The Butyl Acetates

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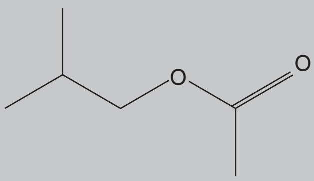
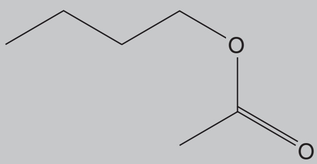
Butyl acetate: The use of lower aliphatic esters to create fruit flavors is most interesting and intriguing. Many of the flavors of our common fruits can be mimicked using a number of mixtures of completely different groups of these esters. This anomaly results from the fact that except for a few unique fruits (lemons-citral), the flavors of most fruits are a complex mixture of esters and other aroma chemicals. Because many of the lower aliphatic esters (C_2-C_5 alcohols) possess similar and overlapping fruity characteristics, mixtures of these esters can be utilized to create a particular type of fruit flavor, even when the major components of that mixture do not appear as part of that fruit's natural constituent's analysis. Remember those strange pineapple-flavored candies you ate as a child?

All of the lower aliphatic esters C_3-C_5 bear a common theme; they are usually ethereal in nature, i.e. volatile and short-lived on the blotter. The terms used for organoleptic descriptions are usually based upon our experiences with foodstuffs in many Western-European based cultures. Since all these esters are found mainly in the fruits consumed in those areas, terms of organoleptic description employed include such terms as: apple, pear, banana, pineapple, strawberry and raspberry. A review of the organoleptic descriptions of these aliphatic esters reveals that the descriptive terms used are very similar and interlaced; all the descriptions include ethereal-fruity. This common theme leads us to question why one structurally similar ester would be relatively popular in its use in flavors while another is relatively shunned. In the practical world, we find that secondary organoleptic characteristics in these esters have only a moderate influence on





	iso-Butyl Acetate	**n-Butyl Acetate**
	Mwt 116	$C_6H_{12}O_2$
	CAS # 110-19-0	CAS # 123-86-4
	FEMA # 2175	FEMA # 2174
	HT Nr. 29153945	HT Nr. 29153300
Physical Data		
Specific Gravity:	0.8748^{20}	0.8825^{20}
Refractive Index:	$1{,}3888^{20}$	$1{,}3941^{20}$
Boiling point:	112°C	126.1°C
Flash Point TCC:	25°C	37°C
Solubility:		
Soluble in H_2O at 25°C:	0.7%	0.43%
Odor Profile:[a]	Fruity-banana-pineapple.	Fruity-banana-pear

Soluble in ethanol, higher alcohols, esters, DEP, propylene glycol, fats, oils, mineral oil, chlorinated solvents and freons.

Classification: Aliphatic esters found in nature.

Additional Names: Banana oil, pear ether, pear oil.[1-4]

French: Acétate de butyle
German: Butyl acetat
Portuguese: Acetato de butila
Spanish: Acetato de butilo

Appearance: Both are clear, colorless, fluid, volatile liquids.

[a] *Samples supplied by Hagelin & Co.*

their use. It appears that their primary attributes, which are similar, and several other fortuitous currents combine to influence their use.

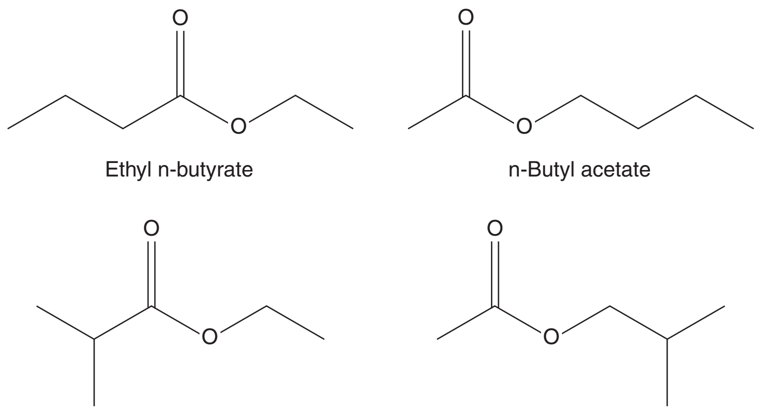
Thus, two esters with similar structures and slightly different secondary toning show surprisingly different usage patterns. Why these esters seem opposite in use development for structurally similar products is an interesting puzzle. The term opposite is used here to provoke the reader. In lower molecular weight chemicals there are only two types of opposites: chemical and chiral. In the fine chemical industry, we currently see an interest in optically active isomers or chiral opposites (right hand-left hand chemicals) as a focus of major activity. This is because the human body responds differently to one of the two antipodes of a chiral material, hence the interest in use of chiral materials in drugs. The organoleptic difference in chiral isomers is just recently becoming a subject of commercial interest in the flavor and fragrance area because it shows promise in the efforts to create better scent- and taste-targeted products.[5]

The other type of opposite that has impact on our industry and has been, at least formally, overlooked—the chemical structural opposite. Ethyl butyrate is the ester of a butyric acid and ethanol. Its chemical structural opposite is butyl acetate, the ester of acetic acid and a butyl alcohol (Figure 1). Both groups (the ethyl butyrates and the butyl acetates) are described as ethereal-fruity and banana-pineapple-pear (with the exception of tert-butyl acetate, which has a very different woody-camphor odor). Cyclobutyl acetate has an unknown odor profile because samples could not be found, but it most likely falls outside of the fruity class into the woody-camphor area. The other three seem to differ only in their secondary organoleptic descriptive terms. Has one never asked the question, why do these esters, so similar structurally; find a different acceptance in our industry? Is it only the secondary attributes in their organoleptic description that causes their difference in usage or some other trick of nature? The secondary organoleptic attributes are certainly one determinate. However, the usage pattern for flavor creation seems to have been developed over a century ago, at a time when the butyl acetates were not available, thus forcing the flavorist to utilize those esters available. The early flavor creation development set a pattern that strongly influences the usage today in new formulas.

In the practical world, these materials suffer two different realities; ethyl butyrate is a low-volume aroma chemical and a very low-volume industrial chemical, while the butyl acetates are very low-volume aroma chemicals and very high-volume commercial chemicals.[6] The butyl group has more than one isomer. Thus, there are five different butyl acetates (Figure 2). Because of this, there are only two ethyl butyrates, but five butyl acetates. However, the flavor and fragrance industry usually uses only two of these butyl esters: n-butyl acetate and iso-butyl acetate. Of the other three esters, sec-butyl acetate and tert-butyl acetate find applications only as industrial chemicals and cyclobutyl acetate is a laboratory curiosity.

The interesting woody-camphor odor of tert-butyl acetate may find use in fragrances to impart a woody volatile top note. In the flavor and fragrance industry, the use of butyl esters is very heavily focussed on the flavor area, with only iso-butyl phenyl acetate normally used in fragrances, and then only at very low volumes. The use of the butyl esters in flavors is concentrated in the fruit formula systems. This reflects their prime organoleptic character—fruity. The main use for the synthetic butyl acetates in the flavor industry today is in chewing gum, where "Juicy-Fruit" flavored gum products consume the highest volume of iso-butyl acetate. Because the flavor industry is currently a "natural flavor industry", the remainder of the butyl acetates being used in the form of isolated esters are of natural origin. However, the world volume of production and consumption of both n-butyl acetate and iso-butyl acetate is overwhelmingly synthetic ester for use as an industrial solvent outside the flavor and fragrance industry.

Figure 1. Chemical opposites: the structural similarities of lower aliphatic esters



Natural Sources

Only two of the five isomers of butyl acetate are found in nature and then mainly in the fruits of plants; n-butyl acetate and iso-butyl acetate. They are often found together in the same fruit along with esters of other similar analog alcohols. Table 1 presents the analysis of the organics found in banana essence, which has a relatively high concentration of butyl acetates, and is found mixed with amyl acetates and butyrates. The areas in which the lower aliphatic esters are not found are animal flesh, cooked meat, fish and seldom in the green parts of plants. There is no plant source, yet discovered, that contains sufficiently high concentrations of the butyl acetates which allow their economical isolation. All the "natural" butyl acetates being offered on the market today are a result of biotechnology systems. The source of the butyl alcohols used for the feedstock is fermentation. Table 2 presents the common natural products that have been reported to contain butyl acetates.

[b]The presence of butyl acetates in rum has been reported in many texts on flavors, yet other investigators have reported that no n-butyl or iso-butyl acetates are present in fruit, wine, whiskey or gin distilled spirits.[7] This might explain their absence in some fusel oils and their only relatively recent isolation and use as an aroma chemical (1920's).

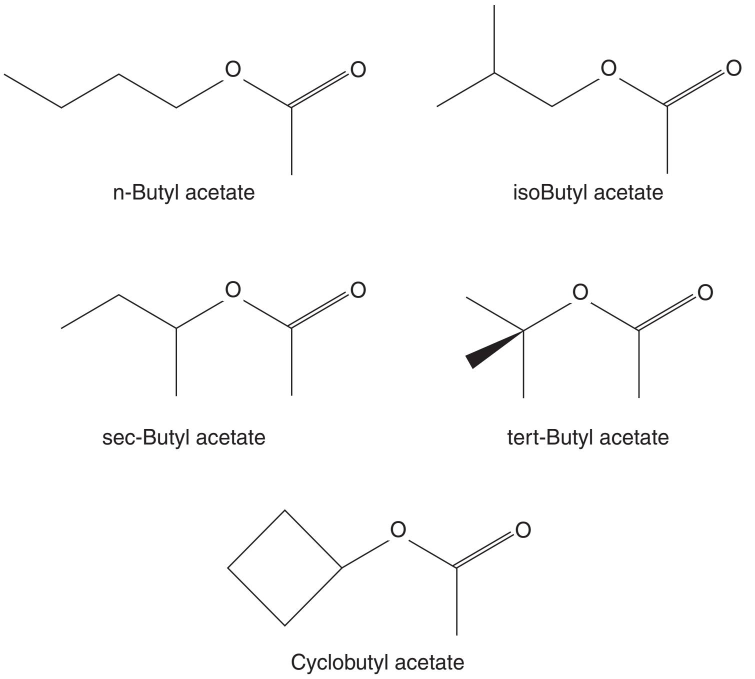
The presence of the butyl acetates in fruits is quite fleeting; these esters seem to arise suddenly during the senessence or ripening stages of the fruits, as the fruit develops from a leafy thing into the ripe finished product.[8] There are two schools of thought on the source of these esters.[9] The straight chain acid-aldehyde-alcohol series arise via the oxidative cleavage of linoleic acid, while the branched acid-aldehyde-alcohols series arise via oxidation of amino acids. However, this could mean that lower straight chain esters are also produced from straight chain amino acids. Both sources of aliphatic acids contribute their products to sets of dynamic acid-aldehyde-alcohol equilibrium systems, which can rapidly convert acid to alcohol thru the aldehyde, as an intermediate.

Whenever one of these materials is removed from the chemical equilibrium system, as it is in the formation of the ester, the system shifts material from one product to the other to balance the system. Thus, ester formation could theoretically drain the system of raw material as it forms. This does not happen as other independent equilibria circulate the ester back into the system. The end result is that the esters' concentrations are held in a dynamic balance; constantly being created and destroyed.

History

As far as the butyl acetates go for the flavor and fragrance industry, it is a case of a too-late development. The references to the butyl acetates in the literature are scant until about 1914, when aviation and WWI arrived with a demand for a quick drying solvent for airplane dope (paints). Nature and man's practicality have seemed to steer this course. There is no natural source of n-butyl acetate or iso-butyl acetate that is of sufficient concentration to allow

Figure 2. The structures of the butyl acetates



its economical isolation. Moreover the butyl acetates are usually found mixed with other esters, making their discovery and isolation difficult for the early chemists. On the other hand, nature provided man with amyl alcohols from the higher boiling fractions found in the distillates of fermented fruits and grains known as fusel oils. The production of alcoholic spirits in large volumes made these still bottoms available as a relatively useless by-product by the year 1785 when Scheele isolated fusel oil from them.

In 1839, Cahours discovered amyl alcohol in these fusel oils, and soon after prepared amyl acetate from the alcohol.[10] Würtz discovered that some fusel oils contained small amounts of butyl alcohols in 1852. In 1867, Erlenmeyer demonstrated that the amyl alcohol present in these fusel oils was the isomer iso-amyl alcohol (3-methyl-1-butanol). By the 1880s, the acetate, butyrate and valerate esters of both ethanol and iso-amyl alcohol were being produced and used in the flavor and fragrance industry, mainly in flavors. Since the iso-amyl alcohol used to prepare the acetate was isolated from fusel oil by crude distillation techniques, it contained minor (10-20 percent) amounts of butyl alcohols, thus the "amyl acetate" used in the early flavor and fragrance industry was a mixture of at least three acetates (see the analysis of banana essence, Table 1). Since each manufacturer's raw material varied in chemical composition, its ester ratio varied and, hence, its secondary organoleptic tone. The recipes employed for the manufacture of esters were similar to those used for the production of diethyl ether and many suppliers and flavor and fragrance houses referred to these ester products as "ethers" in the period 1880-1900. Pear ether was the common name used for "amyl acetate mixture" prepared from the impure amyl alcohol obtained from fusel oil. Amyl acetate was later called "banana oil" or "pear oil". These names were also later used for the butyl acetates. Thus, the flavor and fragrance industry developed its flavor compounding habits around impure Amyl esters and not butyl esters solely because of the availability and price of the items. Thus did the amyl esters become dominant and the butyl esters become only a curiosity. By 1927, the Polak & Schwarz, Ltd. (the forerunner of IFF) catalog listed 11 amyl esters and 14 ethyl esters and no butyl esters.

In 1914, aviation and WWI arrived with a demand for a quick drying solvent for airplane dope. This dope treatment stiffened and held taught the fabric skins of the aircraft. This technology developed using mercerized cotton fabric to cover the airplane's frame, which was then shrunk in place and stiffen with a dope based initially on nitrocellulose and then later on cellulose acetate. The solvents used to apply this dope were based upon amyl and butyl acetates, which evaporated and dried quickly. The availability of large quantities of butyl alcohol for the preparation of the acetate was somewhat fortuitous, as it was a by-product of the fermentation process of corn designed to produce acetone, the solvent needed for the production of the explosive "Cordite".[11]

After WWI, the rise of the automobile industry, especially in the United States, lead to the demand for large quantities of lacquers and, hence, lacquer solvents based upon the butyl acetates. The world's demand for butyl acetates was met by the fermentation of corn and molasses until after WWII, when the petrochemical industry developed the technology to produce synthetic butanols and butyl acetates from olefin feeds. The market development of butyl acetates continued along the commercial solvent usage. As a result, the flavor and fragrance industry adopted the term "solvent" and "finger nail polish remover" to describe these lower esters.[12] The initial petrochemical based synthetic products were not pure even by the standards of the chemical industry of 1950, having only 90 percent content of their designated ester type.

Today some 700,000,000 lb (32,000 Mtons/year) of n-butyl acetate and about 350,000,000 lb (16,000Mtons/year) of iso-butyl acetate are produced and consumed worldwide, mainly as coating and paint solvents. Table 3 presents the major producers of synthetic butyl acetates, while Table 4 gives the domestic capacity of the three major US producers. Table 5 lists the suppliers of natural butyl acetates to the flavor and fragrance industry. Less than 50,000 lb of both n-butyl and iso-butyl acetates are consumed worldwide in the flavor and fragrance industry. Of that amount, only 20,000 lb of these esters are natural in the true sense. The demand for natural aliphatic esters has been dampened by the flavorist's preference for the use of the natural fruit extracts and essences, rather than natural chemical isolates.

The estimated worldwide consumption of the natural butyl acetates is presented in Table 6. The consumption is mainly via the fruit or its products (juices, cider, etc.). Only minor amounts of butyl acetates are consumed via isolated esters in compounded flavors.

Investigators have recognized since the early 1980s that fruit juice flavor diminishes and changes during processing. The classic example of this phenomenon is the loss of juice flavor in orange juice during evaporative concentration to produce frozen orange juice. Recent research has shown that all these changes are not just due to evaporation losses.[14] Apple juice loses about half its flavor impact during processing and a good part of this loss is not evaporation, but chemically induced loss. Enzymatic induced changes increase and decreases the relative amounts of individual aroma chemicals in apple juice during processing and unveiled a new side to the butyl ester story.

Our expectation of what a fruit should taste like is based upon our experience with that fruit or its products at the time we imbibe them. Until the orange became available in large volumes in the northern United States after WWII, the most consumed fruit in America was the apple. Some species of apples could be stored over the winter and consumed over a six-to-eight month period However, the juice of the apple in the form of pasteurized and unpasteurized apple juice and soft and hard cider was the major means of consumption of the fruit.

The formation of the flavor esters in apples occurs quite rapidly in the ripening process and is governed by a dynamic enzymatic system. This enzyme system remains in control until it is eliminated by pasteurization-

Table 1. Analysis of the organics found in banana essence

Material	Wt%
Ethanol	40.0
Butyl acetates (mixed)	10.0
Iso-amyl butyrate	10.0
Ethyl-2-methylbutyrate	10.0
Iso-amyl alcohol	4.5
Acetaldehyde	3.5
Iso-amyl acetate	2.5
E-2-hexenal	1.8
Methyl amyl ketone	1.7
Diacetyl	1.3
Other	14.7
Total	100.0

Table 2. Naturals sources of butyl acetates

	n-Butyl	iso-Butyl
Apples	X	X
Apricots	X	
Bananas	X	X
Beer	X	X
Brandy	X	X
Butter	X	
Grapes	X	X
Mangos	X	
Peaches	X	
Rum[b]	X	X
Rum ether	X	
Strawberries	X	X
Violet leaf	X	
Whisky	X	X
Wine	X	X

Table 3. Producers of synthetic butyl acetates

Producer	n-Butyl	iso-Butyl	sec-Butyl	tert-Butyl
CTC Organics			X	
Eastman	X	X		
Hoechst	X			
Northwest Flavors		X		
Union Carbide	X	X		
Wacker Chemie			X	

Table 4. Estimated 2000 US synthetic ester capacity of the major producers[13]

Eastman	50,000,000kg
Hoechst-Celanese	80,000,000kg
Union Carbide	50,000,000kg
Total	180,000,000kg

Table 5. Producers of natural butyl acetates

Producer	n-Butyl	isoButyl
ABACO	X	X
Advanced Biotech	X	X
Alfrebro	X	X
Britannia	X	X
Danisco	X	X
Elan		X
H&R-Florasynth	X	X
Kato		X
Robertet	X	X
Ungerer		X

Table 6. World consumption of natural butyl esters in 2000

Source	n-Butyl acetate	isoButyl acetate
Apples	550,000kg	3000kg
Bananas	170,000kg	95,000kg
Beer	70,000kg	85,000kg
Other	8000kg	29,000kg
Sub-total	798,000kg	212,000kg
Compounded flavors	4,000kg	16,000kg
Total	802,000kg	228,000kg

microfiltration. It now appears that the aroma chemical composition of apple juice changes when processed, leading to a selective decrease in the n-butyl acetate and iso-butyl acetate content versus other flavor components. The amounts of other esters, such as ethyl-2-methyl butyrate, increase relative to the n-butyl acetate and iso-butyl acetate concentrations and the absolute amounts of green materials. Cis-3-hexanal and *trans*-2-hexenal also increase, leading to a shift in the "flavor of apples" as a liquid product and hence apples as we recognize and remember them. A similar flavor change has been noted for iso-butyl acetate in strawberry juice.[15] Other researchers have found that flavor chemical shifts take place in other fruit juices; i.e. mangos and passion fruit. These enzymatic changes also contributed to the lack of popularity of butyl esters in compounded fruit flavor systems. It now appears that our selective disregard for the flavor of butyl acetates is just not based upon a prejudice from compounding habits due to availability of various esters, but also a shunning of these products because of their failure to fit the profile of fruit flavors as we have come to know them through our modern consumption experience.

Supply and Usage

The supply of synthetic butyl acetates will continue to grow as an industrial solvent, as these esters are deemed environmentally friendly and hence are finding wider usage. The supply of natural butyl acetates will continue as is and will be a very minor player in the flavor industry as users choose to use cheaper, more versatile and organoleptically complex naturally available fruit derived products, such as banana essences. The creative use of isolated natural esters in formulas demands that the flavorist devote more time and formula money to creating a natural fruit complex, that in most cases can be obtained by use of a less expensive natural fruit by-product rather than pure natural esters. Tables 1 and 2 illustrate this point by showing 10 of the major aroma chemicals found in banana essence versus the presence of the butyl acetates in other natural products. Note the crossover between many products and bananas. Moreover the use of these essences in none related fruit formulas is a good way to twist (add color and complex natural tone) a new formula at reasonable prices versus the higher cost of using isolated natural esters. The future market for pure isolated natural butyl acetates is at best bleak. By 2010 the natural butyl acetate volumes seen today will not have changed by more than 10 percent.

Derivatives

Because feedstocks, which can furnish a butyl group, have been available to the research chemist for over 100 years, every derivative that could be conceived of has been made synthetically. Those presented here in Table 7 are a selection of the more popular materials used in our industry. Even then, some of these items are relatively rare or still used in such low volumes and sporadic applications that many formula creators have never heard of them or used them. The

Table 7. Butyl esters and their suppliers

Derivative	FEMA-GRAS Nr.	Supplier
sec-Butyl acetate	-	CTC, Penta
tert-Butyl acetate	-	Wacker Chemie
n-Butyl anthranilate	2181	
Butylated hydroxyanisole (BHA)	2183	
Butyl para-hydroxbenzoate		
Butylated hydroxytoluene (BHT)	2184	
Butyl benzoate		
Butyl benzyl ether	2139	CTC, Penta
Butyl butyrate	2186	
Butyl caproate	2201	
α-Butylcinnamaldehyde		
Butyl cinnamate	2192	
4 -tert-Butyl cyclohexanol		
2 -tert-Butyl cyclohexanol		
4 -tert-Butyl cyclohexanone		
2 -tert-Butyl cyclohexanone		
4 -tert-Butyl cyclohexyl acetate		
2 -tert-Butyl cyclohexyl acetate		
n-Butyl formate	2196	
n-Butyl heptanoate	2199	Fairfield,Grau, Penta
tert-Butylhydroquinone (TBHQ)		
n-Butyl isobutyrate	2188	
n-Butyl isovalerate	2218	
n-Butyl lactate	2205	
n-Butyl -2-methylbutyrate	3393	
para-tert-Butyl-a-methyldi-hydrocinnamaldehyde		
n-Butyl phenylacetate	2209	
n-Butyl propionate	2211	
n-Butyl salicylate	3650	
n-Butyl tiglate		Bedoukian,CTC, Penta
n-Butyl 10-undecylenate	2216	
n-Butyl n-valerate	2217	

following Butyl derivatives are commonly available through a number of suppliers, unless a supplier(s) is indicated.

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