After Louvain: Thinking about Chemical Ecology

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Jeremiah¹ may or may not have been a distinguished chemical ecologist but he understood one of the essential links between the animal and plant world,

... And the wild asses did stand in the high places, they snuffed up the wind like dragons; their eyes did fail, because there was no grass.

George Wald² understood too, and won a Nobel prize. He pointed out that “throughout their entire range these excitations appear to be derived chemically from a single closely knit family of compounds, the carotenoids. This relationship persists from phototropism in moulds to vision in man.”

Tom Eisner³ in his preface to “Chemical Ecology”, stresses the fact we live in a world of sight and sound, and tend to be oblivious of the chemical events in our surroundings and in ourselves. Certainly we rarely reflect that without the golden pigments which plants donate so generously to the animal kingdom (about 100 million tons produced annually⁴) we would be doomed to live like mole rats, tapping or thumping out information to one another in eternal darkness.

On the other hand, on a warm, balmy summer evening we may well be thankful not to be consciously aware of the plethora of chemical messages crossing the air around us – from thousands of sex-starved female insects calling, calling, calling for satisfaction. The hum and ping of their wings is quite enough.

Chemical Ecology is a delightful area of investigation since it is relatively ‘new’, and the weft is dense and provocative, and surprise and discovery inevitable, mainly because the recent improbable advance in technology has ‘opened unknown doors’. Sometimes it is agreeable to ignore the constraints of philogeny! As I have already pointed out, we share pyrazines – aromatic volatiles – with plants and animals⁵ – from passion flowers to nettles, tree trunks to sea anemones, and rabbits to fish. In man – like in mice – they are found in our urine. Pyrazines stimulate recall in chickens and school children⁶ and probably in T-cells; they can regulate ovarian development in mice, signal warnings from toxic plants, enhance the odour of many flowers, and the bouquet of coffee and some white wines. Is their only benefit to man a possible stimulation of T-cells? Is our failure to recall surnames in old age due to a falling off in the production of pyrazines? This is something to think about in traffic jams. If the insect world has really pointed us in the right direction for improving recall we have much to be grateful for – especially to Chemical Ecology and the ladybirds. Probably these charming beetles and their evocative odour were the first insects to be tested by GC.

As larvae monarch butterflies sequester pyrazines from milkweeds⁷ and store them, but if the caterpillars are fed on plants which do not contain any, the butterflies lack them too. Except Danaus plexippus, the Trinidad monarch; these insects secrete pyrazines themselves, if their hosts don’t provide them – but they have not learned how to manufacture carotenoids.

Ingested pyrrolizidine alkaloids – so elegantly described and with such matchless illustrations, by Michael Boppře⁸ – eventually generate sexual arousal in both men and adult danaine butterflies, but this curious and romantic coincidence has not produced a flicker of interest among chemical ecologists.

The late Howard Hinton once remarked that the miracle of all time was the green world. Unquestionably if surprisingly – the plants have won the battle against insects. But how? They are more versatile chemists, but they are static. They use the wind as a pollinator but many of them now depend on insects. How, for instance, can flowering plants protect their pollinators and yet cope with the appetites of hungry herbivores? Do the cardiac glycosides in the latex of Asclepias, which are sequestered by the larvae of danaines, protect these caterpillars from aerial predators and thus preserve the butterfly pollinators? Stephen Malcolm⁹ has suggested that these plants produce a substance in the latex which thins out the population of freshly hatched young larvae. This would ensure a negligible sacrifice of foliage – even of seedlings – for the sake of the future invaluable pollinators.

¹ Old Testament: Jeremiah 14: vi
⁵ Bergström G, Rothschild M, Groth I, Crighton C: present volume
⁹ Malcolm SB: present volume
A glance at the literature concerning the scents produced by flowers indicates that vanilla is their commonest and most persistent odour. It is also recorded as a frequent fragrance on the wings of butterflies and moths. This is a subtle ploy whereby plants attract pollinators and bring the sexes together, offering them simultaneously both food and mates and thus furthering reproduction.

The polyphagous garden tiger moth (Arctia caja) and other members of this ravishing genus, apparently do nothing to assist their host plants – for they are tongueless, and cannot function as pollinators. However, in the Valley of the Butterflies their relative, the Jersey tiger (Euplagia quadripunctaria), after their long summer drowse, bejewels the ivy blossom in their thousands and the flowering Ling in Rhodies. According to Hartman the cinnabar (Tyria jacobaeae) – another relative – seems to have won this round, for it is no pollinator either, but by means of an insect enzyme “specifically processes a plant derived defence compound” to its own advantage. This discovery emphasises the great advances made in the field of chemical ecology for a mere 27 years ago, when the cinnabar larva was first shown to sequester and store PAs, it was only tentatively surmised that these alkaloids might function as part of a defence mechanism.

By far the most exciting news of plants response to predators is Marcel Dicke’s revelation that by means of volatiles released from damaged foliage, carnivores are attracted to the scene and attack the voracious herbivores. A wonderful new vista now lies spread out before us – but one hopes fervently the elimination of the large white (Pieris brassicae) is not envisaged, although it may now be possible.

The Caterpillar on the Leaf
Repeats to thee thy mother’s grief
Kill not the Moth or Butterfly
For the Last Judgement draweth nigh.

Fortunately among the Chemical Ecologists we have Ritsuo Nishida – a gifted scientist who loves butterflies. He and his school of thought give us a glimmer of hope for the whites and blues. The plants’ response to the presence of insect eggs on their leaves is more subtle – by producing deterrent volatiles further oviposition is inhibited but the eggs are not destroyed – thus preventing excessive predation but allowing for the survival of a few useful pollinators. It is worth recording that if the large white female has access to the nectar of crucifers, she lays more rapidly than without this stimulus. Recently, Robert Nash has identified hitherto undescribed glycosidase inhibiting alkaloids in plants, which are sequestered by various larvae and thus eventually stored by the butterflies. Maybe this endows the insects with indigestible qualities. Tropane alkaloids, one surmises, are present in the nectar of various flowers as well as their foliage. Is this yet another plant ploy for protecting pollinators without the sacrifice of a single leaf?

Chemical Ecology began for me when I heard Tom Eisner and Murray Blum read papers at the Entomological Conference in Vienna in 1960. I felt these two invented chemical ecology. Some ten years later Sondheimer and Simeone’s book appeared and I really abandoned my rabbit fleas at that moment. Eli Zlotkin’s fabulous series of publications on animal venoms added flames to the fire. About this time (in the early seventies) it was claimed that 10,000 papers on this topic appeared annually. Zlotkin pointed out that “one is often obliged to make the choice between a superficial but complete coverage of the whole subject or detailed presentation of only a part of it”. This is also true now of Chemical Ecology but fortunately, to begin with, questions and answers were conveniently circumscribed: Do monarch butterflies store cardiac glycosides? Is sinigrin the large white’s oviposition cue? Do captive birds reject mimics after experience with models? But these days are nearly over. Now, if you dare look closely at the chemical defences of any insect you are awestruck, almost appalled, by its complexity which “reveals a confusing variety of diffuse and complex patterns becoming increasingly closer to chaos”. Eli Zlotkin’s present expansion into genetic engineering and molecular biology may well by-pass us, and will add a bit of Brave New World to the toxin scenario. Meanwhile, we follow Keith Brown into the Brazilian forest or the New Forest (in the U.K.) – while they are still there – and reflect how fortunate we are to have lived in a time while there is still an interface to investigate between the Chemical and Natural Worlds!

The monarch butterfly, since it is known to contain cardenolides, PAs, pyrazines, carotenoids and blue bile...