Ground beetles produce lemon/orange-scented aromas as predator repellents

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(PhysOrg.com) -- In a paper to appear in the journal "Naturwissenschaften," Stevens Institute of Technology Professor Athula Attygalle and his research student, Xiaogang Wu, report for the first time that some ground beetles produce the natural repellent limonene as their major defensive chemical. The paper is the result of a collaborative research project with Professor Kipling Will (University of California, Berkeley), and Professor David R. Maddison (University of Arizona, Tucson).

An efficient commercial repellent for dogs, cats, some birds [e.g., Starlings], and even mammals such as deer, limonene is a plant product that belongs to group of chemicals called terpenes. In fact, limonene has been patented as an insect repellent (For example, US Patent 5565208 - Insect repellent aerosol, relates generally to an insect repellent. More particularly, the invention is directed to an insect repellent formulation containing, inter alia, d-limonene, which insect repellent is useful as a concentrate or aqueous mixture for application to humans and animals to repel insects).

The active ingredient in the commercial insect repellent "Orange Guard," is (+)-limonene. It is reported that this broad-based insecticide product will cause mortality in most insects within 15 minutes. The active ingredient d-limonene destroys the wax coating of the insect's respiratory system.

Many higher plants produce essential oils consisting mainly of terpenes

to protect themselves from herbivores.

“Terpenes are well known from some insects such as ants, hemipteran bugs, sawflies, and termites. However, terpenes have not been reported from ground beetles,” said Attygalle, a professor of Chemistry in the Department of Chemistry, Chemical Biology and Biomedical Engineering. “We found that the major constituent in the pygidial gland defensive fluid of the ground beetle Ardistomis schaumii is (R)-(+)-limonene, whereas that of closely related species Semiardistomis puncticollis is (S)-(−)-limonene. This was an unanticipated result, since it is not very common to find the opposite enantiomers (left- and right-handed forms) of the same compound among the secondary metabolites of related species.”

Moreover, said Attygalle, the glandular liquid of A. schaumii contains 1,8-cineole, and that of S. puncticollis has β-pinene, β-phellandrene, sabinene, and p-cymene. Of about 500 carabid species that have been chemically investigated, this is the first report of the presence of such complex mixtures of monoterpenes in their defensive secretions.

Limonene in ground beetles is accompanied by another obnoxious chemical, toluquinone. Many arthropods use benzoquinones as repellents. It is also known that benzoquinones are generally accompanied by hydrocarbons which have been speculated to serve as solvents for uptake of the quinines, which are crystalline at room temperature. Apparently nonpolar compounds facilitate the transport of active polar compounds through the waxed epicuticle of enemy arthropods. It is very likely that limonene acts as a permeation enhancer for benzoquinone. “For example,” said Attygalle, “it has been demonstrated that the transdermal delivery of acetylsalicylic acid, a potent antithrombotic drug, via skin patches can be significantly improved by admixing it with limonene. It appears that the beetles have come up with a winning formulation to enhance the efficacy of their

defensive concoction."

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