Learning Organic Chemistry through a Study of Semiochemicals

Pernaa, Johannes

2011

Pernaa , J & Aksela , M 2011 , ' Learning Organic Chemistry through a Study of
þÿSemiochemicals ' , Journal of Chemical Education , vol. 88 , no. 12 , p

http://hdl.handle.net/10138/339703
https://doi.org/10.1021/ed900050g

unspecified
acceptedVersion

Title: Learning Organic Chemistry Through a Study of Semiochemicals

Corresponding author:
Johannes Pernaa
The Unit of Chemistry Teacher Education, Department of Chemistry, University of Helsinki
Department of Chemistry, P. O. Box 55,
FIN-00014 University of Helsinki,
e-mail: johannes.pernaa@helsinki.fi
telephone: +358 50 4151177
Homepage: http://blogs.helsinki.fi/pernaa/

Other authors:
Maija Aksela
The Unit of Chemistry Teacher Education, Department of Chemistry, University of Helsinki
Department of Chemistry, P. O. Box 55,
FIN-00014 University of Helsinki,
e-mail: maija.aksela@helsinki.fi
telephone: +358-50-5141450
Homepage:
http://kampela.it.helsinki.fi/apumatti/lcms.php?am=11968-11968-1&page=11969

Abstract

The topics of nature, for example semiochemicals are motivating topics, which can be used to teach organic chemistry at high school level. This paper presents the history, classifications and a few important applications of semiochemicals, and an example semiochemical that can be synthetized in the laboratory. Laboratory synthesis is carried out through the well-known Fischer esterification reaction which is easy to implement in a high school laboratory. The paper also demonstrates how computer-based molecular modeling, based on free software, can be used for supporting the characterization of the synthesized molecule. This article can be used as orientation and motivating material for inquiry- and context-based high-school organic chemistry.

Keywords: High School, environmental chemistry, history, organic chemistry, esters, laboratory instruction, molecular modeling

Title: Learning Organic Chemistry Through a Study of Semiochemicals

Corresponding author:
Johannes Pernaa
The Unit of Chemistry Teacher Education, Department of Chemistry, University of Helsinki
Department of Chemistry, P. O. Box 55,
FIN-00014 University of Helsinki,
e-mail: johannes.pernaa@helsinki.fi
telephone: +358 50 4151177
Homepage: http://blogs.helsinki.fi/pernaa/

Other authors:
Maija Aksela
The Unit of Chemistry Teacher Education, Department of Chemistry, University of Helsinki
Department of Chemistry, P. O. Box 55,
FIN-00014 University of Helsinki,
e-mail: maija.aksela@helsinki.fi
telephone: +358-50-5141450
Homepage:
http://kampela.it.helsinki.fi/apumatti/lcms.php?am=11968-11968-1&page=11969

Introduction

Semiochemicals are small organic compounds that transmit chemical messages. They are an essential communication channel in nature, and although the main objective of this paper is to study the chemistry of semiochemicals in the insect world, the readers must keep in mind that semiochemicals are generally also vital in plant and animal communication *(1, 2)*. Insects use semiochemicals for intra- and interspecies communication and detect them directly from the air with olfactory receptors. In most insects, the receptors are located in sensilla hairs on their antennae *(3)*.

The term semiochemical has been in use since 1971 and is derived from the Greek word "semeion", which means a mark or signal *(4)*. The history of semiochemical terminology has been comprehensively reviewed by Nordlund in 1981 *(5)*. The existence of semiochemicals was discovered as early as 1609 *(5)*, and they have been exploited for practical purposes since the 1890s. Although their chemistry was not completely understood at that time, scientists already knew how to use female insects to lure males into traps *(6)*. Semiochemical research in its present form has been conducted since the 1950s. The first pheromones were isolated and identified by Butenandt et al. in 1959 *(7)*. More than 3,500 semiochemicals connected with the chemical communication of insects have been identified from the 1950s *(8)*. Current research on semiochemicals involves continued molecular mapping, synthesis and studies of their biosynthesis. Another research area that has gained importance over the years has been an effort to understand the neurophysiological sensory functions of insects and how hormonal regulation in insects affects pheromone biosynthesis and release. The practical goal of insect semiochemical research is to develop means and methods for exterminating and controlling pests *(9)*.

The Classification of Semiochemicals

The chemical classification of semiochemicals should consider both their effects and structures (see Figure 1). In terms of effect, semiochemicals can be classified as pheromones or allelochemics. Allelochemics can be classified as allomones, kairomones, synomones and apneumones, based on use, benefiter and emitter *(5)*. In terms of structure, semiochemicals can be divided into twenty-four classes according to their functional groups *(8)*.

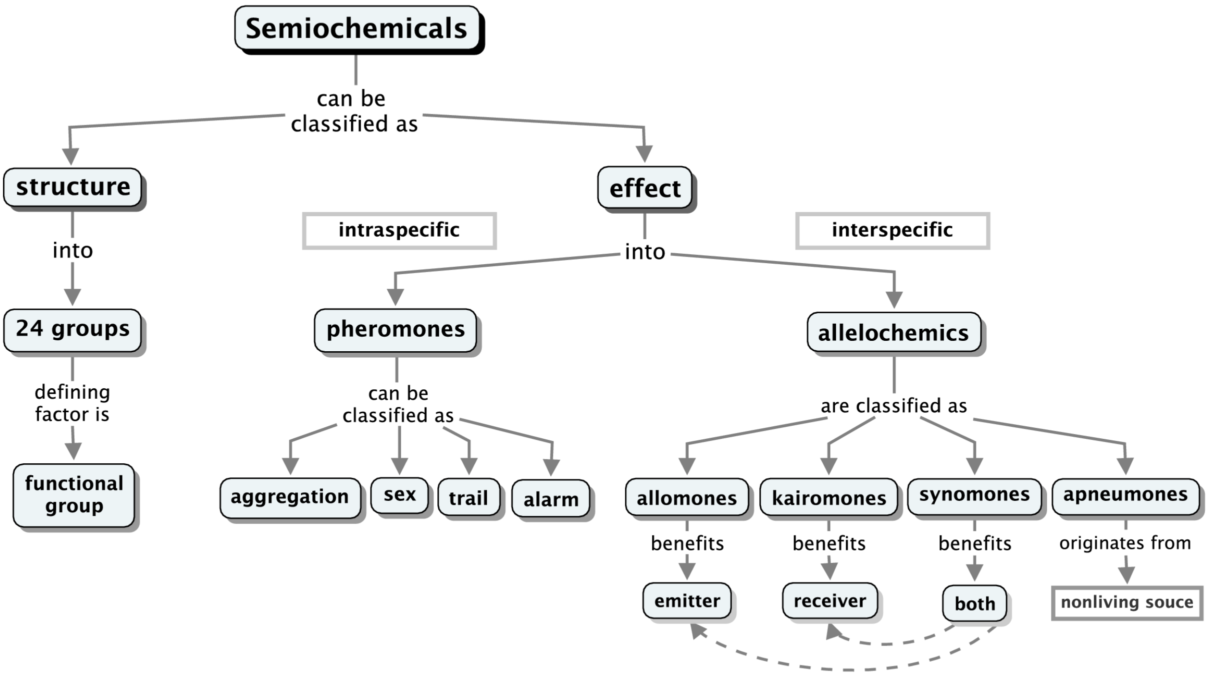


Figure 1. The classification of semiochemicals.

Semiochemical Classification Based on Effect

Based on effect, semiochemicals are divided into two main categories: pheromones and allelochemics. An examination of semiochemicals must take their functions into account, since the same molecule could act as a pheromone for one insect species and as a kairomone or allomone for another *(5, 8)*. In nature, a specific chemical message could be generated based, for example, on synergy effects, an exact molar ratio, a particular form of isomerism, or isomeric mixtures *(10, 11)*.

Pheromones

The term pheromone is derived from the Greek words "pherein" (to carry) and "horman" (to excite/stimulate). The concept was introduced in 1959 in two articles, one written by Karlson and Lüscher *(12)* and the other by Karlson and Butenandt *(13)*. Both papers were clarifying the differences between pheromones and hormones for the public and other scientists. Pheromones are compounds used by insects for intraspecific communication. The difference between pheromones and hormones is that hormones are produced in an insect's endocrine glands and have an effect on the producer, whereas pheromones affect other individuals *(13)*. Based on their effects, insect pheromones can be divided into at least the following main categories *(8)*:

- Aggregation pheromones: compounds that increase the incidence of insects at the pheromone source.
- Alarm pheromones: compounds that stimulate insects' escape or defense behavior.
- Sex pheromones: compounds that help individuals of the opposite sex to find each other.
- Trail pheromones: among social insects, compounds used by workers to mark the way to a food source, for example.

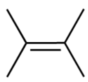
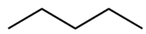
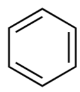
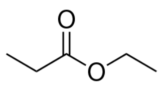
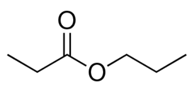
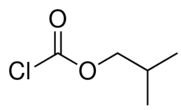
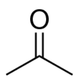
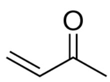
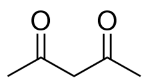
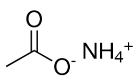
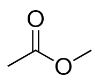
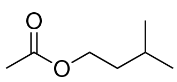
Allelochemics

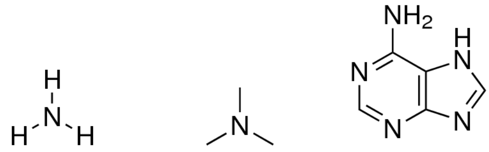
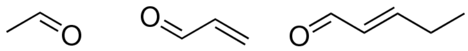
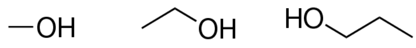
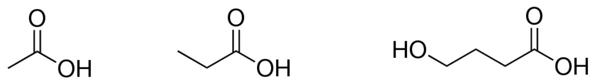
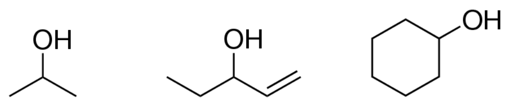
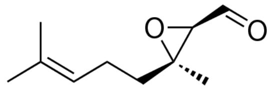
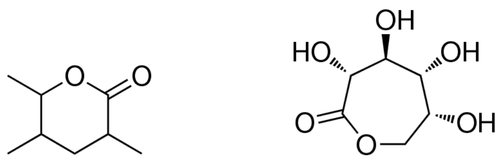
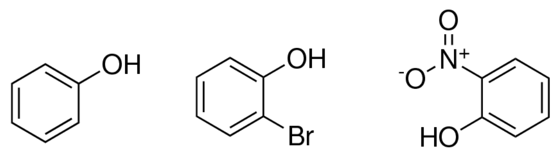
Compounds that deliver interspecific messages among insects have been called allelochemics since 1970. Allelochemics are classified as allomones, kairomones, synomones or apneumones *(5)*. Allomones are a class of compounds that benefit the producer, but not the receiver. Allomones are often found in nature as part of a chemical defense, such as toxic insect secretions or predators can also use them to lure prey. Kairomones (from Greek “kairos”, opportunistic) are a class of compounds that are advantageous for the receiver. Kairomones benefit many predators and bugs by guiding them to prey or potential host insects *(14)*. Synomones (from Greek “syn”, together) on the other hand are compounds that are beneficial to both the receiver and the sender, and apneumones (from Greek “a-pne”, breathless or lifeless) are compounds that originate from a nonliving source. The receiver benefits from apneumones, but they are different from kairomones because the nonliving emitter cannot experience any disadvantage *(15)*.

Semiochemical Classification Based on Structure

Semiochemicals are a diverse category in terms of their chemical structure. They are divided into twenty-four subcategories based on functional groups in the Pherobase, which is a free semiochemical database. The 12 largest semiochemical groups and a few well-known molecules from each structural class are shown in Table 1 *(8)*.

Table 1. Classification of semiochemicals according to chemical structure *(8)*

#	Structural class	Amount	Example molecules		
1	Hydrocarbons	680	 ethene	 pentane	 benzene
2	Carboxylic esters	450	 ethyl propionate	 propyl propionate	 isobutyl chloroformate
3	Ketones	410	 propan-2-one	 3-buten-2-one	 pentane-2,4-dione
4	Acetate esters	350	 ammonium acetate	 methyl ethanoate	 3-methylbutyl ethanoate

5	Amines	290	 ammonia; trimethylamine; adenine
6	Aldehydes	250	 ethanal; prop-2-enal; 2-pentenal
7	Primary alcohols	230	 methanol; ethanol; propan-1-ol
8	Carboxylic acids	210	 ethanoic acid; propanoic acid; gamma-hydroxybutyric acid
9	Secondary alcohols	160	 propan-2-ol; 1-penten-3-ol; cyclohexanol
10	Epoxides	100	 (2R,3R)-2,3-epoxy-3,7-dimethyl-6-octenal
11	Cyclic esters	80	 2,4-Dimethyl-5-hexanolide; gluconolactone
12	Phenols	50	 phenol; 2-bromophenol; 2-nitrophenol

[a] The amounts of the semiochemicals are rounded to the nearest 10.

As can be seen from Table 1, structural subcategories with the largest number of semiochemicals are hydrocarbons, esters, ketones, amines, aldehydes, alcohols and carboxylic acids. The structural categories of semiochemicals cannot be placed within particular categories of behavioral effects because they can be found in all of the effect categories *(8)*.

Semiochemical Applications

Semiochemicals are a fascinating area of research in which chemistry and biology expertise converge. One important application of semiochemicals is insect pest control for cultivated land and stored products. For example, environmental concentrations of semiochemicals can be increased to interfere with insect communication in an attempt to impede reproduction. Other example applications are semiochemical traps, which are used for regulating or monitoring insect population size *(16).*

Studying Semiochemicals in the Laboratory: The Synthesis of Honey Bee Alarm Pheromone

This paper uses the honey-bee as an example insect, because they have a significant role in the history of semiochemistry. According to Nordlund, in 1609 the first semiochemical observations were made by Charles Butler, the Father of English Beekeeping, Butler described how bees performed a massive group sting after being exposed to a substance that is released in a single bee sting *(5).* The substance that Nordlund refers to might be isopentyl acetate ($C_7H_{14}O_2$, isoamyl acetate, 3-methylbutyl ethanoate) (see Figure 2). Isopentyl acetate is an acetate ester pheromone and is one of dozens of honey-bee pheromones. It has been known since the 1960s that isopentyl acetate acts as an alarm pheromone for honey-bees. In addition to functioning as an alarm pheromone in honey-bees, naturally occurring isopentyl acetate also acts as a pheromone and kairomone in some flies and as a pheromone, kairomone and allomone in some beetles *(8)*.

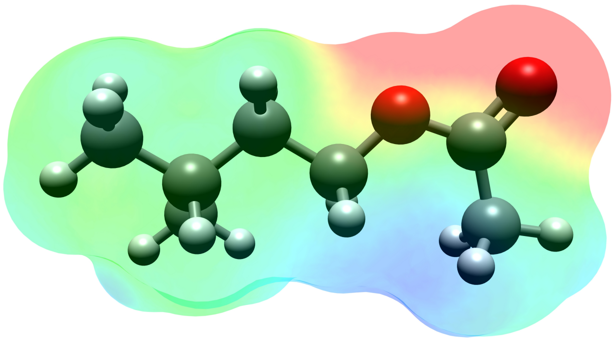


Figure 2. Molecular model of isopentyl acetate

Isopentyl acetate can be synthesized in many different ways. One well-known method is to synthesize it from isoamyl alcohol (3-methylbutan-1-ol) and acetic acid (ethanoic acid) using acid-catalyzed Fischer esterification, which is an important organic reaction (see Figure 3). The acid-catalyzed esterification has the advantage of being a simple process, but still producing pure esters with high, almost 80%, yield. This esterification is suitable for this synthesis because the reactants are common and inexpensive. The disadvantage of this reaction is the high temperature and strong acid catalyst that are required can make it impossible to carry out the synthesis with sensitive substrates *(17).*

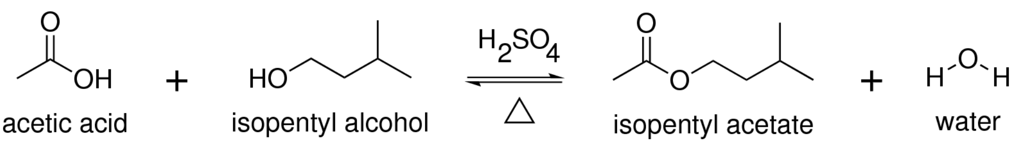


Figure 3. The Chemical reaction equation for isopentyl acetate synthesis

The acid-catalyzed esterification is also a widely used reaction in school chemistry. The synthesis can be implemented e.g. in four sections: reflux, isolation, purification and characterization of the product. Depending on the objectives of the laboratory activity, the synthesis can be carried out either on a normal scale or on a microscale. In the microscale synthesis, the reflux can also be done in a microwave oven. In the reflux section, concentrated sulfuric acid is used as the reaction catalyst, which requires special attention to laboratory safety. After the reflux, the isolation of the organic layer is carried out in a separating funnel using aqueous sodium bicarbonate. The purification of the product can be executed by simple distillation in a sand bath or in an oil bath. The boiling point of the isopentyl acetate is 142 °C, so a temperature 160-180° C is sufficient to separate the product from the final mixture. If the distillation is carried out in an oil bath, it is important to take into account the hazards associated with the use of a hot plate and hot-oil *(18-20)*.

If the characterization section is not included in the synthesis procedure, the distillation is not necessary. The hydrophobic ester has the lowest density in the reaction mixture and it will form the top layer, from which it can be carefully extracted using a pipette *(21)*.

For the characterization of the molecule, we encourage to study the IR-spectrum of the isopentyl acetate. In situations where running the IR-spectrum is not possible, there is a free web-based spectrum database where the spectral data for reactants and products are easily available *(22)*.

In addition, molecules can be studied using computer-based molecular modeling. For example, the Journal of Chemical Education (JCE) presents interactive molecules on its website and isopentyl acetate was one of the monthly molecules in April 2007 *(23)*. JCE molecules are visualized using Jmol software, which is free java-based molecular modeling software *(24)*. Jmol can easily be integrated into chemistry teaching and learning by downloading it freely from the Jmol homepage. It does not require installation. Jmol reads numerous different kinds of chemical file types which are freely available from chemical databases. For example in this synthesis, IR -spectrum database mentioned earlier offers molecular coordinate data files, which can be downloaded from the database and visualized in Jmol.

Discussion

This paper presented a summary of the chemistry of semiochemicals including the history, classifications, and a few applications. The main groups of semiochemicals, classified by structure, are hydrocarbons, esters, ketones, amines, aldehydes, alcohols and carboxylic acids. These are common functional groups found in the high school curriculum, and therefore semiochemicals offer an appropriate topic for supporting context-based organic chemistry learning at high school level *(25).*

This paper can be used as a orientation and motivating material for high school students in inquiry-based chemistry learning. For example, semiochemicals can serve as a main topic for an inquiry-based project where students get familiar with the chemistry of semiochemicals using literature and web sources and study pheromones in the laboratory through the synthesis of isopentyl acetate. The synthesis proposed in this paper is suitable for this purpose, because it includes several basic laboratory techniques, e.g. reflux, extraction and distillation, it does not require expensive or rare chemicals and is safe to carry out, especially on a microscale *(18)*. The characterization of the molecule might cause challenges for some high schools, because IR-spectrophotometers are rare in high schools laboratories. In such case, we recommend contacting nearby colleges, universities or chemical industrial facilities.

Isopentyl acetate was chosen for an example molecule because of its well-known connection to bees, and bees were selected for example insects, because they have an interesting role in the history of semiochemicals and they are familiar to all high school students. Bees are also important pollinators and their role in the global food economy is vital. They have also been a widely published topic in the press and science for the past few years, because of large-scale colony collapse disorder *(26)*.

References

1. Agosta, W. C. *J. Chem. Educ.* **1994**, *71,* 242-246.
2. Burger, B. V. Mammalian semiochemicals. In *The Chemistry of Pheromones and Other Semiochemicals II: Topics in Current Chemistry 240;* Schulz, S., Ed.; Springer: Berlin, 2005; pp 231-278.
3. Leal, W. S. Pheromone Reception. In *The Chemistry of Pheromones and Other Semiochemicals II: Topics in Current Chemistry 240;* Schulz, S., Ed.; Springer: Berlin, 2005; pp 1-36.
4. Law, J. H.; Regnier, F. E. *Annu. Rev. Biochem*. **1971**, *40,* 533-548.
5. Nordlund, D. A. Semiochemicals: a Rewiew of the terminology. In *Semiochemicals: Their Role in Pest Control*; Nordlund, D. A., Jones, R. L., Lewis, W. J., Eds.; John Wiley & Sons: New York, 1981; pp 13-30.
6. Schneider, D. *Naturwissenschaften.* **1992,** *79,* 241-250.
7. Butenandt, A.; Beckmann, R.; Stamm, D.; Hecker, E. *Z. Naturforsch*. **1959**, *14b,* 283-284.

8. El-Sayed, A. M. The Pherobase: Database of Insect Pheromones and Semiochemicals. http://www.pherobase.com (accessed Oct, 2010).

9. Nation, J. L. *J. Chem. Ecol*. **1998**, *24,* 599-600.

10. Slessor, K. N.; Winston, M. L.; Le Conte, Y. *J. Chem. Ecol.* **2005**, *31,* 2731-2745.

11. Mori, K. *Bioorg. Med. Chem.* **2007**, *15,* 7505-7523.

12. Karlson, P.; Lüscher, *M. Nature.* **1959**, *183,* 55-56.

13. Karlson, P.; Butenandt, A. *Ann. Rev. Entomol.* **1959**, *4,* 39-58.

14. Brown, W. L, Jr.; Eisner, T.; Whittaker, R. H. *BioScience.* **1970**, *20,* 21-22.

15. Nordlund, D. A.; Lewis, W. J. *J. Chem. Ecol.* **1976**, *2,* 211-220.

16. Cox, P. D. *J. Stored Prod. Res.* **2004**, *40,* 1-25.

17. Trost, B. M.; Fleming, I. *Comprehensive Organic Synthesis – Selectivity, Strategy & Efficiency in Modern Organic Chemistry,* Vol 6 Heteroatom Manipulation; Pergamon press: Oxford, 1991, pp 325-327.

18. Mayo, D. W.; Pike, R. M.; Forbes, D. C. *Microscale Organic Laboratory: With Multistep and Multiscale Syntheses,* 5th ed.; John Wiley & Sons, Inc.: New York, 2010; pp 205-206.

19. Ault, A. *J. Chem. Educ.* **2010,** *87,* 937–941.

20. Bromfield-Lee, D. C.; Oliver-Hoyo, M. T. *J. Chem. Educ.* **2009,** *86,* 82-84.

21. Cooper, M. M. *J. Chem. Edu.* **1989,** *66,* 663-764.

22. NIST Chemistry WebBook. http://webbook.nist.gov/ (accessed Oct, 2010).

23. Journal of Chemical Education: Molecular Models Candy Compounds . *http://www.jce.divched.org/JCEWWW/Features/MonthlyMolecules/2007/Apr/index.html* (accessed Oct, 2010).

24. Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/.

25. Gilbert, J. K. *Int. J. Sci. Educ.* **2006**, *28,* 957-976.

26. Ratnieks, F. L. W.; Carreck, N. L. Sci. **2010,** *327,* 152-153.