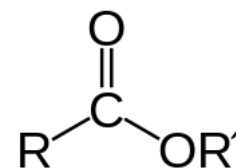


Ester

An **ester** is a chemical compound derived from an acid (organic or inorganic) in which at least one –OH hydroxyl group is replaced by an –O– alkyl (alkoxy) group,^[1] as in the substitution reaction of a carboxylic acid and an alcohol. Glycerides are fatty acid esters of glycerol; they are important in biology, being one of the main classes of lipids and comprising the bulk of animal fats and vegetable oils.



A carboxylate ester.
R' denotes any alkyl
or aryl group.

Esters typically have a nice smell; those of low molecular weight are commonly used as fragrances and are found in essential oils and pheromones. They perform as high-grade solvents for a broad array of plastics, plasticizers, resins, and lacquers,^[2] and are one of the largest classes of synthetic lubricants on the commercial market.^[3] Polyesters are important plastics, with monomers linked by ester moieties. Phosphoesters form the backbone of DNA molecules. Nitrate esters, such as nitroglycerin, are known for their explosive properties.

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Nomenclature

Etymology

The word *ester* was coined in 1848 by a German chemist Leopold Gmelin,^[4] probably as a contraction of the German *Essigäther*, "acetic ether".

IUPAC nomenclature

The names of esters are derived from the parent alcohol and the parent acid, where the latter may be organic or inorganic. Esters derived from the simplest carboxylic acids are commonly named according to the more traditional, so-called "trivial names" e.g. as formate, acetate, propionate, and butyrate, as opposed to the IUPAC nomenclature methanoate, ethanoate, propanoate, and butanoate. Esters derived from more complex carboxylic acids are, on the other hand, more frequently named using the systematic IUPAC name, based on the name for the acid followed by the suffix *-oate*. For example, the ester hexyl octanoate, also known under the trivial name hexyl caprylate, has the formula $\text{CH}_3(\text{CH}_2)_6\text{CO}_2(\text{CH}_2)_5\text{CH}_3$.

The chemical formulas of organic esters usually take the form $\text{RCO}_2\text{R}'$, where R and R' are the hydrocarbon parts of the carboxylic acid and the alcohol, respectively. For example, butyl acetate (systematically butyl ethanoate), derived from butanol and acetic acid (systematically ethanoic acid) would be written $\text{CH}_3\text{CO}_2\text{C}_4\text{H}_9$. Alternative presentations are common including BuOAc and $\text{CH}_3\text{COOC}_4\text{H}_9$.

Cyclic esters are called lactones, regardless of whether they are derived from an organic or inorganic acid. One example of an organic lactone is γ-valerolactone.

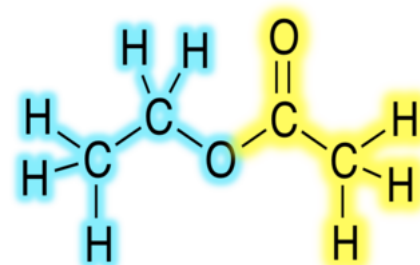
Orthoesters

An uncommon class of organic esters are the orthoesters, which have the formula $\text{RC}(\text{OR}')_3$. Triethylorthoformate ($\text{HC}(\text{OC}_2\text{H}_5)_3$) is derived, in terms of its name (but not its synthesis) from orthoformic acid ($\text{HC}(\text{OH})_3$) and ethanol.

Inorganic esters

Esters can also be derived from inorganic acids.

- Phosphoric acid forms phosphate esters, e.g. triphenylphosphate
- sulfuric acid forms sulfate esters, e.g., dimethylsulfate
- nitric acid forms nitrate esters, e.g. methyl nitrate

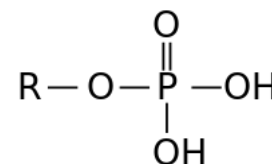


Ethyl acetate derived from an alcohol (blue) and an acyl group (yellow) derived from a carboxylic acid.

- boric acid forms borates, e.g. trimethylborate.
- carbonic acid forms carbonate esters, e.g. ethylene carbonate

Inorganic acids that exist as tautomers form diverse esters

- phosphorous acid forms two kinds of phosphite esters, e.g. triethylphosphite ($\text{P}(\text{OEt})_3$) and diethylphosphite ($\text{HP}(\text{O})(\text{OEt})_2$).



A phosphoric acid ester

Inorganic acids that are unstable or elusive form stable esters.

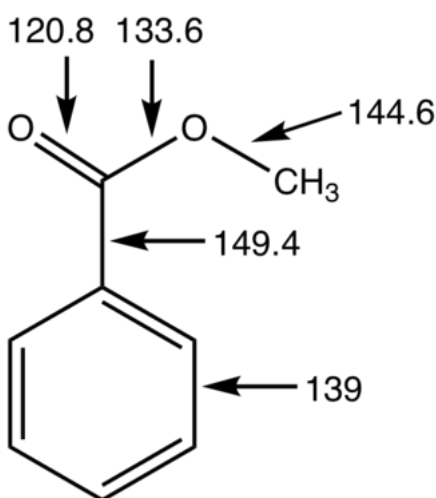
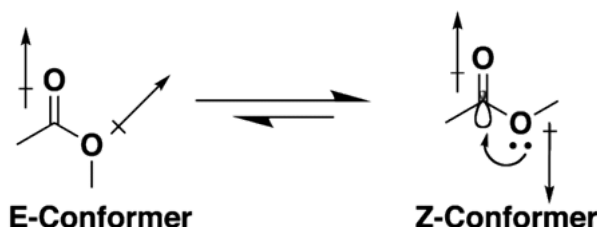
- chromic acid, which has never been detected, forms di-tert-butyl chromate
- sulfurous acid, which is rare, forms dimethylsulfite

In principle, all metal and metalloid alkoxides, of which many hundreds are known, could be classified as esters of the hypothetical acids.

Structure and bonding

Esters contain a carbonyl center, which gives rise to 120° C–C–O and O–C–O angles. Unlike amides, esters are structurally flexible functional groups because rotation about the C–O–C bonds has a low barrier. Their flexibility and low polarity is manifested in their physical properties; they tend to be less rigid (lower melting point) and more volatile (lower boiling point) than the corresponding amides.^[5] The $\text{p}K_{\text{a}}$ of the α -hydrogens on esters is around 25.^[6]

Many esters have the potential for conformational isomerism, but they tend to adopt an *s*-cis (or *Z*) conformation rather than the *s*-trans (or *E*) alternative, due to a combination of hyperconjugation and dipole minimization effects. The preference for the *Z* conformation is influenced by the nature of the substituents and solvent, if present.^{[7][8]} Lactones with small rings are restricted to the *s*-trans (i.e. *E*) conformation due to their cyclic structure.



Metrical details for methyl benzoate, distances in picometers.^[9]

Physical properties and characterization

Esters are more polar than ethers but less polar than alcohols. They participate in hydrogen bonds as hydrogen-bond acceptors, but cannot act as hydrogen-bond donors, unlike their parent alcohols. This ability to participate in hydrogen bonding confers some water-solubility. Because of their lack of hydrogen-bond-donating ability, esters do not self-associate. Consequently, esters are more volatile than carboxylic acids of similar molecular weight.^[5]

Characterization and analysis

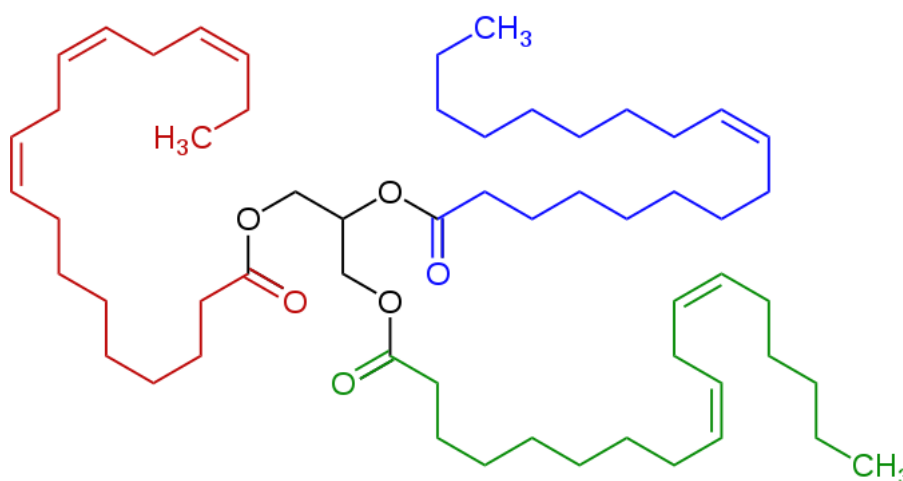
Esters are generally identified by gas chromatography, taking advantage of their volatility. IR spectra for esters feature an intense sharp band in the range $1730\text{--}1750\text{ cm}^{-1}$ assigned to $\nu_{\text{C=O}}$. This peak changes depending on the functional groups attached to the carbonyl. For example, a benzene ring or double bond in conjugation with the carbonyl will bring the wavenumber down about 30 cm^{-1} .

Applications and occurrence

Esters are widespread in nature and are widely used in industry. In nature, fats are in general triesters derived from glycerol and fatty acids.^[10] Esters are responsible for the aroma of many fruits, including apples, durians, pears, bananas, pineapples, and strawberries.^[11] Several billion kilograms of polyesters are produced industrially annually, important products being polyethylene terephthalate, acrylate esters, and cellulose acetate.^[12]

Preparation

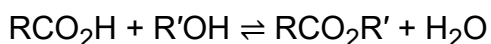
Esterification is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product. Esters are common in organic chemistry and biological materials, and often have a pleasant characteristic, fruity odor. This leads to their extensive use in the fragrance and flavor industry. Ester bonds are also found in many polymers.



Representative triglyceride found in a linseed oil, a triester (triglyceride) derived of linoleic acid, alpha-linolenic acid, and oleic acid.

Esterification of carboxylic acids with alcohols

The classic synthesis is the Fischer esterification, which involves treating a carboxylic acid with an alcohol in the presence of a dehydrating agent:

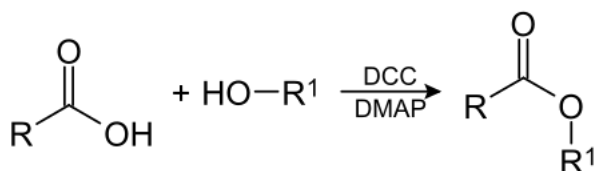


The equilibrium constant for such reactions is about 5 for typical esters, e.g., ethyl acetate.^[13] The reaction is slow in the absence of a catalyst. Sulfuric acid is a typical catalyst for this reaction. Many other acids are also used such as polymeric sulfonic acids. Since esterification is highly reversible, the yield of the ester can be improved using Le Chatelier's principle:

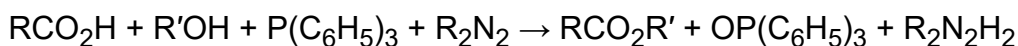
- Using the alcohol in large excess (i.e., as a solvent).
- Using a dehydrating agent: sulfuric acid not only catalyzes the reaction but sequesters water (a reaction product). Other drying agents such as molecular sieves are also effective.
- Removal of water by physical means such as distillation as a low-boiling azeotropes with toluene, in conjunction with a Dean-Stark apparatus.

Reagents are known that drive the dehydration of mixtures of alcohols and carboxylic acids. One example is the Steglich esterification, which is a method of forming esters under mild conditions. The method is popular in peptide synthesis, where the substrates are sensitive to harsh conditions like

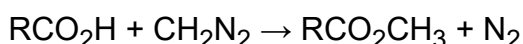
high heat. DCC (dicyclohexylcarbodiimide) is used to activate the carboxylic acid to further reaction. 4-Dimethylaminopyridine (DMAP) is used as an acyl-transfer catalyst.^[14]



Another method for the dehydration of mixtures of alcohols and carboxylic acids is the Mitsunobu reaction:



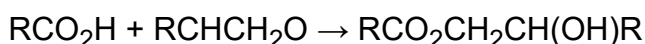
Carboxylic acids can be esterified using diazomethane:



Using this diazomethane, mixtures of carboxylic acids can be converted to their methyl esters in near quantitative yields, e.g., for analysis by gas chromatography. The method is useful in specialized organic synthetic operations but is considered too hazardous and expensive for large-scale applications.

Esterification of carboxylic acids with epoxides

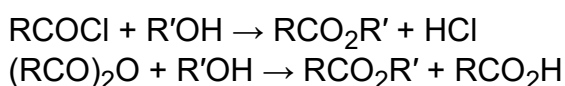
Carboxylic acids are esterified by treatment with epoxides, giving β -hydroxyesters:



This reaction is employed in the production of vinyl ester resin resins from acrylic acid.

Alcoholysis of acyl chlorides and acid anhydrides

Alcohols react with acyl chlorides and acid anhydrides to give esters:



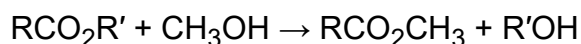
The reactions are irreversible simplifying work-up. Since acyl chlorides and acid anhydrides also react with water, anhydrous conditions are preferred. The analogous acylations of amines to give amides are less sensitive because amines are stronger nucleophiles and react more rapidly than does water. This method is employed only for laboratory-scale procedures, as it is expensive.

Alkylation of carboxylate salts

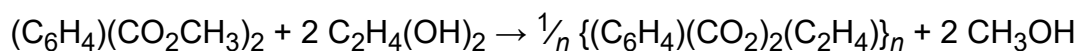
Although not widely employed for esterifications, salts of carboxylate anions can be alkylating agent with alkyl halides to give esters.^[12] In the case that an alkyl chloride is used, an iodide salt can catalyze the reaction (Finkelstein reaction). The carboxylate salt is often generated *in situ*.^[15] In difficult cases, the silver carboxylate may be used, since the silver ion coordinates to the halide aiding its departure and improving the reaction rate. This reaction can suffer from anion availability problems and, therefore, can benefit from the addition of phase transfer catalysts or highly polar aprotic solvents such as DMF.

Transesterification

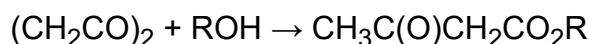
Transesterification, which involves changing one ester into another one, is widely practiced:



Like the hydrolysis, transesterification is catalysed by acids and bases. The reaction is widely used for degrading triglycerides, e.g. in the production of fatty acid esters and alcohols. Poly(ethylene terephthalate) is produced by the transesterification of dimethyl terephthalate and ethylene glycol.^[12]



A subset of transesterification is the alcoholysis of diketene. This reaction affords 2-ketoesters.^[12]

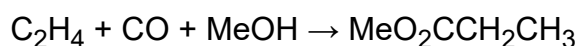


Carbonylation

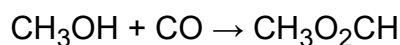
Alkenes undergo "hydroesterification" in the presence of metal carbonyl catalysts. Esters of propanoic acid are produced commercially by this method:



A preparation of methyl propionate is one illustrative example.

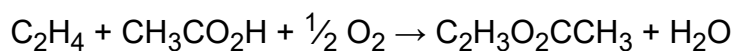


The carbonylation of methanol yields methyl formate, which is the main commercial source of formic acid. The reaction is catalyzed by sodium methoxide:



Addition of carboxylic acids to alkenes and alkynes

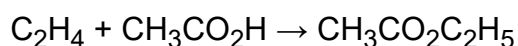
In the presence of palladium-based catalysts, ethylene, acetic acid, and oxygen react to give vinyl acetate:



Direct routes to this same ester are not possible because vinyl alcohol is unstable.

Carboxylic acids also add across alkynes to give the same products.

Silicotungstic acid is used to manufacture ethyl acetate by the alkylation of acetic acid by ethylene:



From aldehydes

The Tishchenko reaction involves disproportionation of an aldehyde in the presence of an anhydrous base to give an ester. Catalysts are aluminium alkoxides or sodium alkoxides. Benzaldehyde reacts with sodium benzyloxide (generated from sodium and benzyl alcohol) to generate benzyl benzoate.^[16] The method is used in the production of ethyl acetate from acetaldehyde.^[12]

Other methods

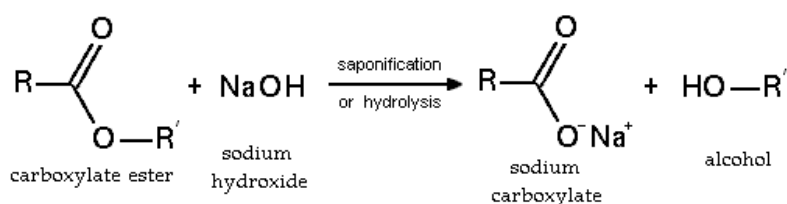
- Favorskii rearrangement of α -haloketones in presence of base
- Baeyer–Villiger oxidation of ketones with peroxides
- Pinner reaction of nitriles with an alcohol
- Nucleophilic abstraction of a metal–acyl complex
- Hydrolysis of orthoesters in aqueous acid
- Cellulolysis via esterification^[17]
- Ozonolysis of alkenes using a work up in the presence of hydrochloric acid and various alcohols.^[18]
- Anodic oxidation of methyl ketones leading to methyl esters.^[19]
- Interesterification exchanges the fatty acid groups of different esters.

Reactions

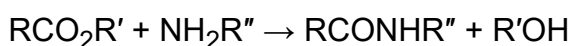
Esters react with nucleophiles at the carbonyl carbon. The carbonyl is weakly electrophilic but is attacked by strong nucleophiles (amines, alkoxides, hydride sources, organolithium compounds, etc.). The C–H bonds adjacent to the carbonyl are weakly acidic but undergo deprotonation with strong bases. This process is the one that usually initiates condensation reactions. The carbonyl oxygen in esters is weakly basic, less so than the carbonyl oxygen in amides due to resonance donation of an electron pair from nitrogen in amides, but forms adducts.

Hydrolysis and saponification

Esterification is a reversible reaction. Esters undergo hydrolysis under acid and basic conditions. Under acidic conditions, the reaction is the reverse reaction of the Fischer esterification. Under basic conditions, hydroxide acts as a nucleophile, while an alkoxide is the leaving group. This reaction, saponification, is the basis of soap making.



The alkoxide group may also be displaced by stronger nucleophiles such as ammonia or primary or secondary amines to give amides: (ammonolysis reaction)

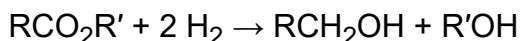


This reaction is not usually reversible. Hydrazines and hydroxylamine can be used in place of amines. Esters can be converted to isocyanates through intermediate hydroxamic acids in the Lossen rearrangement.

Sources of carbon nucleophiles, e.g., Grignard reagents and organolithium compounds, add readily to the carbonyl.

Reduction

Compared to ketones and aldehydes, esters are relatively resistant to reduction. The introduction of catalytic hydrogenation in the early part of the 20th century was a breakthrough; esters of fatty acids are hydrogenated to fatty alcohols.



A typical catalyst is copper chromite. Prior to the development of catalytic hydrogenation, esters were reduced on a large scale using the Bouveault–Blanc reduction. This method, which is largely obsolete, uses sodium in the presence of proton sources.

Especially for fine chemical syntheses, lithium aluminium hydride is used to reduce esters to two primary alcohols. The related reagent sodium borohydride is slow in this reaction. DIBAH reduces esters to aldehydes.^[20]

Direct reduction to give the corresponding ether is difficult as the intermediate hemiacetal tends to decompose to give an alcohol and an aldehyde (which is rapidly reduced to give a second alcohol). The reaction can be achieved using triethylsilane with a variety of Lewis acids.^{[21][22]}

Claisen condensation and related reactions

As for aldehydes, the hydrogen atoms on the carbon adjacent ("α to") the carboxyl group in esters are sufficiently acidic to undergo deprotonation, which in turn leads to a variety of useful reactions. Deprotonation requires relatively strong bases, such as alkoxides. Deprotonation gives a nucleophilic enolate, which can further react, e.g., the Claisen condensation and its intramolecular equivalent, the Dieckmann condensation. This conversion is exploited in the malonic ester synthesis, wherein the diester of malonic acid reacts with an electrophile (e.g., alkyl halide), and is subsequently decarboxylated. Another variation is the Fráter–Seebach alkylation.

Other reactions

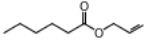
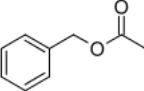
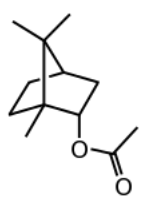
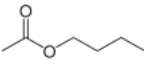
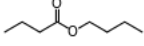
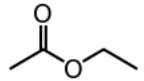
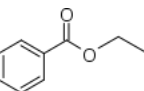
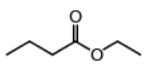
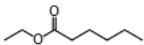
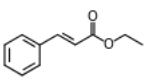
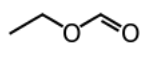
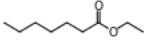
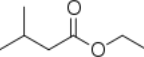
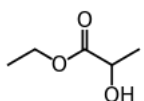
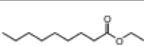
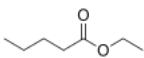
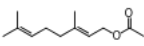
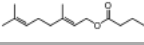
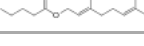
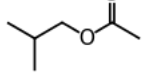
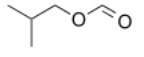
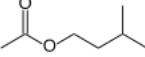
- Phenyl esters react to hydroxyarylketones in the Fries rearrangement.
- Specific esters are functionalized with an α-hydroxyl group in the Chan rearrangement.
- Esters with β-hydrogen atoms can be converted to alkenes in ester pyrolysis.
- A direct conversion of esters to nitriles.^[23]

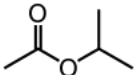
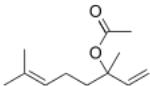
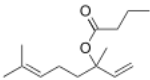
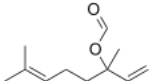
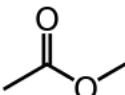
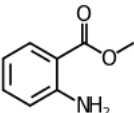
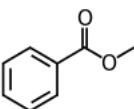
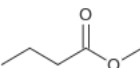
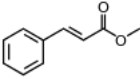
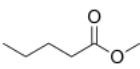
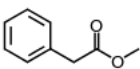
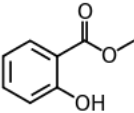
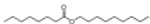


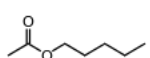
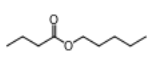
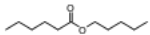
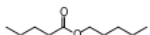
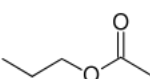
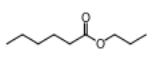
Protecting groups

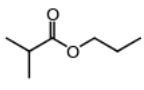
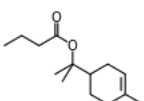
As a class, esters serve as protecting groups for carboxylic acids. Protecting a carboxylic acid is useful in peptide synthesis, to prevent self-reactions of the bifunctional amino acids. Methyl and ethyl esters are commonly available for many amino acids; the *t*-butyl ester tends to be more expensive. However, *t*-butyl esters are particularly useful because, under strongly acidic conditions, the *t*-butyl esters undergo elimination to give the carboxylic acid and isobutylene, simplifying work-up.

List of ester odorants

Many esters have distinctive fruit-like odors, and many occur naturally in the essential oils of plants. This has also led to their common use in artificial flavorings and fragrances which aim to mimic those odors.

Ester name	Structure	Odor or occurrence
<u>Allyl hexanoate</u>		<u>pineapple</u>
<u>Benzyl acetate</u>		<u>pear</u> , <u>strawberry</u> , <u>jasmine</u>
<u>Bornyl acetate</u>		<u>pine</u>
<u>Butyl acetate</u>		<u>apple</u> , <u>honey</u>
<u>Butyl butyrate</u>		<u>pineapple</u>
<u>Butyl propanoate</u>		<u>pear drops</u>
<u>Ethyl acetate</u>		<u>nail polish remover</u> , <u>model paint</u> , <u>model airplane glue</u> , <u>pears</u>
<u>Ethyl benzoate</u>		<u>sweet</u> , <u>wintergreen</u> , <u>fruity</u> , medicinal, <u>cherry</u> , <u>grape</u>
<u>Ethyl butyrate</u>		<u>banana</u> , <u>pineapple</u> , <u>strawberry</u>
<u>Ethyl hexanoate</u>		<u>pineapple</u> , <u>waxy-green banana</u>
<u>Ethyl cinnamate</u>		<u>cinnamon</u>
<u>Ethyl formate</u>		<u>lemon</u> , <u>rum</u> , <u>strawberry</u>
<u>Ethyl heptanoate</u>		<u>apricot</u> , <u>cherry</u> , <u>grape</u> , <u>raspberry</u>
<u>Ethyl isovalerate</u>		<u>apple</u>
<u>Ethyl lactate</u>		<u>butter</u> , <u>cream</u>
<u>Ethyl nonanoate</u>		<u>grape</u>
<u>Ethyl pentanoate</u>		<u>apple</u>
<u>Geranyl acetate</u>		<u>geranium</u>
<u>Geranyl butyrate</u>		<u>cherry</u>
<u>Geranyl pentanoate</u>		<u>apple</u>
<u>Isobutyl acetate</u>		<u>cherry</u> , <u>raspberry</u> , <u>strawberry</u>
<u>Isobutyl formate</u>		<u>raspberry</u>
<u>Isoamyl acetate</u>		<u>pear</u> , <u>banana</u> (flavoring in <u>Pear drops</u>)

<u>Isopropyl acetate</u>		fruity
<u>Linalyl acetate</u>		<u>lavender</u> , <u>sage</u>
<u>Linalyl butyrate</u>		<u>peach</u>
<u>Linalyl formate</u>		<u>apple</u> , <u>peach</u>
<u>Methyl acetate</u>		<u>glue</u>
<u>Methyl anthranilate</u>		<u>grape</u> , <u>jasmine</u>
<u>Methyl benzoate</u>		fruity, <u>ylang ylang</u> , <u>feijoa</u>
<u>Methyl butyrate</u> (methyl butanoate)		<u>pineapple</u> , <u>apple</u> , <u>strawberry</u>
<u>Methyl cinnamate</u>		<u>strawberry</u>
<u>Methyl pentanoate</u> (methyl valerate)		<u>flowery</u>
<u>Methyl phenylacetate</u>		<u>honey</u>
<u>Methyl salicylate</u> (oil of <u>wintergreen</u>)		Modern <u>root beer</u> , <u>wintergreen</u> , <u>Germolene</u> and <u>Ralgex</u> ointments (UK)
<u>Nonyl caprylate</u>		<u>orange</u>
<u>Octyl acetate</u>		fruity- <u>orange</u>
<u>Octyl butyrate</u>		<u>parsnip</u>
<u>Amyl acetate</u> (pentyl acetate)		<u>apple</u> , <u>banana</u>
<u>Pentyl butyrate</u> (amyl butyrate)		<u>apricot</u> , <u>pear</u> , <u>pineapple</u>
<u>Pentyl hexanoate</u> (amyl caproate)		<u>apple</u> , <u>pineapple</u>
<u>Pentyl pentanoate</u> (amyl valerate)		<u>apple</u>
<u>Propyl acetate</u>		<u>pear</u>
<u>Propyl hexanoate</u>		<u>blackberry</u> , <u>pineapple</u> , <u>cheese</u> , <u>wine</u>
<u>Propyl isobutyrate</u>		<u>rum</u>

		
<u>Terpenyl butyrate</u>		<u>cherry</u>

See also

- List of esters
- Amide, an ester analog with oxygen replaced by nitrogen
- Cyanate ester
- Oligoester
- Polyolester
- Thioester, an ester analog with oxygen replaced by sulfur
- Transesterification
- Ether lipid

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Original text:

b. Ester oder sauerstoffsäure Aetherarten.
Ethers du troisième genre.

Viele mineralische und organische Sauerstoffsäuren treten mit einer Alkohol-Art unter Ausscheidung von Wasser zu neutralen flüchtigen ätherischen Verbindungen zusammen, welche man als gepaarte Verbindungen von Alkohol und Säuren-Wasser oder, nach der Radicaltheorie, als Salze betrachten kann, in welchen eine Säure mit einem Aether verbunden ist.

Translation:

b. Ester or oxy-acid ethers.
Ethers of the third type.

Many mineral and organic acids containing oxygen combine with an alcohol upon elimination of water to [form] neutral, volatile ether compounds, which one can view as coupled compounds of alcohol and acid-water, or, according to the theory of radicals, as salts in which an acid is bonded with an ether.

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External links

- An introduction to esters (<http://www.chemguide.co.uk/organicprops/esters/background.html>)
- Molecule of the month: Ethyl acetate and other esters (<http://www.chm.bris.ac.uk/motm/ethylacetate/ethylh.htm>)

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