Nature’s Chemical Weapons: Beetle Defenses

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Abstract: The defense chemicals secreted by beetles are very diverse. They are exemplified by those of members of the families Carabidae (ground beetles) and Coccinellidae (ladybirds).

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Beetles are insects in the enormous order Coleoptera comprising over 400,000 species worldwide. The wings of beetles are covered by a hard case (elytra) and, compared to other insects, the need to open the elytra to trigger wing movement reduces the speed at which a beetle can take off in flight. This may be one of the reasons that beetles, in particular ground beetles (family Carabidae), have evolved a huge array of chemical defenses.\(^1\) Perhaps the most well known example is the explosive spray ejected by bombardier beetles;\(^2\) hot 1,4-benzoquinones (Scheme 1)\(^3\) are expelled from a pair of abdominal glands called the pygidial glands. The structure and mode of function of these glands vary with the type of beetle and they may discharge chemicals in the form of a spray, an explosive ejection or a slower release. In bombardier beetles, the benzoquinones are expelled explosively at temperatures of around 100 °C at velocities of ≈10 m s\(^{-1}\). Even more amazing is the fact that this ejection is not a single event but consists of pulsed explosions with a remarkably high frequency (up to \(\approx 800\) s\(^{-1}\)).\(^1\)\(^,\)\(^4\) Each of the two pygidial glands of a bombardier beetle consists of two chambers: a reservoir storing aqueous 1,4-hydroquinone (Scheme 1) and hydrogen peroxide, and a reaction chamber containing peroxidase and catalase. (A peroxidase is an enzyme that catalyses the one-electron oxidation of a substrate by hydrogen peroxide and a catalase catalyses the decomposition of hydrogen peroxide to \(O_2\) and \(H_2O\).) The two chambers are separated by a muscle-controlled valve. When the beetle is triggered to defend itself, the valve opens allowing reactants and enzymes to mix. This results in the formation of benzoquinones, \(O_2\) and \(H_2O\) which are ejected through a vent near the tip of the abdomen.\(^2\) The reactions are highly exothermic and this in conjunction with the build up of pressure caused by the formation of \(O_2\) leads to the explosive ejection of defensive spray. The reaction chamber in a bombardier beetle is sclerotized (i.e. composed of the hard biomaterial sclerotin which is formed by cross-linking of proteins) so as to withstand the extreme reaction conditions.

The chemical defense mechanism of bombardier beetles is a special case. Typically the defense chemicals of Carabidae beetles are saturated and unsaturated carboxylic acids, often formic, acetic, methacrylic or tiglic acids (Scheme 2). The family of Carabidae includes large sub-Saharan African ground beetles such as the two-spotted ground beetle Anthia thoracica (Fig. 1).

Although aliphatic organic acids are most usual, some Carabidae beetles produce salicylaldehyde (Scheme 3), and tiger beetles (subfamily Cicindelinae) are unusual in producing benzaldehyde in their pygidial glands. Tiger beetles (Fig. 2) are recognized for their aggressive predatory behaviour and for their impressive speed of running. Their mean velocity is 30.5±6.9 cm s\(^{-1}\) which translates to 22.9 body lengths per second; running...
speeds of up to 35.5±4.9 cm s⁻¹ can be achieved.⁶ The formation of benzaldehyde in the pygidial glands is accompanied by hydrogen cyanide in some millipedes. This pathway is likely to be in Scheme 4. Proposed pathway for the formation of benzaldehyde and hydrogen cyanide in some millipedes. This pathway is likely to be involved in the formation of benzaldehyde and HCN in tiger beetles.

We now turn our attention to the instantly recognizable family of Coccinellidae beetles, commonly known as ladybirds (Marienkäfer in German, coccinelle in French, coccinella in Italian). One of the most distinctive is the harlequin ladybird (Fig. 3), a large Coccinellidae beetle which has been introduced into Europe from Asia to control aphids and scale insects. When alarmed, ladybirds ‘reflex-bleed’ which involves loss of orange-coloured haemolymph (the circulating fluid in insects). Alkaloids (naturally occurring, nitrogen-containing organic bases) in this orange fluid give rise to its strong smell and bitter taste. In particular, azaphenalenes which are tricyclic amines are responsible for the unpleasant taste.⁹,¹⁰ Coccinellidae beetles seem to be a unique example of the natural occurrence of azaphenalene alkaloids.¹⁰ The nine azaphenalene alkaloids found in ladybirds differ in their stereochemistries and the presence of a C=C bond or N-oxide. Four examples are shown in Scheme 5.

In summary, this column has introduced examples of the defense chemicals of some Carabidae (ground beetles) and Coccinellidae (ladybirds). These are but a few of the chemicals produced by beetles to defend themselves against predators.

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**Scheme 3.** The structure of salicylaldehyde, and the structure of benzaldehyde which is produced from (R)-mandelonitrile in the pygidial glands of tiger beetles.

**Scheme 4.** Proposed pathway for the formation of benzaldehyde and hydrogen cyanide in some millipedes. This pathway is likely to be involved in the formation of benzaldehyde and HCN in tiger beetles.

**Scheme 5.** Four of the nine azaphenalene alkaloids found in Coccinellidae beetles.

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