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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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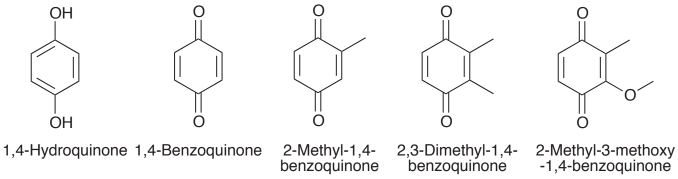
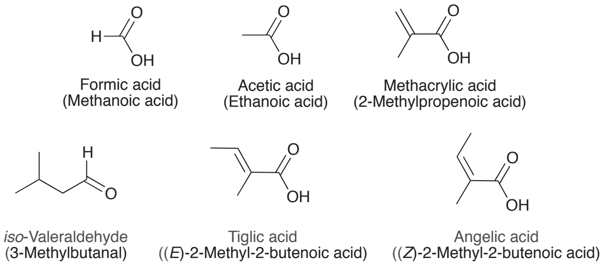
Beetles are insects in the enormous order *Coleoptera* comprising over 400,000 species worldwide. The wings of beetles are covered by a hard case (*elytra*) and, compared to other insects, the need to open the elytra to trigger wing movement reduces the speed at which a beetle can take off in flight. 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 *ca.* 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.



Scheme 1. The structure of 1,4-hydroquinone and the 1,4-benzoquinones in the defensive sprays of bombardier beetles.

The chemical defense mechanism of bombadier 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). *Anthinae* beetles tend to have bold markings which act as a warning to predators – the beetles are capable of spraying highly concentrated acids over distances of a metre or more. Formic acid accounts for 98% of the defensive spray from *A. thoracica* with minor amounts of *iso*-valeraldehyde, acetic acid and the (*E*)- and (*Z*)-isomers of 2-methyl-2-butenoic acid (Scheme 2).[5]



Scheme 2. The structures of typical components of the defensive sprays of *Carabidae* beetles.

Fig. 1. The two-spotted ground beetle (*Anthia thoracica*) with prey. ©Edwin C. Constable 2019.

Although aliphatic organic acids are most usual, some *Carabidae* beetles produce salicylaldehyde (Scheme 3), and tiger beetles (subfamily *Cicindelinae*) are unusual in producing benzaldehye 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

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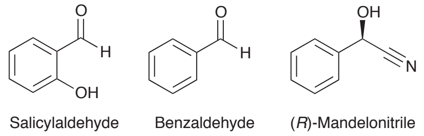
speeds of up to 35.5±4.9 cm s^{-1} can be achieved.[6] The formation of benzaldehyde in the pygidial glands is accompanied by hydrogen cyanide, and mandelonitrile (Scheme 3) is also present.[1,7] This points to the mechanism being *cyanogenic* in origin. Although not well documented for tiger beetles, the enzyme-catalysed conversion of (*R*)-mandelonitrile to benzaldehyde and HCN in *Polydesmida* millipedes has been well-studied[8] and it seems likely that a similar mechanism operates in tiger beetles. A proposed synthetic pathway for the production of defensive chemicals in some millipedes starting from the naturally occurring amino acid L-phenylalanine is shown in Scheme 4.[8]



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

Fig. 2. Tiger beetle *Myriochila melancholica.*
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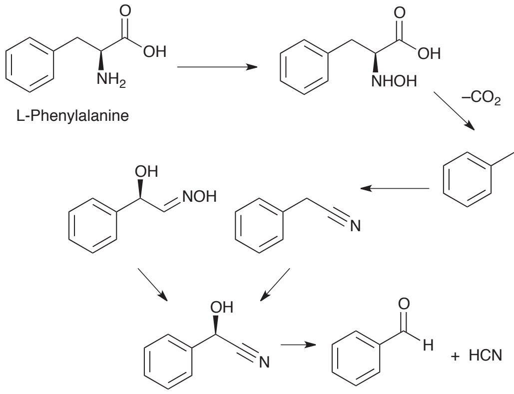

Scheme 4. Proposed pathway for the formation of benzaldehyde and hydrogen cyanide in some millipedes. This pathway is likely to be involved in the formation of benzaldehye and HCN in tiger beetles.

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 addition to azaphenalene alkaloids, a wide variety of other alkaloids are found in *Coccinellidae* beetles, and have been surveyed by King and Meinwald[10] and Daloze *et al*.[11] In the first 'Chemistry in Nature'' column,[12] we introduced aposematism – the association of colour with a defense strategy. The red coloration of many ladybirds is another example of aposematism, and is associated with the presence of 2-methoxy-3-alkylpyrazines (also alkaloids) which give rise to the strong smell detected when these insects undergo reflex-bleeding.

Fig. 3. Pair of mating harlequin ladybirds (*Harmonia axyridis*).
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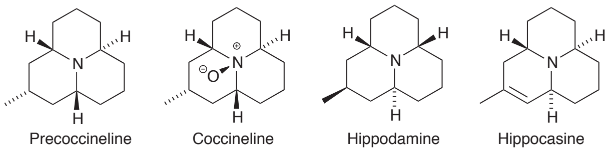

Scheme 5. Four of the nine *azaphenalene* alkaloids found in *Coccinellidae* beetles.

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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