An Aroma Chemical Profile

Ethyl Butyrate

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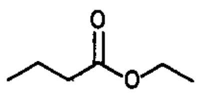
Ethyl butyrate is one of a group of aroma chemicals, which is often slighted or even held in the minds of many in our industry in benign contempt. One industrial colleague summed up this mental niche to which ethyl butyrate has been relegated in the statement: "Ethyl butyrate, I've always thought of it as finger nail polish remover."

There is some organoleptic validity to this attitude, as there exists a large group of C_4-C_{12} esters and ketones, which present fruity impressions in an almost unending spectrum of overlap in one tone or another (see "substitutes"). Some of these materials do find use in the industrial solvent area. Ethyl butyrate's isomer, n-butyl acetate, shares some of its organoleptic profile, yet commercially (with respect to consumption values) is a lacquer solvent, although some small volumes are consumed in flavors. About 230,000,000 lbs. a year of n-butyl acetate are consumed in the paint industry in the U.S. every year,[5] while probably less than 20,000 lbs. are used in the flavor and fragrance industry the world over.

Ethyl butyrate is a prime example of a large grouping of aliphatic esters found in nature mainly in the fruit of plants. For about a century, it has been produced synthetically for use mainly in the flavor industry. Only minute amounts of this product are consumed in the fragrance industry. What peaks one's interest in ethyl butyrate is the recent activity in its commercial production via biotechnology. The result is in effect that ethyl butyrate is really a number of products—one synthetic and the others natural.

The synthetic product currently available from the prime suppliers are very close in organoleptic profile and, thus, convey what can be considered the true notes of ethyl butyrate.

Ethyl Butyrate



Mwt 116 $C_6H_{12}O_2$

CAS 105-54-4 **FEMA-GRAS** 2427

Classification:

Ethyl Ester of a lower straight chain aliphatic acid

Additional Names:[1-3]

Ethyl n-butyrate
Ethyl n-butanoate
Butyric ether[4]—this term applies to a mixture of ethyl esters prepared from mixed acids isolated from butter.
French—Butyrate d'ethyle
German—Aethyl Butyrat
Spanish—Butirato de etilo
Portugese—Butirato de etila

Physical Data:

Appearance: clear, colorless, volatile liquid
Specific Gravity: 0.876 (25°C)
Refractive Index: 1,390-1,395 (20°C)
Boiling Point: 121°C
Flash Point TCC: 75 F flammable liquid
ca. 26°C (DIN 51758)
Solubility: Soluble in H_2O at 25°C ca. 0.5% wt.
Soluble in ethanol, higher alcohols, esters, DEP, propylene glycol, fats, oils, mineral oils and chlorinated solvents.

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The natural products on the market today show a fair degree of variation (especially in top note), which makes many of them individual non-interchangeable materials. Such variation in organoleptic profile was also common in synthetic ethyl butyrate during its early years of production, when most flavor houses manufactured their own ingredients.

Ethyl butyrate from all sources displays a high impact, ethereal, fruity-juice impression that when smelled neat can be overpowering, almost choking. Since it is found in so many fruits, its secondary descriptive terms often vary, but the general consensus is: banana - pineapple - apple - pear (in that order).

Amost all of the products commercially available today displayed clean profiles. Not in one case did burned, still notes prevail. However, one sample of natural ethyl butyrate displayed a persistant isoamyl salicylate dry-out, when all of the other samples had fled the blotter.

Samples of crudely produced ethyl butyrate or material stored under indifferent conditions will display butyric acid notes.

Natural Sources

Ethyl butyrate is found in nature almost exclusively in fruits, their juices and their fermented analogues. The major exception to this statement is its presence in certain dairy products, namely cheeses, and fermented grain and sugar beverages.

Materials reported to contain ethyl butyrate are:

apple	mangos
banana	melons
beer	orange juice
brandy	papaya
butter	passion fruit
cheese	pineapples
cider	rum
grapes	strawberries
grapefruit	whiskey
kiwi fruit	wine

This grouping of materials containing ethyl butyrate illustrates the idea of the general fruit juice effect it imparts in formulations. Thus, it is not surprising, when reviewing old flavor formulations published over half a century ago (before the encroachment of the GLC), to find ethyl butyrate being used to duplicate the flavors of the above items and even the following, where its presence has not been observed:

apricots	butterscotch
cherries	grenadine
caramel	custard

More surprising is the replacement of ethyl butyrate by ethyl acetate in some usages with notations in the formula that either one may be used interchangeably.

Despite the presence of ethyl butyrate in a number of fruit products, no plant source has yet been discovered where it is present at a high enough level to allow it to be commercially isolated.[6] Its presence in orange juice and hence orange juice essence oils is most likely the fruit source with the highest concentration allowing its isolation.

Human consumption of this ester in the U.S. via natural food stuffs is estimated at about 72,000 lbs., while consumption of this ester via flavors will be in the area of 500,000 lbs. of added synthetic and natural ethyl butyrate. Small amounts of natural ethyl butyrate are being produced by isolation from essence oils, but their cost is substantially higher than either synthetic ester or that produced via fermentation. Thus, the emerging source of natural ethyl butyrate is biotechnology.[7,8]

The following are producers of orange essence oils and juice fractions:

Aromachemie Erich Ziegler GmbH
Citrus & Allied Essences Ltd.
Hercules Corp.
Sunkist Essential Oils
Treatts PLC

History

Just who first produced synthetic ethyl butyrate in our industry is a fact lost to time. Once Emil Fischer had elucidated the esterification reaction that bears his name in 1895, production of various esters began in Germany. The U.S. market seems to have been supplied with these esters mainly from Schimmel & Co. and Haarmann & Reimer until 1914. After the war, U.S. production was carried out by a number of firms including Northwestern Chemical, Fritzsche and Felton in the 1920s and then Trubek Labs entered the market in the 1930s. Today, the U.S. manufacturers of synthetic ethyl butyrate are FD&O (now Givaudan) and Northwestern Flavors Inc., a division of Wm. Wrigley Jr. Co.

Suppliers

The demand for natural flavors, which mushroomed during the late 1970s and 1980s, has resulted in a frantic search for natural aroma chemicals from every possible source. Even firms that have traditionally shunned involvement in production of aroma chemicals have explored the manufacture of natural aroma chemicals.

The present supplier picture reflects the interest in sythetic and natural ethyl butyrate, as presented in Table I.

Synthetic Routes

The reaction employed by all synthetic manufacturers is basically that of Fischer esterification of n-butyric acid with slight excess of ethanol (Reaction 1).

Reaction I

$$CH_3CH_2OH + CH_3CH_2CH_2C(=O)OH \xrightleftharpoons{H^+} CH_3CH_2O{-}C(=O){-}CH_2CH_2CH_3 + H_2O$$

Table I. World Producers of Ethyl Butyrate

Firm	Natural	Synthetic
Arofine (India)		x
BASF	x	
China (Shanghai Native Products)		x
Elan	x	
F & C International	x	
Fries & Fries	x	
Givaudan (FD&O)	x	x
H&R GmbH	x	x
IFF	x	
Inoue		x
Northwestern Flavors		x
Oxford	x	
PFW/Hercules	x	
Quest International	x	
Schimmel (Hüls)		x
Shiono		x
Universal Flavors (Mexico)		x

The reaction is an equilibrium which is driven to the ester side of the equation by removal of the water, usually by azeotropic distillation with a solvent, such as hexane or toluene. After the theoretical amount of water has been removed, the batch is worked up by neutralizing the acid catalyst, washing the product with water, and then separating the mixture by fractional distillation. Each manufacturer practices its own variation of this reaction according to the raw material feed stock source, catalysts and solvents employed. The result is a fairly constant synthetic ethyl butyrate quality around the world.

Capacity/Supply—Synthetic Ethyl Butyrate

As ethyl butyrate is produced in general plant equipment in campaigns, the capacity of the synthetic manufacturers is difficult to assess. Capacity is more of a decision to allocate reactor and still time to produce an inexpensive product versus utilizing the equipment for items of higher return. World reactor and still volumes for the production of esters in place today are far in excess of demand in the aroma chemical industry.

In the U.S., a rough estimate of current synthetic ethyl butyrate production is as follows:

Northwestern Flavors Inc.	400,000 lbs/year +
Fritzsche D & O	150,000 lbs/year +

Natural Ethyl Butyrate

Interest in natural flavors has grown so rapidly over the last 15 years that a number of firms have investigated potential methods for the production of natural aroma chemicals. This activity has resurrected fermentation as a key method for the production of natural aroma chemicals and raw material for them.

The volumes of natural ethyl butyrate being produced by fermentation on a global scale are relatively small, about 7% of total usage, but significant and growing. In the U.S., natural ethyl butyrate will command 11% of consumption in 1991.

The technology for the product of natural ethyl butyrate is analogous to that of synthetic ethyl butyrate (Reaction I). Natural raw materials, both acid and alcohol, are produced via fermentation and then coupled by esterification using an enzyme as the catalyst. Although biotechnology captures the imagination as the forefront of science, in many ways, it is just a finer tuning of reactions and processes known for ages.

History—Chemicals by Fermentation

The use of fermentation by man goes back to the dawn of history with the production of wine and beer. The first standard grade chemical, or possibly aroma chemical, produced by biotechnology was Cologne Spirits (95% ethanol) which was first mentioned by Kardanus in his "de subtilitate" as having been produced in Cologne, Germany, in the year 1554.

The last century saw the commercial production via fermentation of lactic acid in 1857, followed by glycerine in 1858, n-butanol in 1876 and citric and oxalic acid in 1893.[9]

In the U.S., commercial production of lactic acid began in 1881 and by 1907 more than eight natural ethanol plants were in operation with a production volume of 1,750,000 gallons.

One of the early pioneers of fermentation science was Chaim Weizmann who developed specific micro-organisms for the production of various chemicals and was the head of the British Admirality's Laboratories from 1916-1919.

World War I gave a boost to fermentation technology as the increased demand for acetone to produce the explosive "Cordite" was met by large scale fermentation plants using Weizmann's organisms. So critical was this need for Great Britain that the Balfours declaration was issued, as requested by Weizmann, which supported at least the concept of a Jewish homeland in Palestine. Weizmann later became the first president of the new state of Israel.

After the war, a number of firms began producing commercial quantities of ethanol, acetone and n-butanol by fermentation on scales unimaginable only ten years before. In the U.S., Commercial Solvents Corp. was founded for that purpose in 1919. Northwestern Chemical, founded in 1882, began the production of ethyl butyrate in the 1920s using fermentation technology for at least one of the steps. Shortly after, the firm was acquired by the Wm. Wrigley Jr. Co.

The production of chemicals by fermentation continued until about the mid-1940s when petrochemical advances slowly displaced much of the fermentation routes. It was the renewed demand for natural aroma chemicals that resurrected the fermentation routes in the early 1980s and resulted in the number of natural aroma chemicals being produced by this method today.[9,10]

Production of Natural Ethyl Butyrate

The production of natural ethyl butyrate can be divided into two steps:

1. The production of raw materials, and
2. The formation of the ester.

1) *Natural Ethanol and Butyric Acid*—The raw materials necessary for natural ethyl butyrate production are natural ethanol and natural butyric acid, both of which are produced via fermentation of carbohydrate feed stock using specific micro-organisms. Natural butyric acid can also be isolated from dairy products, however, the ethyl butyrate generated from it cannot be certified kosher.

2) *Esterification*[10]—The reaction of the raw materials, ethanol and butyric acid, is analogus to Reaction I. The modification that creates a natural ethyl butyrate is the use of natural ethanol and natural butyric acid which is esterified by a natural catalyst (an enzyme) rather than a synthetic acid. The reaction's equilibrium is shifted to the ester side by the removal of water using a hydrophobic reaction media, such as hexane.

World Consumption

Worldwide consumption of ethyl butyrate, both natural and synthetic, is estimated at 1,835,000 lbs. in 1991.

The regional breakdowns for consumption of synthetic and natural ethyl butyrate are as follows:

Area	Natural	Synthetic
North America	74,000 lbs.	600,000 lbs.
Europe	41,000 lbs.	735,000 lbs.
Japan	5,000 lbs.	200,000 lbs.
Others	5,000 lbs.	175,000 lbs.
Sub Totals	125,000 lbs.	1,710,000 lbs.
Combined Totals:		**1,835,000 lbs.**

Pricing

A statement was made earlier in this article that ethyl butyrate resembles not one product but many. The pricing found in today's market reflects that reality.

Synthetic Ethyl Butyrate
1970-1990

Year	$/lb.
1970	0.62
1975	0.82
1980	1.30
1985	1.35
1990	1.50

In general, the depressed pricing for this product will reduce the number of manufacturers involved in its production until prices rise enough to provide adequate returns.

Natural Ethyl Butyrate: These products vary in price from $50/lb. to $80/lb. for similar quantities according to organoleptic profile. Competition is slowly bringing prices down due to excess fermentation reactor capacity.

Supply/Usage

No shortages are foreseen for either synthetic or natural ethyl butyrate due to excess production capacity now in place.

The U.S. market will grow more slowly than in the past and Europe should show more rapid consumption increases over the next five years for natural product.

The overall growth of ethyl butyrate will be about 3-4% per year with most of the growth in natural ester with sales of synthetic ester remaining relatively flat.

Substitutes

The question of substitutes for ethyl butyrate is most interesting, since this ester belongs to a group of materials with similar impressions and overlapping tones. It seems a flavor requiring materials with ethyl butyrate type notes can also be constructed without it; using other esters, ketones and specialty products. Table II is illustrative of its phenomena of organoleptic overlapping of tones in esters, as some 37 materials are represented which display pineapple-like

Table II. Materials with Pineapple Tones, with FEMA Number

allyl cyclohexane acetate	2023
allyl cyclohexane butyrate	2024
allyl cyclohexane propionate	2026
allyl cyclohexane valerate	2027
allyl hexanoate	2032
allyl α-ionone	2033
allyl nonanoate	2036
allyl phenoxyacetate	2038
allyl 10-undecenoate	2044
benzyl ethyl ether	2144
benzyl formate	2145
benzyl isovalerate	2152
n-butyl acetate	2174
n-butyl hexanoate	2201
ethyl acetate	2414
ethyl cyclohexane propionate	2431
ethyl hexanoate	2439
ethyl 3-hexenoate	3342
ethyl propionate	2456
3-hexanone	3290
hexyl butyrate	2568
4-hydroxy-2,5-dimethyl-3-furanone	3174
isoamyl propionate	2082
isobutyl butyrate	2187
isobutyl isobutyrate	2189
isopropyl hexanoate	2950
2-methyl allyl butyrate	2678
methyl butyrate	2693
methyl hexanoate	2708
methyl hexenoate	3364
methyl isobutyrate	2694
methyl 4-methyl butyrate	2721
phenethyl hexanoate	3221
n-propyl n-butyrate	2934
n-propyl isobutyrate	2936
rhodinyl isobutyrate	2983
tetrahydro furfuryl butyrate	3057

impressions. Only four of these items are not esters (FEMA #2033, 2144, 3290 and 3174). Of the remaining esters, the greatest acid grouping represented is butyric 30% (11 esters), with hexanoates following at 19% (7 esters). The most represented alcohol grouping is allyl with 24% (9 esters), followed by the ethyl group at 14% (5 esters). The four non-ester materials chemically can be classified as two ketones and two ethers.

Moreover, the reader should remember that this list is probably not complete with respect to FEMA/GRAS items with pineapple tone. There do exist non-GRAS items with the impression. The same exercise can be carried out for the other organoleptic descriptive tones used for ethyl butyrate, i.e., banana, apple and pear. When such lists are constructed, it is found that esters predominate with a majority of the esters different than the pineapple list, but with a minor number shared with it. Hence, the use of the term "overlapping tones".

Analogues - The Ethyl Series

	Mwt		Arc. Nr.*
Ethyl formate	74	sweet, ethereal, fruity	1235
Ethyl acetate	88	ethereal, fruity, brandy	1137
Ethyl propionate	102	sweet, fruity, ethereal, rum, apple, banana	1344
Ethyl valerate	130	powerful ether, fruity, apple	1361
Ethyl isovalerate	130	powerful ether, apple, fruity	1362
Ethyl caproate	144	powerful fruity, wine, apple, banana, pineapple	1183
Ethyl heptanoate	158	powerful fruity, wine, brandy-berry	1255
Ethyl caprylate	172	fruity, wine, sweet, apricot, banana, pineapple	1185
Ethyl nonanoate	186	fruity, fatty winey	1312
Ethyl decanoate	200	sweet, oily, nut, wine, brandy	1208
Ethyl undecanoate	214	winey, fatty, fruity	1359

Isomeric Esters
Mwt 116 $C_6H_{12}O_2$

Ester	Impression
Methyl valerate	pungent, ethereal, green, fruity, apple
Methyl isovalerate	pungent, ethereal, fruity, apple
Ethyl isobutyrate	sweet, ethereal, fruity, pineapple
n-Propyl propionate	ethereal, fruity, apple
Isopropyl propionate	ethereal, wine-like
n-Butyl acetate	ethereal, fruity
Isobutyl acetate	ethereal, fruity, banana
n-Amyl formate	ethereal, wine-like
Isoamyl formate	ethereal, green, fruity, apple

These isomers illustrate the point that even among isomers of the same molecular weight of ethyl butyrate, the organoleptic profile remains fruity with shifting secondary tones.

* Refers to Arctanders Perfume & Flavor Chemical

References

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1. Ethyl Butyrate, Natural, Givaudan Data Sheet (1990).
2. Ethyl Butyrate, Natural, H&R Data Sheet (1990).
3. Ethyl Butyrate, Natural, Hercules Ferment-Arom Data Sheet (1986).
4. S Arctander, *Perfume and Flavor Chemicals*, Nr. 1178 (1969).
5. n-Butyl Acetate, Chemical Profile, *Chemical Marketing Reporter*, p 5, Dec 17 (1990).
6. J Stofberg, Consumption Ratio and Food Predominance of Flavoring Materials, *Perf & Flav*, **12** (Aug/Sep), 41 (1987).
7. Juan-Ramon Mor, Brochure: Biotechnology - An Introduction by Givaudan, Givaudan Dübendorf Ltd (1989).
8. Ian Gatfield, Production of Flavor and Aroma Compounds by Biotechnology, *Food Technology*, p 110-122, Oct (1988).
9. C S Boruff and J M Van Lanen, Fermentation Chemistry...Key to Better Living, Diamond Jubilee Volume, American Chemical Society, pp 87-89 (1951).
10. F W Welsch, et al, Lipase Mediated Synthesis of Low Molecular Weight Flavor Esters, *Journal of Food Science*, **55**(6), 1679-1682 (1990).