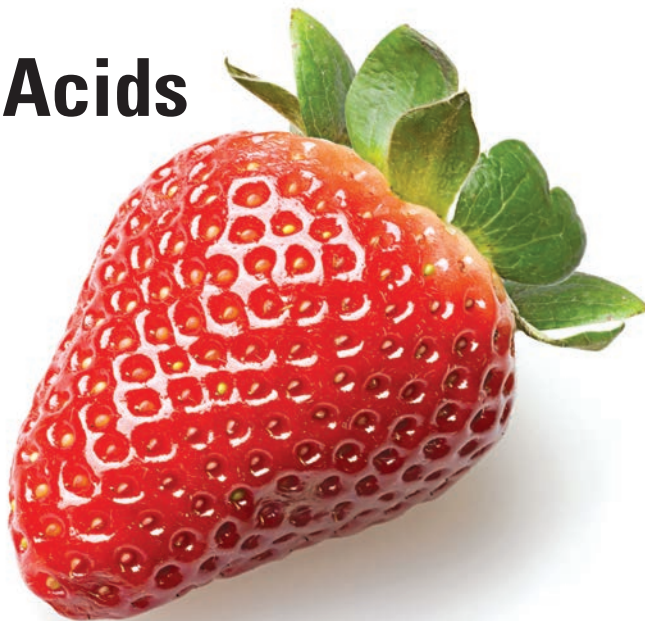


Unsaturated Aliphatic Acids

Chemistry and application in flavor

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Five- and six-carbon atom unsaturated acids have an important role, mostly in cheesy and fruity flavors.

For example, *trans*-2-hexenoic acid (FEMA# 3169, CAS# 13419-69-7) (**F-1**)—which occurs in apple, banana, grape, strawberry, beer, wine, pork and tea—has a cheesy, fatty, herbal, warm odor, and is applied to cheesy, berry and fruity flavorings^a.

The most important 5–7 carbon atom unsaturated carboxylic acids can be seen in **F-2**.

As a special case, the addition of a methyl group to *trans*-2-hexenoic acid skeleton gives *E*-3-methyl-2-hexenoic acid (CAS# 27960-21-0). The human axilla is a unique area that produces a characteristic odor, called axillary odor. In the axillary region of humans, various compounds are secreted by apocrine, eccrine, apoecrine and sebaceous glands. The characteristic odor is generated when microorganisms on the skin surface interact with apocrine secretions. It has been suggested that the characteristic odor in axillary secretion is due to the volatile steroids (androstanol, CAS#1153-51-1; androstenone, CAS# 18339-16-7; and androstadienone, CAS# 4075-07-4), having musky and urinary odors, and isovaleric acid (FEMA# 3102, CAS# 503-74-2) (**F-3**), having an acidic odor.

However, axillary odor is more distinct and pungent, suggesting the presence of other volatile compounds. In particular, (*E*)-3-methyl-2-hexenoic acid (**F-4**) was identified as having a strong malodor.¹

It seems that other isomers of this acid can contribute to beer flavor. Thus, a hop essence flavor consisting of ethanol, water and an ethanol solution of a mixture of

(*E*)-4-methyl-3-hexenoic acid (CAS# 34935-26-7) and (*E*)-4-methyl-2-hexenoic acid (CAS# 51724-49-3) (**F-5**) were mixed to give a beer flavor. A beer flavored beverage containing the flavor had the fresh, sharp, and green flavor of hop.²

Another interesting hexenoic acid is the *cis* isomer, *cis*-3-hexenoic acid (CAS# 1775-43-5) (**F-6**). Even the most popular raw materials potentially emit a repulsive odor if smelled in their undiluted form, including *cis*-3-hexenoic acid, with its unattractive miasma of stale sweat. Consequently, this raw material shows no visible flavor connections. However, it has been found that *cis*-3-hexenoic acid exhibited a much stronger influence and helped create a fresher, more natural-tasting effect.³ *cis*-3-Hexenoic acid is found also in tea (*Camellia sinensis*, Theaceae), in which the roasted, smoky character of black tea is supported by the sweaty odor of the acid.⁴

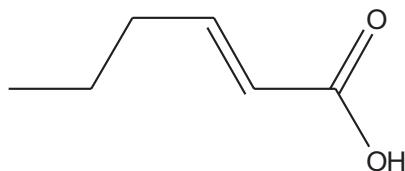
trans-2-Hexenoic acids is one of the volatile compounds of merlot and cabernet Gernischt in a Chinese wine, Chateau Changyu-Castel, which might contribute to its acidic taste.⁵

One of the methods to prepare *trans*-2-hexenoic acid comprises sequentially adding diethyl malonate (FEMA# 2375, CAS# 105-53-3), *n*-butanal (CAS# 123-72-8) and a catalyst into reactor, stirring the reaction mixture with heat, then adding base solution, stirring and refluxing,

^a Most information on organoleptic properties and uses (unless otherwise noted) are taken from FRM2001 *Database of Flavour Raw Materials*, Boelens Aroma Chemicals Information Services, The Netherlands.

trans-2-Hexenoic acid

F-1



Physical Data for *trans*-2-Hexenoic acid

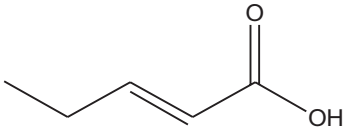
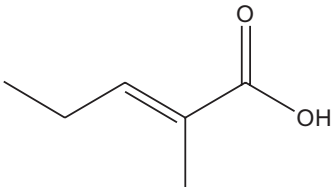
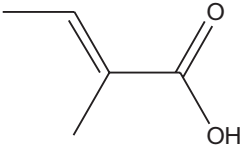
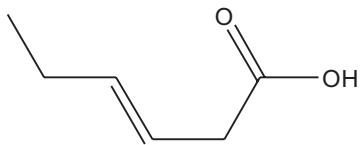
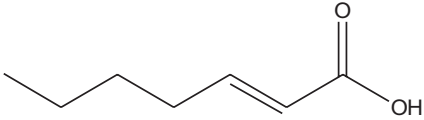
Appearance: Colorless to pale yellow liquid above the congealing point

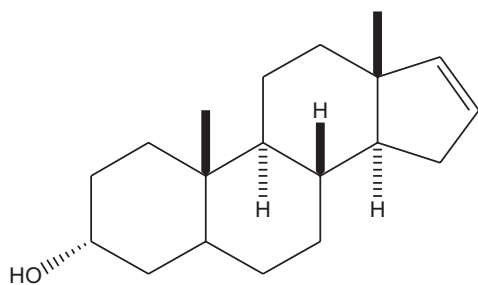
Molecular weight: 114.15

Molecular formula: C₆H₁₀O₂

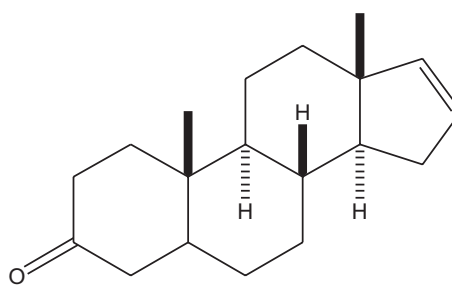
Congealing point: 28–35°C

Solubility point: Soluble in one and more parts of 70% alcohol

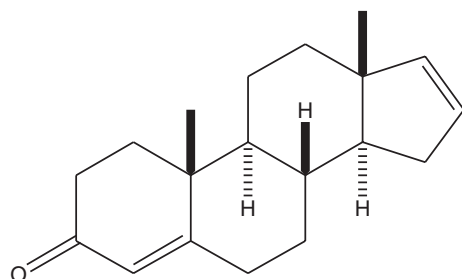
Structure, Name, FEMA# (where applicable), CAS# CAS No.	Occurrence	Organoleptic characteristics	Applications in flavors
 <p>trans-2-Pentenoic acid CAS# 13991-37-2</p>	Banana, beer	Green fruity, caprylic	Fruit flavors
 <p>2-Methyl-2-pentenoic acid FEMA# 3195, CAS# 3142-72-1</p>	Strawberry	Sour fruity, cheeselike	Fruity (strawberry), dairy (cheese) flavorings
 <p>2-Methyl-trans-2-butenoic acid (tiglic acid) FEMA# 3599, CAS# 80-59-1</p>	Strawberry, celery, aniseed, coffee, soybean, mango, bonito, croton oil	Sweet, brown, fruity, with ripe and jammy nuances	Fruity, caramellic, bakery, dairy and spicy flavorings, rum, caramel, bread, cheese, fruit and berry nuances
 <p>trans-3-Hexenoic acid FEMA# 3170, CAS# 1577-18-0</p>	Banana, raspberry, beer, sherry, tea, passion fruit	Diffusive cheese, somewhat fruity	Alcoholic beverages, bakery, cheese, passion fruit, raspberry, soft fruits, tea
 <p>trans-2-Heptenoic acid CAS# 10352-88-2</p>	Pork	Caprylic, fatty	Dairy and meat flavors



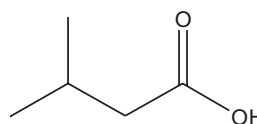
Androst-enol



Androstenone



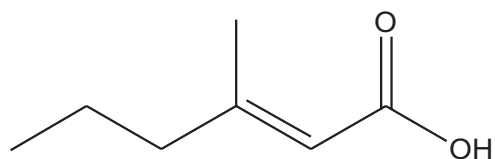
Androstadienone



Isovaleric acid

(E)-3-Methyl-2-hexenoic acid

F-4

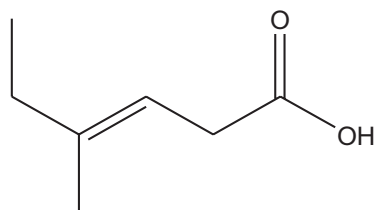


(E)-3-Methyl-2-hexenoic acid

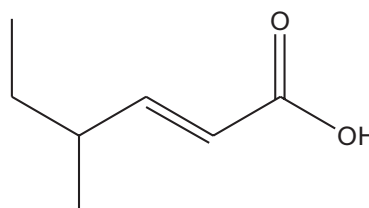
then adding acid solution, acidifying, stirring and refluxing for more time.⁶ When the reaction is completed, distillate under decompression is carried out to obtain *trans*-2-hexenoic acid. The catalyst can be TBAB (tetrabutylammonium bromide, CAS# 10549-76-5), TEBA (triethylbenzylammonium chloride, CAS# 56-37-1), dioctadecyldimethylammonium bromide (CAS# 3700-67-2), or similar materials. The base is NaOH (CAS# 1310-73-2), KOH (CAS# 1310-58-3) or even Ca(OH)₂ (CAS# 1305-62-0), and the acid is HCl (CAS# 7647-01-0) or H₂SO₄ (CAS# 7664-93-9). The solvent is water. The method is environmentally friendly and easy in industrialization, and has few side reactions and high yield (75–85%) (F-7).

(E)-4-Methyl-3-hexenoic acid and (E)-4-methyl-2-hexenoic acid

F-5



(E)-4-Methyl-3-hexenoic acid



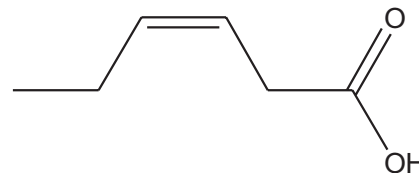
(E)-4-Methyl-2-hexenoic acid


References

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cis-3-Hexenoic acid

F-6

*cis*-3-Hexenoic acid

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Method to prepare *trans*-2-hexenoic acid

F-7

