Chemistry? Set...

Clouds of noxious gas, stink bombs and purple smokescreens may sound like schoolboy pranks, but the animal world is just as capable of executing arresting chemical warfare, says **Deborah Nicholls-Lee**

JUST as David defeated Goliath, so it is that some of our smallest creatures are all too often underestimated. The bombardier beetle, for example, although less than half an inch long, is a master of chemical warfare. Its tiny abdomen conceals two chambers, each containing a different chemical. When the beetle is threatened, the substances combine to create an almighty reaction. With an audible pop, a scalding cloud of noxious gas explodes from its rear end, causing the predator—a toad, perhaps, or a shrew—to retreat. Even Charles Darwin fell foul. With his hands full of other specimens he was collecting, he seized the innocent-looking creature between his teeth: 'To my unspeakable disgust and pain, the little inconsiderate beast squirted his acid down my throat,' he wrote in a letter of 1846.

Our native wildlife is typically seen as rather benign, yet the bombardier beetle is only one in an army of animals weaponising chemistry in the fight for survival. The ant is a case in point. In the mid 1600s, the esteemed natural historian Revd John Ray was intrigued by the vapour and vinegary odour that emanated from ant hills and resolved to investigate. Chicory, Nature's litmus paper, had already suggested strange goings on. 'Cast the flowers of Cycory among a heape of Ants or pismires, and they wil soone become as red as blood,' reported William Langham in 1597's *The Garden of Health*. Putting science before sanctity, our parson-naturalist crushed up some ants and, on distilling the pulp, discovered a chemical that, in honour of his victims, was named formic acid (from the Latin *Formica*, for ants).

Unsurprisingly, given its acid arsenal, close contact with a defensive ant can cause the skin to smart, but most European and North American varieties have no functional sting. Instead, as noted by the entomologist Neal A. Weber in his 1937 article *The Sting of an Ant*, 'many of these ants, when biting the skin, curve their abdomen forward to eject acid into the cut and thus give to the layman the impression of stinging'.

Corvids, sparrows and robins are among the birds that have learnt to harness the ant's chemical defences to indulge in a natural spa treatment known as 'anting'. This involves disturbing an ant settlement so that its tenants crawl energetically over the intruder, anointing the birds' feathers with their chemical juices, which deter parasites and fungi. As the poet Ogden Nash remarked:

> The ant has made herself illustrious
> By constant industry industrious…
> Would you be calm and placid
> If you were full of formic acid?

Despite its name, formic acid is not limited to ants. If predators ignore the war dance of the puss moth caterpillar, for example, as it waves its whip-like tail, it will squirt it from a gland beneath its ghastly, red-painted mouth.

For some moths, formic acid is all too ordinaire. The red markings of the six-spot burnet moth send out a warning that it's →

Left: **The tiny bombardier beetle takes no prisoners with its noxious-gas protection—even Darwin fell victim when he held the insect in his teeth.** *Below:* **Packed lunch: a black darter dragonfly, immobilised in a spider's web, is destined to be dinner**

packing some serious poison. If attacked, it will release hydrogen cyanide, making it a bitter and potentially lethal mouthful. For creatures of its own species, however, an abundance of this chemical, associated with high fertility, affords bragging rights. During mating, it becomes a nuptial gift as the male transfers some of his own cyanide stores to the female.

The distinctive whiff of bitter almonds, associated with the presence of hydrogen cyanide, can also be smelled on millipedes. During a staged battle between a millipede and a toad, the chemical ecologist Dr Thomas Eisner observed 'what amounted to a most grotesque gesture', as the toad spat out the millipede and 'in obvious discomfort was left "pawing" his tongue with his front feet'. In fact, so powerful is the poison of our native flat-backed millipede that an encounter with it can cause organ failure in small mammals and birds. No wonder millipedes were once placed in the 'killing jars' of entomologists, their natural cyanide extinguishing all life but their own.

Spot of bother: six-spot burnet moths can ward off attackers using hydrogen cyanide

Call to arms: as honey bees sting an intruder, an alarm pheremone is also released

Chemical romance

'All around us, animals are living in a hidden world of smells and information,' explains Tristram Wyatt, senior research fellow in biology at Oxford University and author of the 2014 book *Pheromones and Animal Behaviour*. Creatures, from moths to mice, he says, use pheromones to attract a mate, releasing a chemical blend that only their own species can detect—but it's not all lovey-dovey.

'Pheromones can also signal an alarm,' says Dr Wyatt, giving the example of honey bees. 'When the nest is attacked by a predator seeking honey and bee grubs, the worker bees sting the intruder. The embedded sting continues to release poison and an alarm pheromone, which calls in other workers to sting the predator.'

Chemicals released by threatened ants can also help coordinate an attack. 'Other wood ants in the colony are alerted by the formic acid… and join the defenders,' he explains. 'In this way, they can deter predators such as badgers in search of succulent ant pupae deep in the nest.'

Under the sea, the chemical warfare continues. 'We underestimate exactly how important using chemicals is to marine life,' says Elizabeth Mills, a marine biologist and award-winning science communicator who shares her enthusiasm via her YouTube channel, Marine Mumbles. So many sea creatures are 'soft and squidgy', she remarks, that it makes sense that 'some of these species turn to using chemicals as a defence mechanism… or utilise chemicals to attack'. One of Dr Mills's most memorable chemical encounters was with a sea hare (a marine snail with long, ear-like tentacles) that, as an undergraduate, alerted her study group to its presence by coating her lecturer's hand in 'bright purple ink'. The ink, which contains hydrogen peroxide, creates

Bug spray: a jay disturbs a red wood ant hill aiming to encourage its occupants to emit formic acid—a defence against avian parasites

a smoke screen that overwhelms its enemy's sensory systems so the sea hare can slip away.

A group of sea slugs, known as aeolids, are more, well, sluggish. 'Aeolids don't actually go through the energy-intensive experience of creating their own chemicals and instead steal stinging cells (nematocysts) from anemones or hydroids, which are in their food,' explains Dr Mills. They then 'store the stolen cells in balloon-like structures on their back,' she says, 'ready to be released in defence'.

Back on dry land, our native spiders are poised for their own chemical attacks. By either injecting or spitting venom, they immobilise their prey; swaddling them in silk to enjoy later or eating them on the spot by regurgitating digestive fluids over their victims to create a liquid meal.

> 'Millipedes were placed in the "killing jars" of entomologists, their natural cyanide extinguishing all life but their own'

Perhaps our most intimidating chemical warrior is the common European viper (which also goes under the more familiar name of adder), Britain's only venomous snake, which discharges a powerful cocktail of proteins and peptides from its hollow, hinged fangs. A bite to a human, according to a 1976 issue of the *British Medical Journal* (now *BMJ*), may cause 'local swelling and discolouration, vomiting, diarrhoea, and early collapse', as well as 'recurrent shock'. The publication gives victims short shrift, however, noting that 'most bites occurred in men who foolishly picked up the adder'.

Other creatures deal with adversaries by detonating stink bombs made of pungent compounds called methoxypyrazines. In the case of the deceptively endearing ladybird, →

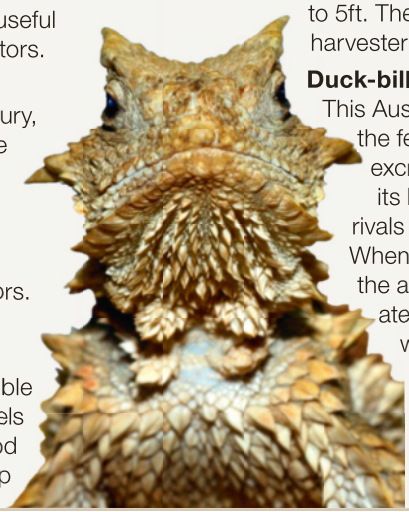
Weird science

Around the world, creatures of all shapes and sizes are teaching antagonists a chemistry lesson they'll never forget. Here are four of the most curious:

Hooded pitohui (*above left*)
A simple stroke of the black-and-orange plumage of the hooded pitohui bird of New Guinea unleashes a burning sensation and eating its flesh can cause cardiac arrest. No wonder locals call it the 'rubbish bird' and give it a wide berth. The batrachotoxins in its feathers are manufactured via its diet of choresine beetles and are useful in protecting it from parasites and predators.

Boxer crabs (*above right*)
Some animals don't have their own armoury, so they borrow a creature that does. The coral-dwelling, Indo-Pacific boxer crab is also known as a 'pom pom crab', as it defends itself by clutching a stinging anemone in each claw and doing a little cheerleading to fend off passing predators.

Horned lizard (*right*)
In the deserts and prairies of North and Central America lurks a lizard with a terrible temper. Provoked, it ruptures blood vessels around its eyes and squirts noxious blood at its aggressor, reaching distances of up to 5ft. The foul-tasting blood owes its toxicity to the venomous harvester ants consumed by the lizard, to which it is immune.



Duck-billed platypus (*below right*)
This Australian mammal defies its taxonomy. Not only does the female lay eggs, but the male produces venom, excreted from spurs on its hind legs, to see off rivals during the mating season. When rescuing a stranded platypus, the aptly named Keith Payne, a decorated war veteran, was rewarded with an excruciating sting that lasted weeks and proved resistant to standard analgesics. It was worse than being struck by shrapnel, he remarked.

the origin of the stench is yellow reflex blood, excreted from its leg joints. Some mammals, too, can make a real stink if attacked. The pole cat—the Latin name for which, *Mustela putorius* (smelly mustelid), says it all—is one of several mustelids that expel a foul-smelling, musky liquid from its anal scent glands to send assailants packing.

Beyond Britain, animals' plundering of the periodic table has been a feature of planet life since the dinosaurs. Sealed in prehistoric amber, and analysed by Oregon State University in 2007, is a Burmese soldier beetle, engulfed in sap just as it doused its foe with dihydromatricaria acid. Lead researcher Prof George Poina, commented: 'That this type of defence has been preserved through 100 million years of evolution is evidence that it works pretty well.'

Purple haze: a spotted sea hare's ink 'smoke screen' defence contains hydrogen peroxide

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