

Table 1 Product yields from different lithium compounds

Run	A	Solvent	B	Organo-F yield (%)
1	LiPF ₆	EC	—	0
2	LiPF ₆	EC	LiCoO ₂	80
3	Li[(CF ₃ SO ₂) ₂ N]	EC	LiCoO ₂	0
4	LiBF ₄	EC	LiCoO ₂	80
5	LiBF ₄	EC	LiMn ₂ O ₄	80
6	LiBF ₄	EC	LiNiO ₂	80
7	LiPF ₆	EC + DMC	LiCoO ₂	35

Yields of fluoro-organics are shown for ethylene carbonate reacting with lithium compounds A and B at 240 °C for 30–60 min in different solvents. EC, ethylene carbonate; DMC, dimethyl carbonate.

and their failure rate has dropped to about 0.3 per million. The consequences of runaway reactions have so far focused mainly on the risks of fire, burns and the release of hydrogen fluoride.

The compound 2-fluoroethanol is highly toxic (the 50%-lethal dose, LD₅₀, in mice is 0.1 mg kg⁻¹) and is readily formed by nucleophilic attack of fluoride ion on ethylene carbonate¹. Although no example of electrophilic fluorination using coordination anions such as LiPF₆ is known, we investigated whether a similar reaction could occur by this route.

Ethylene carbonate and LiPF₆ alone do not form fluoro-organics, but these are generated in abundance when any of the positive-electrode materials (Li_xMO₂, where M is Co, Ni or Mn) is also present. Gas chromatography with mass spectrometry (110 mass units) indicates that the fluoroethanol ether is formed under these conditions: two moles of ethylene carbonate react with one mole of LiPF₆ to yield one mole each of (FCH₂CH₂)₂O, LiF and volatile PO₂F₃ (boiling point, -39.7 °C), providing the driving force with the loss of two moles of CO₂.

Ethylene oxide (formed by the loss of CO₂ from ethylene carbonate and catalysed by the transition metal) is a likely transient intermediate. The compound bis-(2-fluoroethyl)-ether, which has an LD₁₀₀ in rats of 10 mg kg⁻¹ (estimated LD₅₀ of 4 mg kg⁻¹, ref. 2), represents 80% of the total fluoro-chemicals in runs 2 and 4–6, which are summarized in Table 1. The carbon anion with covalently bonded fluorine (CF₃⁻) is inert.

Our experiments are *ex situ* and relate only to the reaction of electrolyte with the material of the positive electrode. However, the conditions triggering the ring-opening fluorination of ethylene carbonate could easily occur in large batteries (weighing more than 500 g), such as those proposed for use in electric vehicles, where a short-circuit might cause the temperature in the electrolyte to rise instantly above 250 °C. Although these batteries are in principle highly desirable for saving energy and preventing pollution and for CO₂ abatement, their safety should be rigorously investigated under protected conditions. Further exploration of the chemicals evolved in runaway reactions should be undertaken with

extreme caution and only where *ad hoc* facilities are available.

Amer Hammami, Nathalie Raymond, Michel Armand

Laboratoire International sur Les Matériaux Electro-actifs CNRS-UdM, UMR 2289, Université de Montréal, PO Box 6122, Montréal, Québec H3C3J7, Canada
e-mail: michel.armand@umontreal.ca

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Palaeontology

Spider-web silk from the Early Cretaceous

The use of viscid silk in aerial webs as a means to capture prey was a key innovation of araneoid spiders and has contributed largely to their ecological success¹. Here I describe a single silk thread from a spider's web that bears glue droplets and has been preserved in Lebanese amber from the Early Cretaceous period for about 130 million years. This specimen not only demonstrates the antiquity of viscid silk and of the spider superfamily Araneoidea, but is also some 90 million years older than the oldest viscid spider thread previously reported in Baltic amber from the Eocene epoch².

The silk glands that produce the gluey coating on viscid silk may be the best single character to define the Araneoidea, the superfamily that includes all ecribellate orb-weavers and the comb-footed spiders

(Theridiidae)³. A fossil spider from the Early–Middle Jurassic (which is about 190 Myr old) has been described — on the basis of characters other than its silk-producing glands — as belonging to the Araneoidea⁴, and araneoid spiders have been recorded from the Early Cretaceous^{5,6}.

Spiders are known to have been able to produce silk since the Mid-Devonian period, about 410 Myr ago⁷. It is unclear, however, how today's intricate araneoid webs with viscid silk evolved from the probably primitive silk that was used by Devonian spiders. Current ideas about the evolution of aerial webs and of viscid silk are based on the phylogeny of the spiders, which in turn is based on morphological characters — mostly genitalic ones — whose evolution is generally not directly linked to the spider's ability to build webs or to produce viscid silk.

The present specimen (C19/2, held at the Staatliches Museum für Naturkunde in Stuttgart, Germany) was collected by Dieter Schlee in 1969 from amber beds located near Jezzine in Lebanon. These deposits are dated to the Hauterivian (about 127–132 Myr) and represent the oldest known amber with insect inclusions⁸.

The specimen contains a single thread of about 4 mm in length, which shows a striking resemblance to recent araneoid spider threads, with 38 distinct fossilized glue droplets arranged at regular intervals along two sections (Fig. 1a). The thread diameter (3 μm) and the size (7–29 μm), density (22 droplets per mm), arrangement (small droplets alternating with larger ones) and shape (semi-transparent globules, slightly elongated along the thread) of most glue droplets (Fig. 1b) closely match those in recent araneoid webs⁹. Some droplets have a larger diameter of up to 85 μm (Fig. 1c), probably as a result of water uptake from the resin (araneoid glue droplets are highly hygroscopic¹⁰) and subsequent merging with neighbouring droplets.

As the specimen contains only a single thread, we cannot identify with certainty the type of web of which this thread was a part. It may have been part of an orb-web or of a gum-footed web, as built by some

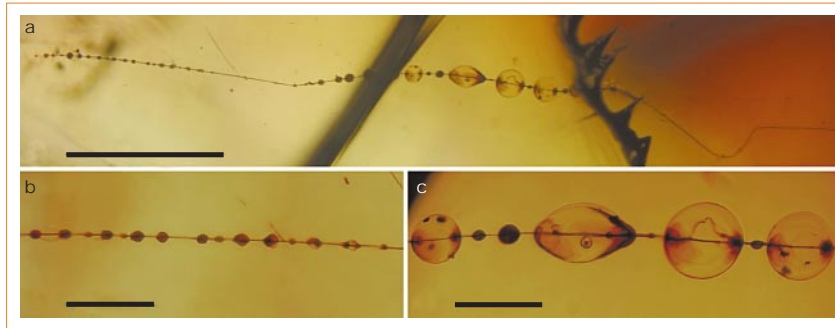


Figure 1 Fossil araneoid spider thread with glue droplets in Lebanese amber. **a**, Overall view: the thread runs at an angle of 50° to the upper surface of the amber; the left-hand end of the thread reaches the lower surface of the amber. **b**, A region of the thread showing regularly arranged glue droplets. **c**, Distended glue droplets with clearly visible core threads. Scale bars: **a**, 500 μm; **b**, **c**, 100 μm.

recent theriid spiders. In these webs, only the gumfeet, the peripheral parts of the threads extending from a central structure to the substrate, are equipped with glue droplets¹¹.

It is likely that the present specimen was such a gumfoot, because viscid threads in other araneoid webs are always surrounded by non-sticky threads, and because gumfeet are the only type of viscid thread that is built near the bark of a tree, where the probability of becoming engulfed in resin is largest. In addition, the thread is only partly covered with glue droplets, another feature that it shares only with gumfeet.

However, the fossil thread could have been part of a web type that no longer exists today. In any case, the present specimen is direct evidence for the antiquity of viscid spider silk and provides independent evidence for the antiquity of the Araneoidea.

Samuel Zschokke

Department of Integrative Biology, Section of Conservation Biology, University of Basel, 4056 Basel, Switzerland
e-mail: samuel.zschokke@alumni.ethz.ch

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Insect signalling

Components of giant hornet alarm pheromone

Up to 74 people die each year in Japan after being stung by Hymenopteran insects, with hornets (*Vespa* spp.) being among the worst offenders¹. Here we identify a volatile, multi-component alarm pheromone in the venom of the world's largest hornet, *V. mandarinia*, and use field bioassays to show that 2-pentanol is its principal active component, and that 3-methyl-1-butanol and 1-methylbutyl 3-methylbutanoate act synergistically with it. The compound 1-methylbutyl 3-methylbutanoate, which may also be a foraging-site-marking pheromone, elicits a strong defensive reaction in the sympatric prey hornet *V. simillima xanthoptera*. As these chemicals are sometimes used in food flavourings and as fragrances in cosmetics^{2,3}, it is possible that they might provoke a seemingly unwarranted hornet attack on humans.

We investigated whether the strongly defensive behaviour of *V. mandarinia* could be due to the presence of a powerful alarm pheromone in the venom by capturing the volatile components from the venom sacs of three frozen worker hornets by solid-phase micro-extraction (SPME) and analysing them by gas chromatograph mass spectrometry. These volatile components were absorbed onto SPME fibre (with a 100- μ m coating of polydimethylsiloxane), which was then inserted into the injection port of the spectrometer at 250 °C.

Three biologically active chemicals — 2-pentanol, 3-methyl-1-butanol and 1-methylbutyl 3-methylbutanoate — were identified from the venom. Analysis against synthetic enantiomers and using a chiral column revealed that the (*S*) enantiomer was predominant, with eight times less (*R*) enantiomer for 2-pentanol and 1-methylbutyl 3-methylbutanoate.

In field bioassays, the crude venom extract caused intense alarm and defensive behaviour, with worker hornets flying excitedly around the nest and rushing towards the target. Authentic (*R*), (*S*) and racemic 2-pentanol elicited the same response. A synergistic effect was observed with the addition of 1-methylbutyl 3-methylbutanoate and 3-methyl-1-butanol (Figs 1, 2). Several commercial products containing these chemicals also elicited this defensive reaction. The use of these extremely volatile chemicals as alarm signals may allow a hornet colony to resume normal behaviour rapidly — that is, very soon after an intruder has been driven away and pheromone release ceases.

We also identified 1-methylbutyl 3-methylbutanoate as a major component of the extract from the van der Vecht gland of *V. mandarinia*. This ester elicits a strong defensive reaction in the smaller sympatric prey, *V. simillima xanthoptera*; the behaviour



Figure 1 Bioassay to evaluate alarm-pheromone activity of samples. Guard hornets rush towards filter paper impregnated with a single-worker equivalent of 2-pentanol, 3-methyl-1-butanol and 1-methylbutyl 3-methylbutanoate. The insects did not respond to filter paper impregnated only with diethyl ether.

is identical to the defensive reaction by *V. simillima* when it detects the foraging-site-marking pheromone⁴ secreted by *V. mandarinia* scouts. This 'kairomone' detection is an example of adaptation to predation by sympatric species.

The synergistic interaction and the kairomonal function described here indicate that hornets probably use semiochemicals in a complex form. Single-component alarm pheromones are found in the venom of other insects (for example, 2-methyl-3-buten-2-ol in *Vespa crabro*⁵, *N*-(3-methylbutyl)acetamide in *Vespula squamosa*⁶ and (2*S*,6*R*,8*S*)-2,8-dimethyl-1,7-dioxaspiro [5.5] undecane in *Polybia occidentalis*⁷).

A preliminary analysis of the volatile components in venom from all seven Japanese hornet species confirms that they contain alcohols and esters that are also common in manufactured food and cosmetic products (our unpublished results). It may therefore be sensible to screen these commercial products for the presence of

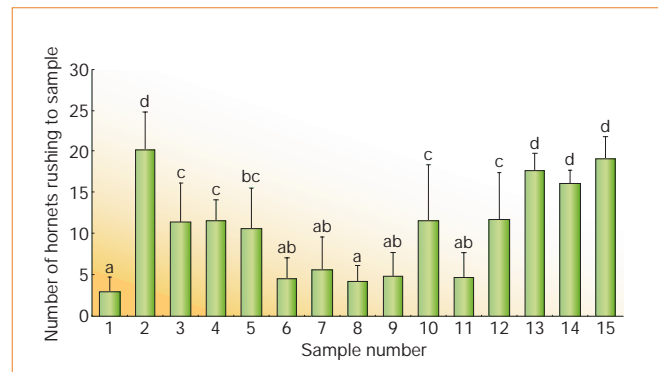


Figure 2 Response by guard hornets (*Vespa mandarinia*) to impregnated filter paper placed at the entrance to a feral giant-hornet colony containing about 200 workers. Samples 1 and 2 were 100 μ l each of diethyl ether and venom extract, respectively; samples 3–15, which were each diluted in diethyl ether (10 nl per 100 μ l) were as follows: 3, (*S*)-2-pentanol; 4, (*R*)-2-pentanol; 5, (\pm)-2-pentanol; 6, 3-methyl-1-butanol; 7, (*S*)-1-methylbutyl 3-methylbutanoate; 8, (*R*)-1-methylbutyl 3-methylbutanoate; 9, (\pm)-1-methylbutyl 3-methylbutanoate; 10, (\pm)-2-pentanol and (\pm)-1-methylbutyl 3-methylbutanoate; 11, (\pm)-1-methylbutyl 3-methylbutanoate and 3-methyl-1-butanol; 12, (\pm)-2-pentanol and 3-methyl-1-butanol; 13, (*S*)-2-pentanol, 3-methyl-1-butanol and (*S*)-1-methylbutyl 3-methylbutanoate; 14, (*R*)-2-pentanol, 3-methyl-1-butanol and (*R*)-1-methylbutyl 3-methylbutanoate; 15, (\pm)-2-pentanol, 3-methyl-1-butanol and (\pm)-1-methylbutyl 3-methylbutanoate. Venom extract and 2-pentanol each elicited a defensive reaction, which increased when the filter paper was impregnated with all three volatile components. Data are mean responses \pm s.d. (five replicates); letters indicate a significant difference ($P < 0.01$) by Tukey's test.