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Topics for Teaching: Chemistry in Nature

The Growing Problem of the Spruce Bark Beetle

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Abstract: The European spruce bark beetles release aggregation pheromones to trigger attack on Norway spruce trees; attracting beetles through the use of pheromone traps proves less effective than conventional forest management.

Keywords: Bark beetles · Chemical education · Diastereoisomers · Forest management · Pheromones

Severe weather phenomena are linked to climate change. At the end of 1999, the storm ‘Lothar’ caused immense destruction across parts of northern Europe, including Switzerland. Apart from structural damage and loss of life, ‘Lothar’ devastated forests. A quarter of a century later, new trees have grown back (Fig. 1), but the period in which trees lay uprooted (so-called *windthrow* areas) was highly favourable for a dramatic increase in the population of European spruce bark beetles *Ips typographus* (Fig. 2a, German: der Buchdrucker; French: le Bostryche typographe). Beetles seek out damaged wood into which they burrow and mate. A female lays around 30 eggs in a maternal gallery, and after hatching, the beetle larvae feed on the inner tree bark (*phloem* tissue). In doing so, they create tunnels radiating from the maternal gallery (Fig. 2b). After a period of pupation, the adult beetles emerge by excavating a hole through the tree bark. Beetles of the genus *Ips* can produce up to five generations per year when climatic conditions are favourable.[1] Bark beetles *I. typographus* thrive when substantial windthrow areas caused by storms are available. Although weakened trees are the primary target of the beetles, population explosions linked to extreme climatic events result in attacks on healthy Norway spruce trees (*Picea abies*) with substantial economic consequences. Essential forest management relies on clearing windthrow areas to limit beetle infestations. After the storm ‘Lothar’, large amounts of Swiss public funds were invested in both windthrow clearance and felling of beetle-infested trees.[2]

One method of preventing bark beetle attack is to use pheromone traps which exploit the natural pheromones of *I. typographus*. The first beetles to locate a food source (so-called pioneer beetles) release aggregation pheromones that attract mass numbers of the same species. In *I. typographus*, aggregation pheromones comprise a mixture of (*S*)-*cis*-verbenol, 2-methyl-3-buten-2-ol, and ipsdienol (Scheme 1).[3] Verbenol is an interesting bicyclic compound that can exist in the form of four diastereoisomers related by the relative positions of the bridgehead methyl groups and the OH substituent (Scheme 2). The spatial arrangement of these groups on the same or opposite side of the 6-membered ring is described by the use of the *cis*- and *trans*-descriptors. The (*R*)- and (*S*)-labels, *e.g.* in (*R*)- and (*S*)-*cis*-verbenol, refer to pairs of enantiomers (Scheme 2). Nature is very specific, and *I. typographus* releases only the *cis*-diastereoisomers of verbenol with an apparent preference of the (*S*)-enantiomer. It is noteworthy that Kovalenko *et al.* point out that although various aspects of the biological activity of *cis*-verbenol have been described, “little attention was paid to the contribution of individual enantiomers”.[4]

Fig. 1. A reminder of the destruction in forests around Hochwald, Canton Solothurn, of the severe storm ‘Lothar’. Photo credit: Catherine Housecroft.

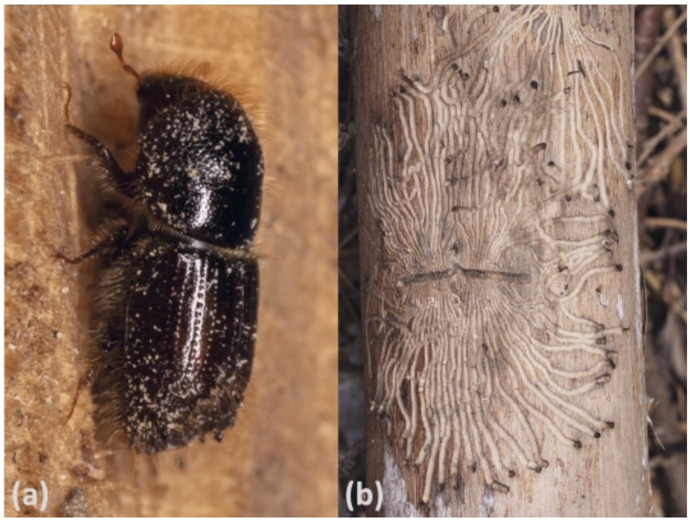

Fig. 2. (a) A bark beetle of the genus *Ips* (length around 4 mm), and (b) galleries made by bark beetles; the maternal gallery is central to tunnels produced by larvae. Photo credit: Edwin Constable.

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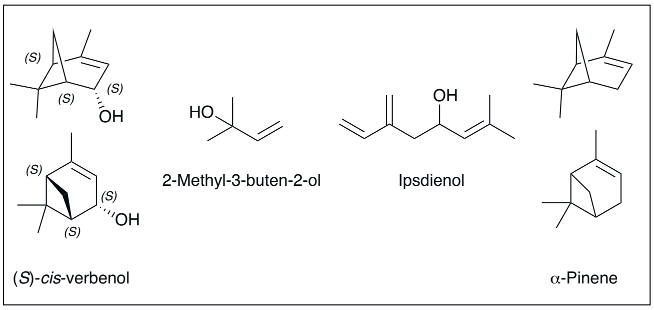
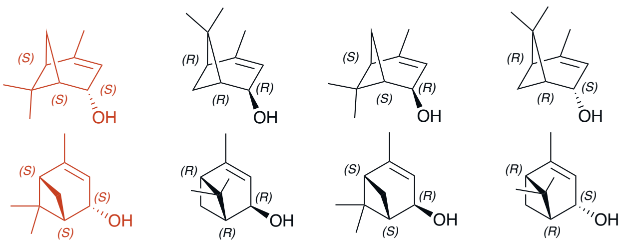


Scheme 1. Structures of (*S*)-*cis*-verbenol (IUPAC name (1*S*,2*S*)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-ol), 2-methyl-3-buten-2-ol, ipsdienol (IUPAC name 2-methyl-6-methylideneocta-2,7-dien-4-ol), and α-pinene (IUPAC name 2,6,6-trimethylbicyclo[3.1.1]hept-2-ene). Note that, despite the trivial name of ipsdienol, the structure has three double bonds; 'dienol' arises from the IUPAC name. The structures of (*S*)-*cis*-verbenol and α-pinene are each displayed in two representations.



(*S*)-*cis*-verbenol (*R*)-*cis*-verbenol (*S*)-*trans*-verbenol (*R*)-*trans*-verbenol

Scheme 2. The four diastereoisomers of verbenol: (*S*)-*cis*-verbenol (IUPAC: (1*S*,2*S*,5*S*)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-ol), (*R*)-*cis*-verbenol (IUPAC: (1*R*,2*R*,5*R*)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-ol); (*S*)-*trans*-verbenol (IUPAC: (1*S*,2*R*,5*S*)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-ol); (*R*)-*trans*-verbenol (IUPAC: (1*R*,2*S*,5*R*)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-ol). The diastereoisomer shown in red is the principal aggregation pheromone of *I. typographus.*

There has been considerable debate as to the origins of the pheromones (*S*)-*cis*-verbenol, 2-methyl-3-buten-2-ol, and ipsdienol in *Ips* beetles. Does the beetle produce them in a biosynthetic pathway, or from tree-based precursors? A review by Blomquist *et al*. provides a historical perspective.[5] Current views are that 2-methyl-3-buten-2-ol and ipsdienol are produced in the hindgut of the beetle. In contrast, (*S*)-*cis*-verbenol originates from α-pinene (Scheme 1) which occurs in spruce trees and is ingested by the beetles. α-Pinene is present in tree bark as a natural chemical defense, and is one of a range of defense chemicals comprising phenolic compounds, monoterpenes, and diterpene resin acids.[3] The interplay of the Norway spruce tree's chemical defenses and the production of aggregation pheromones by *I. typographus* is complex. For example, beetle damage to phloem tissue in the tree bark stimulates the buildup and release of monoterpenes from the bark. Pheromones attract natural predators of *I. typographus*, of which ant beetles (*Thanasimus formicarius*, Fig. 3) are some of the most important. Ipsdienol (Scheme 1) is a key pheromone which attracts *T. formicarius*.[5]

Commercial pheromone products for use in traps targetting *I. typographus* include Pheroprax® (produced by BASF) and Ipstyp® (produced by Alpha Scents Inc.) which contain (*S*)-*cis*-verbenol, 2-methyl-3-buten-2-ol, and (*S*)-ipsdienol, Typosan® (produced by Sintagro AG, and containing (*S*)-*cis*-verbenol and 2-methyl-3-buten-2-ol), Ipsowit® (produced by Witasek, and comprising (*S*)-ipsdienol and (*S*)-*cis*-verbenol), and IT Ecolure Extra® (produced by Fytofarm and containing (*S*)-*cis*-verbenol).[6] Despite the availability of such lures which mimic *I. typographus* aggregation

Fig. 3. Ant beetles (*Thanasimus formicarius*, length around 10 mm) are natural predators of *I. typographus*. Photo credit: Edwin Constable.

pheromones, their effectiveness in controlling bark beetles is not clearcut. In a recent study focusing on the use of Ipsowit®, Kuhn *et al.* concluded: "Overall, we found no evidence in favor of the efficacy of pheromone trapping during spring to reduce economic damages at the local scale when combined with sanitation felling and during a severe outbreak".[7]

Currently, in Switzerland and worldwide, the effects of severe storms, drought, hot weather and the consequent beetle infestations are leading to significantly increased quantities of damaged wood. In 2019 in Switzerland, the volume of spruce wood infested by *Ips* beetles doubled to 1.4 million m^3 in one year.[8] Pheromone traps only account for eradicating 3–10% of bark beetles. Forest management continues to rely primarily on mechanical clearance of windthrow areas and felling of infested trees. For maximum benefit, this must be carried out in a period between beetle infestation and the emergence of next generation of beetles. Beetle-infested trees are felled before emergence of adult beetles, and are stripped of their bark leading to the extermination of 93% of *Ips* species.[2]

In this article, we have described the increasing environmental problem of European spruce bark beetles which has major economic consequences on forestry. Natural aggregation pheromones which are also used in pheromone traps include verbenol, and its structure provides an opportunity to reinforce the topic of diastereoisomers.

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This column is one of a series designed to attract teachers to topics that link chemistry to Nature and stimulate students by seeing real-life applications of the subject.