85-0] which is then conjugated with glycine [56-40-6], and rapidly eliminated in the urine as hippuric acid [495-69-2] (54).

National Toxicology Program (NTP) carcinogenicity studies in rats and mice were negative and benzyl alcohol was not mutagenic when tested in the NTP Genetic Toxicology Program (49, 55).

2. β-Phenethyl Alcohol

Of all the aromatic organic molecules β-phenethyl alcohol (PEA) (2) is probably the most prestigious aroma chemical in the world of perfumery. This is because of its exquisite odor of natural rose petals.

Twenty-four years before its detection in nature PEA was first synthesized in 1876 (56) by reducing phenylacetaldehyde [122-78-1] with sodium amalgam. Then, in 1900, it was independently identified in otto of rose (57) and rose water (58). Subsequently, PEA has been identified in numerous flower oils such as ylang-ylang, narcissus, hyacinth, lily, neroli, and geranium as well as various other natural products like tea, tobacco, orange juice, beer, cigarette smoke, etc.

Physical properties of PEA are shown in Table 1. The pure compound is extremely difficult to crystallize because it tends to supercool to a glass. In addition, it forms a number of azeotropes (59).

The compound undergoes the usual chemical reactions of alcohols or aromatic compounds. The hydroxyl group can be replaced by halogens and can be readily esterified with practically any organic acid in the presence of sulfuric acid as a catalyst. It combines with anhydrous calcium chloride to give a solid addition compound formerly used in purifying the alcohol. It forms acetals with many aldehydes. Phenethyl alcohol dehydrates in the presence of acids to bis(phenethyl)ether [93-96-9], whereas with alkali, it gives styrene. With other alcohols, it forms mixed ethers. Dehydrogenation to phenylacetaldehyde can be effected with finely divided metallic catalysts, such as copper and silver or zinc oxide in the presence of oxygen. Oxidation with dichromate or permanganate yields phenylacetic acid [103-82-2], and finally benzoic acid. With nitric oxide the primary product of oxidation is phenylacetic acid with similar amounts of phenylacetaldehyde (60). Since it contains an aromatic ring, PEA can be nitrated, sulfonated, and chlorinated; it can be hydrogenated to 2-cyclohexylethanol [4442-79-9] (61–64), which is not only a natural product (65, 66), but also a perfume chemical. It has also been found in fresh tearose leaves (67).

In insect control, PEA has been considered as a mosquito repellant (68), and its acetate has been used as an ingredient in Japanese beetle bait (69). The alcohol also has bacteriostatic action and antifungicidal properties (70–73), and it has been claimed as a surface-active agent (74).

Phenethyl alcohol may be identified as the phenethyl *p*-nitrobenzoate [57455-00-2] (mp 106–108°C), as phenethyl *p*-nitrobenzyl phthalate [65997-34-4] (mp 84.3°C), and also by its formation of styrene on treatment with alkali. Use of these derivatives has, however, been superseded by physical methods. Infrared (75, 76), mass spectroscopy (77), and nmr spectra (78) are useful for identification.

Pure PEA possesses an extremely mild roselike odor. Commercial grades of PEA which are $>99\%$ pure vary in odor because of the impurities present which depend on the method of manufacture. The common impurities are benzaldehyde [100-52-7], benzylacetone [2550-26-7], 1-phenyl-2-propanol [14898-87-4], and phenylacetaldehyde. It is claimed that the presence of phenylacetaldehyde imparts a honeylike by-odor resembling the odor of dried rose leaves with a faint suggestion of otto of rose which has a honey by-note. However, the presence of phenylacetaldehyde above 0.01% greatly distorts the delicate rose odor of PEA.

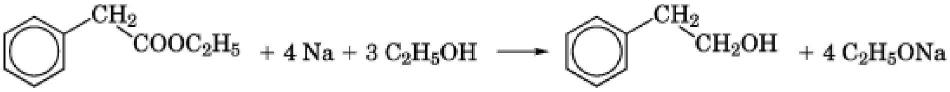
Because of factors of low cost, stability, and odor quality, PEA is ideally suited for use in bar soap fragrances where its use can be up to 30–50% of the fragrance.

2.1. Manufacture

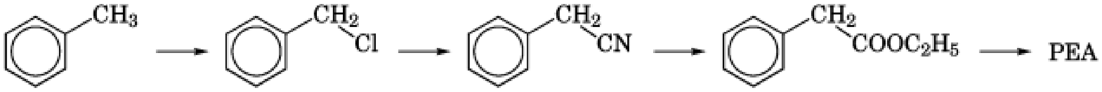
Commercial methods for making PEA can be broadly divided into three categories: historical, present, and future methods.

2.1.1. Methods Primarily of Historical Interest

In the *Bouveault-Blanc Reduction* (79, 80) phenylacetic ester is reduced with sodium and alcohol to PEA.

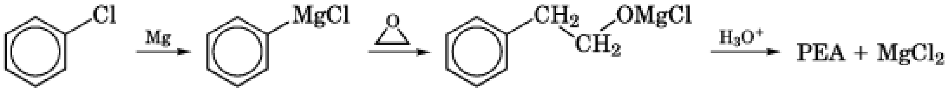


In *Leonard's Method* (81) toluene is chlorinated to benzyl chloride which is, in turn, converted to phenylacetic ester, and then to PEA.

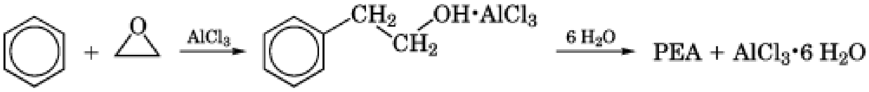


2.1.2. Present Day Methods

In the *Grignard Synthesis* (82, 83), chlorobenzene [108-90-7] is converted to phenylmagnesium chloride which reacts with ethylene oxide [75-21-8] at 100°C to give β-phenylethoxy magnesium chloride which is then decomposed with sulfuric acid to give PEA.

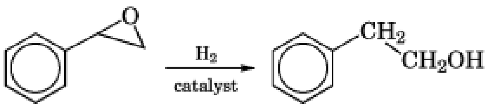


The *Friedel-Crafts* process (84, 85) produces most of the PEA presently being manufactured.



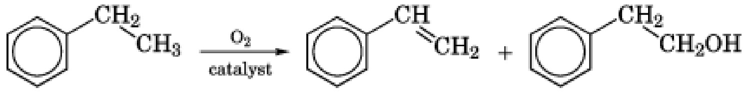
Because PEA is such an important fragrance material this simple, essentially one-step process has been exhaustively studied to optimize reaction conditions and purification procedures. Because of the high reactivity of the intermediates and the tendency toward polymer formation, critical factors such as throughput, temperature, molar ratios of reactants, addition rates, reactor materials and design, and agitation rate must be carefully balanced to provide an economical product with acceptable odor properties.

Catalytic hydrogenation of styrene oxide (86–99) is another process currently used for the manufacture of PEA. The main requirements for this reaction are a low operating temperature to avoid side reactions and a good quality of styrene oxide [76-09-3] starting material.



2.1.3. Future Methods

A by-product stream containing 60–80% PEA can be obtained from the catalytic air oxidation of ethylbenzene [100-41-4] (100). Perfumery-grade material can be isolated from this stream by complexing the PEA with a metal halide (such as $CaCl_2$), separation of the adduct, and thermal decomposition followed by distillation.



2.1.4. Microbiological Oxidation

Styrene [100-42-5] can be oxidized to PEA by aerobic culturing with a *Pseudomonas* bacterium in the appropriate medium (101). For a medium containing peptone, $(NH_4)_2SO_4$, $Na_2HPO_4{\cdot}12H_2O$, KH_2PO_4, $MgSO_4$, and corn steep liquor, the yield is 2.34 mg/mL.

2.2. Purification

Purification problems are primarily solved by two methods: continuous vacuum fractionation and chemical combination to yield a high boiling ester, separation of the noncombining impurities by distillation, and hydrolysis of the ester. Although the product produced by continuous vacuum fractionation satisfies most needs, shows no impurities by glc, is odor-acceptable, and thus is used to produce most of the PEA for commercial use, for highest requirements chemical purification by the borate ester is required.

2.3. World Consumption

The estimated total world consumption of PEA and its esters for 1990 was 7000 t. Of this figure, one-fourth was used in North America and 43% in East and West Europe. Approximately 85% of the PEA is employed for fragrance use (102).

2.4. Health and Safety

The use of β-phenethyl alcohol generally presents no health problems. PEA is listed on the U.S. (TSCA), (EINECS), *Australian Care Inventory of Chemical Substances*, and the Canadian (DSL) (39–42). This material has Generally Recognized As Safe (GRAS) status as indicated by the Flavor and Extract Manufacturers Association and is approved by the U.S. Food and Drug Administration and the Council of Europe for use in flavors (43–45). PEA satisfies the most current guidelines published by the International Fragrance Association (IFRA) which governs the use of fragrance materials (46).

PEA was negative when tested at 8% in human dermal sensitization and irritation studies (103). Undiluted material caused slight to moderate irritation when applied to guinea pig skin (48, 49), and moderate irritation on rabbit skin (48, 49); it was severely irritating to the rabbit eye (50). Oral rat LD_{50} values of 1.5, 1.79, and 2.46 g/kg have been reported (47, 48, 104). Mouse LD_{50} values of 0.8–1.5 g/kg and a dermal rabbit LD_{50} of 0.79 g/kg have been recorded (49). An 8-h exposure to a saturated vapor atmosphere caused no mortality in rats (50). No significant effects other than decreased weight gain at high doses were observed after a 90-d dermal study in rats (105). Maternally nontoxic dermal doses of PEA caused no adverse fetal effects in rats (106).

BIBLIOGRAPHY

"Benzyl Alcohol and β-Phenylethyl Alcohols" in *ECT* 1st ed., Vol. 2, pp. 483–489, by H. L. Simons and F. F. Polger, Harold L. Simons, Inc. (Benzyl alcohol), and E. T. Theimer, van Ameringen-Haebler, Inc. (β-Phenylethyl alcohol); "Benzyl Alcohol and β-Phenylethyl Alcohol" in *ECT* 2nd ed., pp. 442–449, by William F. Ringk, Benzol Products Company (Benzyl alcohol), and E. T. Theimer, International Flavors & Fragrances, Inc. (β-Phenylethyl alcohol); in *ECT* 3rd ed., Vol. 3, pp. 793–802, by W. F. Ringk (Benzyl Alcohol) and E. T. Theimer (β-Phenethyl Alcohol), Consultants.

Cited Publications

1. P. Z. Bedoukian, *Perfumery and Flavoring Synthetics*, 2nd revised ed., Elsevier Publishing Co., New York, 1967, p. 55.
2. Cannizzaro, *Ann.* **88**, 129 (1853).
3. Jpn. Kokai 85 118573 (May 31, 1985), H. Takigawa and co-workers (to Kao Corp.).
4. A. Bujold, *Chem. Econ. Handbook Program*, Stanford Research Institute, Menlo Park, Calif., 1990.
5. W. T. Hansen, Jr. and W. I. Kisner, *Soc. Motion Pict. Telev. Eng.* **61**, 667 (1953).
6. U.S. Pat. 2,304,925 (Dec. 15, 1942), E. E. Jelley (to Eastman Kodak Co.).
7. U.S. Pat. 2,965,484 (Dec. 20, 1960), V. Tulagin and R. D. Jackson (to General Aniline and Film Corp.).
8. U.S. Pat. 3,146,105 (Aug. 25, 1964), K. L. Wrisley and W. E. Guthrie (to Eastman Kodak Co.).
9. Ger. Offen. Pat. 2,216,419 (Oct. 12, 1972), K. Kobayashi and co-workers (to Fuji Photo Film Co., Ltd.).
10. Jpn. Kokai 75 26,601 (Mar. 19, 1975), K. Kobayashi and co-workers (to Fuji Photo Film Co., Ltd.).
11. U.S. Pat. 2,584,337 (Feb. 5, 1952), K. Famulener and H. Hoerlin (to General Aniline and Film Corp.).
12. U.S. Pat. 2,844,465 (July 22, 1958), L. Chalkley.
13. W. Beal and co-workers, *J. Soc. Dyers Colour.* **76**, 331 (1960).
14. L. Peters and co-workers, *J. Soc. Dyers Colour.* **76**, 543 (1960).
15. C. H. Giles and co-workers, *Text. Res. J.* **32**, 99 (1962).
16. *The IRGA Solvent Process, Dye 6*, Technical Bulletin, Geigy Dyestuffs, Geigy Chemical Corp., Dec. 1960.
17. U.S. Pat. 2,686,145 (Aug. 10, 1954), L. J. Klotz and J. B. Vaughan (to Lloyd Bros., Inc.).
18. R. W. Vander Wyk and A. E. Granston, *J. Am. Pharm. Assoc.* **47**, 193 (1958).
19. U.S. Pat. 2,671,750 (Mar. 9, 1954), T. J. Macek (to Merck and Co., Inc.).
20. A. F. Leyden and co-workers, *J. Am. Pharm. Assoc.* **45**, 771 (1956).
21. U.S. Pat. 3,471,927 (Oct. 14, 1969), H. H. Eisenberg.
22. U.S. Pat. 3,261,754 (July 19, 1966), L. Peters and C. B. Stevens (to Rapidol Ltd.).
23. U.S. Pat. 3,663,716 (May 16, 1972), M. E. Stolar (to Miles Laboratories, Inc.).
24. U.S. Pat. 2,625,515 (Jan. 13, 1953), G. G. Wittwer (to W. B. Chemical Co.).
25. Brit. Pat. 872,506 (July 12, 1961), H. E. Nurston and co-workers.
26. Ger. Pat. 1,073,663 (Jan. 21, 1960), W. Bolzau and co-workers (to Badische Anilin- und Soda-Fabrik A.G.).
27. Fr. Pat. 1,564,133 (Apr. 18, 1969), M. Potter and co-workers (to International Business Machine Corp.).
28. U.S. Pat. 3,089,829 (May 14, 1963), A. F. Millikan (to Pure Oil Co.).
29. U.S. Pat. 3,031,383 (Apr. 24, 1962), A. F. Millikan (to Pure Oil Co.).
30. Fr. Pat. 982,003 (June 4, 1951), J. Labie and S. Warchavsky.
31. U.S. Pat. 3,652,300 (Mar. 28, 1972), J. N. Sharma (to Zenith Processing Corp.).
32. Brit. Pat. 796,863 (June 18, 1958) (to E. I. du Pont de Nemours & Co., Inc.).
33. U.S. Pat. 3,085,907 (Apr. 16, 1963), R. E. Zdanowski and co-workers (to Rohm and Haas Co.).
34. U.S. Pat. 2,755,261 (July 17, 1956), H. A. Clark (to The Dow Chemical Company).
35. U.S. Pat. 3,794,609 (Feb. 26, 1974), I. Metil (to Ameron, Inc.).
36. U.S. Pat. 3,860,475 (Jan. 14, 1975), W. J. Simmons (to E. I. du Pont de Nemours & Co., Inc.).
37. Jpn. Kokai 75 06,652 (Jan. 23, 1975), (to . 4, 1975), H. Takemoto and co-workers (to Toyo Soda Mfg. Co. Ltd.).
38. U.S. Pat. 3,525,206 (Aug. 25, 1970), S. P. Hersh and co-workers (to Monsanto Co.).
39. *Toxic Substances Control Act (TSCA) Chemical Substances Inventory*, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C., Jan. 1986.
40. *European Inventory of Existing Commercial Chemical Substances*, (EINECS), Luxembourg, The Netherlands, 1987.

41. *Australian Core Inventory of Chemical Substances*, 1984.
42. *Canadian Domestic Substances List (DSL)*, 1990.
43. *Flavor and Fragrance Materials*, Flavors and Extracts Manufacturers Association, 1989.
44. *Code of Federal Regulations*, Title 21 Food and Drugs, Part 172.515, United States Food and Drug Administration, Washington, D.C., Apr. 1, 1989.
45. *Natural Flavoring Substances and Added Artificial Flavoring Substances, List 3*, Council of Europe, 1981.
46. *Code of Practice*, International Fragrance Association, 1989.
47. D. L. J. Opdyke, *Food Chem. Toxicol.* **13**, (Special issue No. 2) 903 (1975).
48. J. F. Treon, in G. D. Clayton and F. E. Clayton, eds., *Patty's Industrial Hygiene and Toxicology*, 3rd ed., Vol. **2**, Wiley-Interscience, Inc., New York, 1982, p. 4638.
49. D. V. Sweet, ed., *Registry of Toxic Effects of Chemical Substances*, U.S. Department of Health and Human Services, Washington, D.C., 1990.
50. H. F. Smyth, Jr., C. P. Carpenter, and C. S. Weil, in Ref. 48, p. 4637.
51. F. K. Bar and F. Griepentrog, *Med. Frnaher* **8**, 244 (1967).
52. B. E. Graham and M. H. Kuizenga, *J. Pharm.* **84**, 358 (1945).
53. H. F. Smyth and co-workers, *J. Pharm.* **84**, 4639 (1945).
54. J. A. Stekol, in Ref. 48, p. 4640.
55. *Toxicology and Carcinogenesis Studies of Benzyl Alcohol*, National Toxicology Program, U.S. Department of Health and Human Services, Washington, D.C., May 1989.
56. B. Radziszewski, *Ber.* **9**, 372 (1876).
57. H. Walbaum, *Ber.* **33**, 1904, 2299 (1900).
58. H. V. Soden and W. Rojahn, *Ber.* **33**, 3063 (1900).
59. L. H. Horsley, *Anal. Chem.* **19**, 577 (1947).
60. W. Langenbeck and M. Richter, *Chem. Ber.* **89**, 202 (1956).
61. J. Lee and co-workers, *Jubilee Vol.* Emil Barell, 1946, p. 264.
62. H. Adkins and H. R. Billica, *J. Am. Chem. Soc.* **70**, 695 (1948).
63. Y. R. Naves, *Helv. Chim. Acta* **27**, 261 (1944).
64. Fr. Pat. 1,235,542 (Oct. 28, 1960), G. Bo and P. Perras.
65. A. C. Thompson, P. A. Hedin, R. C. Gueldner, and F. M. Davis, *Phytochemistry* **13**(9), 2029 (1974).
66. N. V. Chuyen and H. Kato, *Agric. Biol. Chem.* **46**(11), 2795 (1982).
67. B. D. Mookherjee and R. W. Trenkle (International Flavors and Fragrances, unpublished data).
68. L. A. O. Roadhouse, *Can. J. Zool.* **31**, 535 (1953).
69. G. S. Langford and E. Gilbert, *J. Econ. Entomol.* **42**, 146 (1949).
70. J. C. Maruzella and E. Bramnick, *Soap Perfum. Cosmet.* **34**, 743 (1961).
71. B. D. Lilley and J. H. Brewer, *J. Am. Pharm. Assoc.* **42**, 6 (1953).
72. I. W. Groto and M. Woods, *J. Am. Pharm. Assoc.* **44**, 9 (1955).
73. C. F. Lord and W. J. Husa, *J. Am. Pharm. Assoc.* **43**, 438 (1954).
74. Brit. Pat. 789,444 (Jan. 22, 1958) (to Daimler-Benz Aktiengesellschaft).
75. C. J. Ponchert, ed., *Aldrich Library of Infrared Spectra, Spectrum No. 520 C*, Aldrich Chemical Co., Milwaukee, Wis., 1970.
76. *Coblentz Society Spectra, Spectrum No. 3712*, Sadoler Research Laboratories, Philadelphia, Pa., 1963.
77. A. Cornu and R. Massot, *Compilation of Mass Data, Code No. 19AD2*, 1966.
78. C. J. Ponchert and J. R. Campbell, eds., *Aldrich Library of NMR Spectra, Spectrum No. 20C*, Aldrich Chemical Co., Milwaukee, Wis., 1974.
79. L. Bouveault and G. Blanc, *Compt. Rend.* **136**, 1676 (1903).
80. *Ibid.*, **137**, 60 (1903).
81. C. S. Leonard, *J. Am. Chem. Soc.* **47**, 1774 (1925).
82. V. Grignard, *Compt. Rend.* **141**, 44 (1905).
83. USSR Pat. 36,400 (1932), P. P. Schorygin and co-workers.
84. A. Schaarschmidt, L. Hermann, and B. Szemzo, *Ber.* **58**, 1914 (1925).
85. H. Horiguchi and T. Yumoto, *Rept. Govt. Chem. Ind. Res. Inst.* **46**, 261 (1951).
86. Brit. Pat. 678,589 (Sept. 3, 1952) (to U.S. Rubber Co.).

87. Brit. Pat. 681,183 (Oct. 22, 1952) (to L. Givaudan et Cie, S.A.).
88. U.S. Pat. 2,524,096 (Oct. 3, 1950), T. F. Wood (to Burton T. Bush, Inc.).
89. Can. Pat. 512,236 (Apr. 26, 1955), H. R. Frisch (to Dominion Rubber Co., Ltd.).
90. Brit. Pat. 760,768 (Nov. 7, 1956) (to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler).
91. U.S. Pat. 2,822,403 (Feb. 4, 1958), H. Hopff and co-workers (to Pittsburgh Coke and Chemical Co.).
92. Brit. Pat. 1,115,145 (May 29, 1968) (to Degussa).
93. A. Sokl'skaya and co-workers, *Sb. Statei Aspir. Soiskatelei Minist. Vyssh. Sredn. Spets. Obrazov. Kaz. SSR Khim. Khim. Teknol.* **3** (1966); *Chem. Abstr.* **69**, 627027g (1968).
94. U.S. Pat. 3,579,593 (May 18, 1971), T. F. Wood (to Givaudan Corp.).
95. E. J. Mistrik and T. Rendko, *Petrochemia* **11**(3), 74 (1971).
96. Ger. (East) Pat. 86,812 (Jan. 5, 1972), O. Priese.
97. Ger. Offen. 2,206,805 (Aug. 16, 1973), K. Adem, W. Hoffmann, and K. Schneider (to BASF).
98. Jpn. Kokai 74 05,933 (Jan. 19, 1974), T. Hashimoto and co-workers (to Mitsubishi Petrochemical Co., Ltd.).
99. Jpn. Kokai 74 05,932 (Jan. 19, 1974), M. Tanaka and T. Aoka (to Mitsubishi Petrochemical Co., Ltd.).
100. U.S. Pat. 4,400,558 (Aug. 23, 1983), M. I. Nemet-Mavrodin and J. F. White (to Atlantic Richfield Co.).
101. Jpn. Kokai 78 64,906 (June 1, 1978), K. Shirai, S. Ishiyama, N. Murakami, and K. Hisatuka (to Idemitsu Kosan Co., Ltd.).
102. G. S. Clark, *Perfum. Flavorist* **15**, 37 (Sept./Oct. 1990).
103. N. Greif, *Am. Perfum. Cosmet.* **82**, 54 (1967).
104. P. M. Jenner and co-workers, *Food Cosmet. Toxicol.* **2**(3), 327 (1964).
105. E. Owston and R. Lough, *Food Cosmet. Toxicol.* **19**, 713 (1981).
106. R. A. Ford and A. M. Api, Research Institute for Frag. Materials, Inc., 1986.

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