# cis-3-HEXENAL, trans-2-HEXENAL

#### and 'GREEN GRASS' SMELL

Simon Cotton Uppingham School, Rutland, UK

Molecule of the Month March 2005 Also available: JSmol version.



#### What's the connection with grass?

cis-3-hexenal is the key aroma substance emitted when grass is cut and other types of vegetation are damaged. It has a very low odour threshold of 0.25 parts per billion.



# What's an Odour Threshold?

The Odour Threshold is the lowest concentration of a vapour in air which can be detected by smell.

# Can you bottle it?

Unfortunately, cis-3-hexenal is unstable and tends to rearrange to the more stable trans-2-hexenal ("leaf aldehyde"), which has an odour threshold of 17 ppb. The related cis-3-hexen-1-ol ("leaf alcohol") has an odour threshold of 70 ppb it's used in perfumes.

# How is it formed?

When grass is cut, breakdown of fats and phospholipids leads to a-linolenic acid (and lineoleic acid). This is oxidised to 12hydroperoxylinoleinic acid by a lipoxygenase enzyme. In turn, the C<sub>18</sub> chain in this molecules is split by another enzyme, hydroperoxide lyase , usually into C<sub>6</sub> and C<sub>12</sub> fragments. The initial C<sub>6</sub> product is *cis*-hex-3-enal (3E-hexenal).









#### What role do these molecules have?

One may be in protecting the plant from bacteria, for example, allowing the cut ends to heal. *trans*-2-hexenal is one of a number of aldehydes found in coriander, widely used in cooking. Spices have long been associated with preserving food, and both *trans*-2-hexenal and *trans*-3-hexenal have been found to be active against a range of bacteria, including *Salmonella choleraesuis* (the most common cause of septicaemia).

# Why do these smells have such an impact?

There is no doubt that smell taps into our memories and into subconscious emotions. The classic example linking smell with memory occurs in the masterpiece of the French novelist Marcel Proust (1871-1922, right), "A la Recherche du Temps Perdu" ("In Search of Lost Time"). Very early on, in the first book ("Swann's Way"), the protagonist Charles Swann found that the smell from a piece of a small madeleine cake soaked in tea acted as the trigger for a whole raft of memories from his childhood. On Sunday mornings at Illiers, near Chartres (Combray in the novel), Proust would go to the bedroom of his aunt Elizabeth (Léonie, in the novel) to say good morning, before Mass, and she would give him a small piece of madeleine that had been dipped in her cup of lime blossom tea.





Players of the traditional English summer game, cricket, are familiar with the smell of cut grass. It is very potent. Alan Dixon played first class cricket for Kent. He was an all-rounder, both a middle-order batsman and a bowler at medium pace and of off-spinners. He decided to retire in the autumn of 1957 at the age of 23 as he was not sure of a place in the First XI. He went off to become a travelling salesman.

"But it came round to the spring [1958], and I stopped the car by a cricket field where they were mowing the grass. And the smell of that new-mown grass meant so much. I got out of my car and rang Les Ames [the Secretary of Kent County Cricket Club]. 'Leslie,' I said, 'it looks as if I've made a mistake'".

Dixon played for another 13 seasons and did not retire until 1970, when he was a member of the Kent XI that won the County Championship.

#### How does it work?

We are hot-wired for memory. Olfaction is closely linked with the limbic system, of which the hippocampus and amygdala are a part, and which is responsible for emotions and memory. The sense of smell has a direct link to the cerebral cortex in the brain; messages involving other senses like touch or taste have a more circuitous route. How the message gets through is another matter, with both the traditional "lock and key" theory and the "vibrational" theory linking molecules and smell currently in vogue.



# And, of course, people sing songs about grass...

Tom Jones for one, in "Green Green Grass Of Home" and the Inkspots, with "Whispering Grass".



Tom Jones



The Inkspots

#### Where else do these molecules occur?

trans-2-hexenal, and hexyl acetate are chief among molecules responsible for the freshness of apple juice flavour, and thus hexenals can be used as additives to make flavours have a greener texture. Animals use them too.

#### **Really?**

The Japanese scarab beetle, *Phyllopertha diversa*, has olfactory receptor neurones that are specific for green-leaf volatiles, namely *trans*-2-hexenal, *cis*-3-hexenyl acetate, and *cis*-3-hexenol.

Some ants use trans-2-hexenal as an alarm pheromone.

Stink bugs, important agricultural predators (picture, right), use *trans*-2-hexenal as a attractant and pheromone, and it is a potential weapon to protect crops.

Green leaf volatiles, including *trans*-2-hexenal, disrupt responses by the spruce beetle, *Dendroctonus rufipennis*, and the western pine beetle, *Dendroctonus brevicomis* to attractant-baited traps.

# And Green Grass smell really does seem to be good for you...

Behavioural studies involving PET (Positron emission tomography) have shown that the "green odour" mixture of *trans*-2-hexenal and *cis*-3-hexen-1-ol has a healing effect on the psychological damage caused by stress. The mixture activates regional blood flow in the primary olfactory cortex (like other smelly molecules) and also the anterior cingulated gyrus, the latter being linked with the "healing effect".

# Bibliography

#### **Devon prayer meadow**

http://www.bbc.co.uk/devon/faith/2004/prayer\_meadow.shtml

#### **Antibacterial Activity**

I. Kubo, K. Fujita, A. Kubo, K. Nihei, and T. Ogura, J. Agric. Food Chem., 2004, 52, 3329.

#### **Smell and memory**

- http://www.leffingwell.com/olfaction.htm
- http://www.cf.ac.uk/biosi/staff/jacob/teaching/sensory/olfact1.html
- http://www.csa.com/crw/home.html
- http://www.macalester.edu/~psych/whathap/UBNRP/Smell/memory.html

#### **Alan Dixon**

- Stephen Chalke, The Wisden Cricketer, October 2004, p.61
- http://www.cricketarchive.com/Kent/Players/29/29085/29085.html
- http://aus.cricinfo.com/link\_to\_database/ARCHIVE/CRICKET\_NEWS/2004/SEP/054783\_WCM\_23SEP2004.html

#### Apples

- J.H.F. Bult, H.N.J. Schifferstein, J.P. Roozen, E.D. Boronat, A.G.J. Voragen and J.H.A. Kroeze, Chem. Senses, 2002, 27, 485.
- J. Dixon and E.N. Hewett, New Zealand Journal of Crop and Horticultural Science, 2000, 28, 155.
- http://www.fks.com/flavors/tech/Science%20of%20Flavor%20Creation.asp

#### Insects

- B.S. Hansson, M.C. Larsson and W.S. Leal, Physiological Entomology, 1999, 24, 121 (scarab beetle)
- http://www.pherobase.com/database/compounds-detail-E2-6Ald.html
- B. Holldobler and E.O. Wilson, *The Ants*, Belknap Press, Harvard, 1990, p.263
- M. Jacobson, Insect Pheromones, Academic Press, New York, 1972, p.82
- T.M. Poland, J.H. Borden, A.J. Stock and L.J. Chong, J. Entomol. Soc. Brit. Columbia., 1998, 95, 17 (disruptor)





Jean-Yves Tadie, Marcel Proust: A Life, Viking, 2000

Green Grass Smell is good for you

T. Sasabe, M. Kobayashi, Y. Kondo, H. Onoe, S. Matsubara, S. Yamamoto, H. Tsukada, K. Onoe, H. Watabe, H. Iida, M. Kogo, K. Sano, A. Hatanaka, T. Sawada, and Y. Watanabe, Chem.Senses, 2003, 28, 565.

0025831

**E** Back to Molecule of the Month page.

[DOI:10.6084/m9.figshare.5245834]