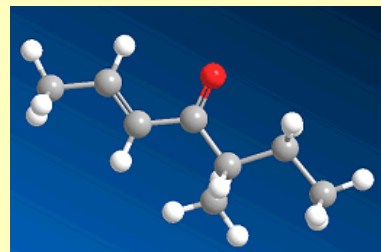


# FILBERTONE

(the smell of hazelnuts)

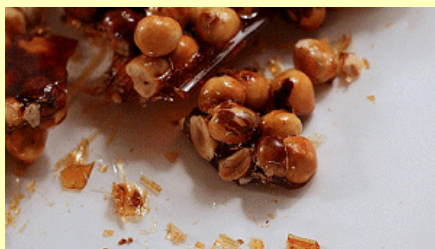
Simon Cotton  
University of Birmingham

Molecule of the Month September 2012  
Also available: [JSMol](#) version.



## The smell of filberts?

Yes, though in many places they are known as hazelnuts (*Corylus maxima* and *Corylus avellana*), the fruit of the hazeltree (photo, right). And the molecule was only identified in hazelnuts in 1989. Hazelnuts are used as a flavouring in cakes, famously Viennese hazelnut torte and Kiev cake; confectionary (pralines) and chocolates; liqueurs; and other food products (like Nutella).



Hazelnut pralines



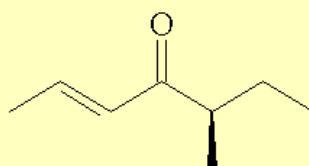
Kiev cake



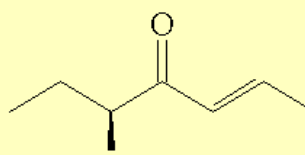
Nutella

## Filbertone is shown as enantiomers, do they both occur in nature?

In nature, there is a slight excess of the (*S*)-isomer, the amount varies depending upon the source of the filberts. The enantiomeric excess in the extracted filbertone is greater under mild extraction conditions.



(-)-(E,R)-filbertone

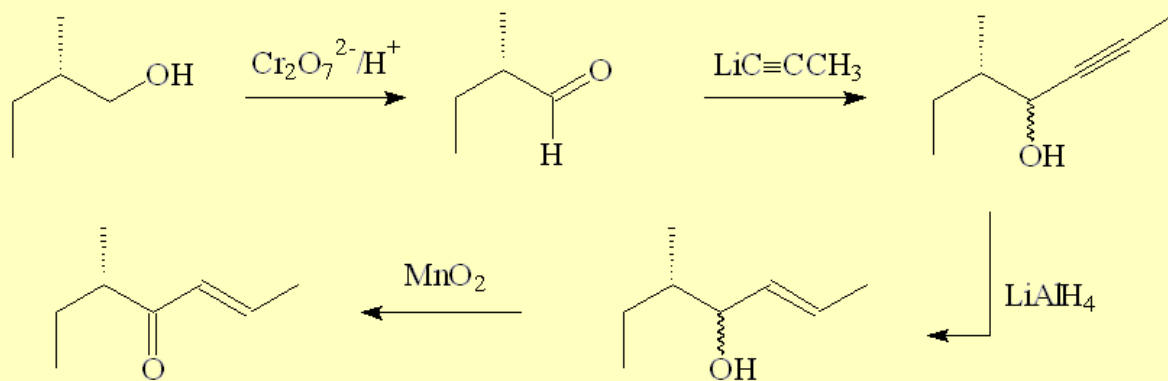


(+)-(E,S)-filbertone

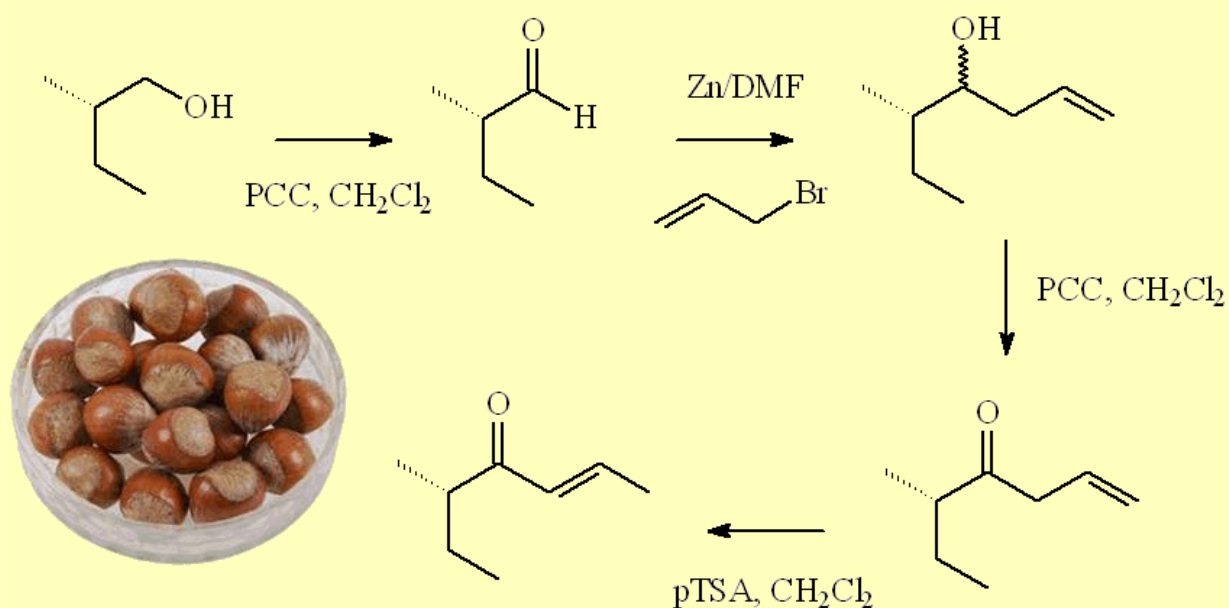
## Can you tell the isomers apart?

They have been separated by chromatography using a chiral column. The two mirror-image isomers (enantiomers) have significantly different smells. Both smell of "hazelnuts", but the (+)-(E,S)-isomer has a more fatty smell than the (-)-(E,R)-isomer, which has notes of butter and chocolate, as well as having a stronger impact, with a 10 times greater odour threshold.

## How do you make it?



In the original laboratory synthesis, (+)-(E,5S)-filbertone was prepared starting from (S)-(-)-2-methylbutan-1-ol. First it was oxidised to the corresponding aldehyde, which underwent nucleophilic attack at the carbonyl carbon by propynyl lithium, forming a mixture of the isomers (4R,5S)-5-methylhept-2-yn-4-ol and (4S,5S)-5-methylhept-2-yn-4-ol. Reduction with LiAlH<sub>4</sub> proceeded stereospecifically at the triple bond to give (E,4R,5S)-5-methylhept-2-en-4-ol and (E,4S,5S)-5-methylhept-2-en-4-ol, which on oxidation with MnO<sub>2</sub> formed just (E,5S)-5-methylhept-2-en-4-one.

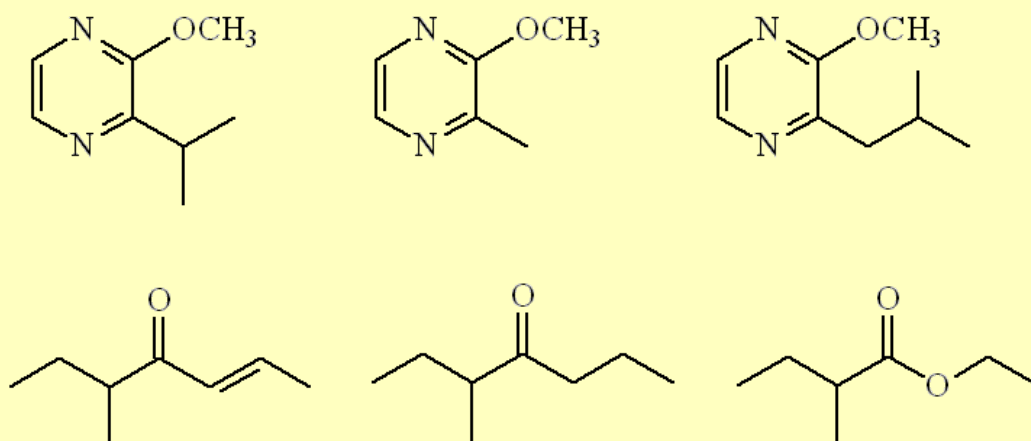


A second route uses oxidation in the first step, with pyridinium chlorochromate oxidant, but introduces the additional chain in a different way, by a coupling with allyl bromide. The alcohol product was oxidised using PCC again to afford (5S)-5-methylhept-1-en-4-one, which was isomerised on treatment with *p*-toluenesulfonic acid.

In a modification of the original route, NaOCl was used as the stoichiometric oxidant in the first step, with 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) catalyst. Yields were improved by better work-up procedures.

## Is filbertone the only molecule responsible for the smell of hazelnuts?

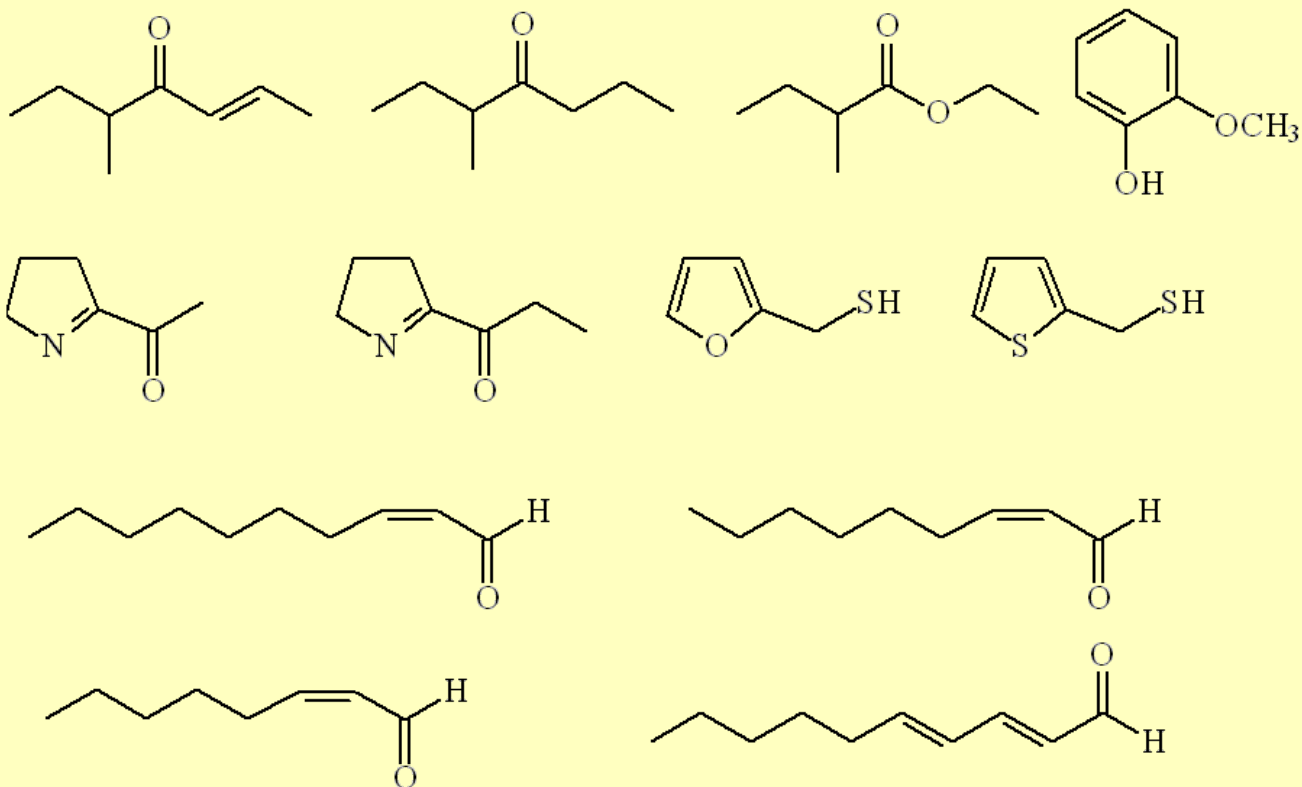
Not at all. A recent paper on Italian hazelnuts (2010) identified 37 odour-active compounds in the raw nuts. Important ones include three substituted pyrazines, especially 2-methoxy-3-isopropylpyrazine and 2-methoxy-3,5-dimethylpyrazine, as well as 5-methyl-4-heptanone and ethyl 2-methylbutanoate, in addition to 5-methyl-(E)-2-hepten-4-one.



Raw hazelnut odourants

Rather more (46) aroma-active compounds were detected in roasted nuts, with some additional new molecules present, notably unsaturated aldehydes (Z)-2-octenal, (Z)-2-nonenal, (Z)-2-

decenal and (*E,E*)-2,4-decadienal, 2-thienylthiol, 2-acetyl-1-pyrroline and 2-propionyl-1-pyrroline.



Roast hazelnut odourants

## And what's this about using Hazelnut oil to adulterate olive oil?

It's true. Olive oil is a cornerstone of the Mediterranean diet. It's more expensive than hazelnut oil, so unscrupulous people adulterate olive oil with cheaper hazelnut oil, as small amounts can be hard to detect, though GC-MS has been successfully used.



The Abbey at Tournus

## And why are they called filberts?

They are linked with St. Philibert, the 7th-century monk who founded several monasteries in France, and whose feast day of August 20th coincides with the nutting season. He was buried at Noirmoutier, on the western coast of France, but the 9th-century Viking attacks caused the monks to move. They eventually settled at Tournus in the Rhone valley, where the great abbey church of St. Philibert still holds his relics.



The casket (or reliquary) holding the relics of St. Philibert.



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