C. H. Walker

ORGANIC POLLUTANTS

An Ecotoxicological Perspective

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Preface

This book is intended to be a companion volume to *Principles of Ecotoxicology*, first published in 1996 and now in its second edition. Both texts have grown out of teaching material used for the MSc course Ecotoxicology of Natural Populations, which was taught at Reading University between 1991 and 1997. At the time of writing both of these books, a strong driving force was the lack of suitable teaching texts in the areas covered by the course. Although this shortcoming is beginning to be redressed in the wider field of ecotoxicology, with the recent appearance of some valuable new teaching texts, this is not evident in the more focused field of the ecotoxicology of organic pollutants viewed from a mechanistic biochemical point of view. Matters are further advanced in the field of medical toxicology, and there are now some very good teaching texts in biochemical toxicology.

Principles of Ecotoxicology deals in broad brush strokes with the whole field, giving due attention to the 'top-down' approach – considering adverse changes at the levels of population, community and ecosystem, and relating them to the effects of both organic and inorganic pollutants. The present text gives a much more detailed and focused account of major groups of organic pollutants and adopts a 'bottom-up' approach. The fate and effects of organic pollutants are seen from the point of view of the properties of the chemicals, and their biochemical interactions. Particular attention is given to comparative metabolism and mechanism of toxic action and these are related, where possible, to consequent ecological effects. Biomarker assays that provide measures of toxic action are given some prominence because they have the potential to link the adverse effects of particular types of pollutant at the cellular level to consequent effects at the levels of population and above. In this way the top-down approach is complementary to the bottom-up approach; biomarker assays can provide evidence of causality when adverse ecological effects in the field are associated with measured levels of pollutants. Under field conditions, the discovery of a relationship between the level of a pollutant and an adverse effect upon a population is no proof of causality. Many other factors (including other pollutants not determined in the analysis) can have ecological effects, and these factors may happen to correlate with the concentrations of pollutants determined in ecotoxicological studies. The text will also address the question, 'To what extent can ecological effects be predicted from the chemical properties and the biochemistry of pollutants?', which is relevant to the utility or otherwise of use of quantitative structure–activity relationships (QSARs) of chemicals in ecotoxicology.

The investigation of the effects of chemicals upon the numbers and genetic composition of populations has inevitably been a long-term matter, the fruits of which are now becoming more evident with the passage of time. The emergence of resistant strains in response to the selective pressure of pesticides and other pollutants has given insights into the evolutionary process. The evolution of detoxifying enzymes such as the monooxygenases which have cytochrome P450 at their active centre is believed to have occurred in herbivores and omnivores with the movement from water to land. The development of detoxifying mechanisms to protect animals against plant toxins is a feature of 'plant–animal warfare', and is mirrored in the resistance mechanisms developed by invertebrates against pesticides. In the present text, the ecological effects of organic pollutants are seen against the background of the evolutionary history of chemical warfare.

The text is divided into three parts. The first deals with the basic principles underlying the environmental behaviour and effects of organic pollutants; the second describes the properties and ecotoxicology of major pollutants in reasonable detail; the last discusses some issues that arise after consideration of the material in the second part of the text and looks at future prospects. The groups of compounds represented in the second part of the book are all regarded as pollutants rather than simply contaminants, because they have the potential to cause adverse biological effects at realistic environmental levels; in most cases these effects have been well documented under environmental conditions. The term 'adverse effects' includes harmful effects upon individual organisms as well as effects at the level of population and above.

The layout of Chapters 5–12, which constitute Part 2, follows the structure of the text *Principles of Ecotoxicology* as far as possible. Where there is sufficient evidence to do so, the presentations for individual groups of pollutants are arranged as follows:

Topic in this book	Part in *Principles of Ecotoxicology*
Chemical properties Metabolism Environmental fate	1 Pollutants and their fate in ecosystems
Toxicity	2 Effects of pollutants on individual organisms
Ecological effects	3 Effects on populations and communities

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Colyton
January 2001

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Last but not least, I am grateful to all the research students and postdoctoral research workers at Reading who have contributed in so many ways to the production of this text.

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Contents

PART 1

Basic principles

CHAPTER 1

Chemical warfare

1.1 *Introduction*

Chemical warfare has been taking place since very early in the history of life on earth, and the design of chemical weapons by humans is an extremely recent event on the evolutionary scale. The synthesis by plants of secondary compounds ('toxins') that are toxic to invertebrates and vertebrates that feed upon them, together with the development of detoxication mechanisms by the animals in response, has been termed a 'co-evolutionary arms race' (Ehrlich and Raven, 1964; Harborne, 1993). Animals, too, have developed chemical weapons, both for attack and for defence. Spiders, scorpions, wasps and snakes possess venoms that paralyse their prey. Bombardier beetles and some slow-moving herbivorous tropical fish produce chemicals that are toxic to other organisms that prey upon them (see Agosta, 1996). Microorganisms produce compounds that are toxic to other microorganisms that may compete with them (e.g. penicillin produced by the mould *Penicillium notatum*).

A very large number of natural chemical weapons have already been identified and characterised, and many more are being discovered with each passing year – in plants, marine organisms, etc. Like pesticides and other man-made chemicals, they are, in a biochemical sense, 'foreign compounds' (xenobiotics). They are 'normal' to the organism that synthesises them but 'foreign' to the organism against which they express toxicity. During the course of evolution, defence mechanisms have evolved to provide protection against the toxins of plants and other naturally occurring xenobiotics.

The use of pesticides and 'chemical warfare agents' by man should be seen against this background. Many defence mechanisms already exist in nature, mechanisms that have evolved to give protection against natural xenobiotics. These systems may work, to a greater or lesser extent, against man-made pesticides when they are first introduced into the environment. Many pesticides are not as novel as they may seem. Some, such as the pyrethroid insecticides, are modelled upon natural insecticides (in the present case pyrethrins) with which they share a common mode of action and similar routes of metabolic detoxication. Also, many detoxication mechanisms are relatively non-specific, operating against a wide range of compounds that have common structural features, e.g. benzene rings, methyl groups or ester bonds. Thus, they can metabolise both man-made and natural xenobiotics, even where overall structures are not closely related.

We are dealing here with an area of science where pure and applied approaches come together. The discovery of natural products with high biological activity (toxicity in the present case), the elucidation of their modes of action and of the defence systems that operate against them can all provide knowledge that aids the development of new pesticides, the development of mechanistic **biomarker assays** which can establish their side-effects on non-target organisms, and the elucidation of mechanisms of resistance that operate against them. Whether compounds are natural or man-made, the molecular basis of toxicity remains a fundamental issue; whether biocides are natural or unnatural, similar mechanisms of action and of metabolism apply. Much of what is now known about the structure and function of enzymes that metabolise xenobiotics has been elucidated during the course of 'applied' research with pesticides and drugs, and the knowledge gained from this is immediately relevant to the metabolism of naturally occurring compounds. The development of this branch of science illustrates how misleading the division between 'pure' and 'applied' science can be. Here, at a fundamental scientific level, they are one and the same; the difference is a question of motivation – whether or not the work is done with some view to a 'practical' outcome (e.g. development of a new pesticide).

The phenomenon of plant–animal warfare will now be discussed, before moving on to a brief review of toxins produced by animals.

1.2 *Plant–animal warfare*

1.2.1 Toxic compounds produced by plants

A formidable array of compounds of diverse structure which are toxic to invertebrates and/or vertebrates has been isolated from plants. Some examples are given in Figure 1.1. Many of the known toxic compounds produced by plants are described in Harborne and Baxter (1993). Information about the mode of action of a few of them is given in Table 1.1, noting cases where man-made pesticides act in a similar way.

Let us consider, briefly, the compounds featured in Table 1.1. Pyrethrins are lipophilic esters that occur in *Chrysanthemum* spp. Extracts of flower heads of *Chrysanthemum* spp. contain six different pyrethrins and have been used for insect control (Chapter 12). Pyrethrins act upon sodium channels in a similar manner to *p,p′* -DDT (*p,p′* -

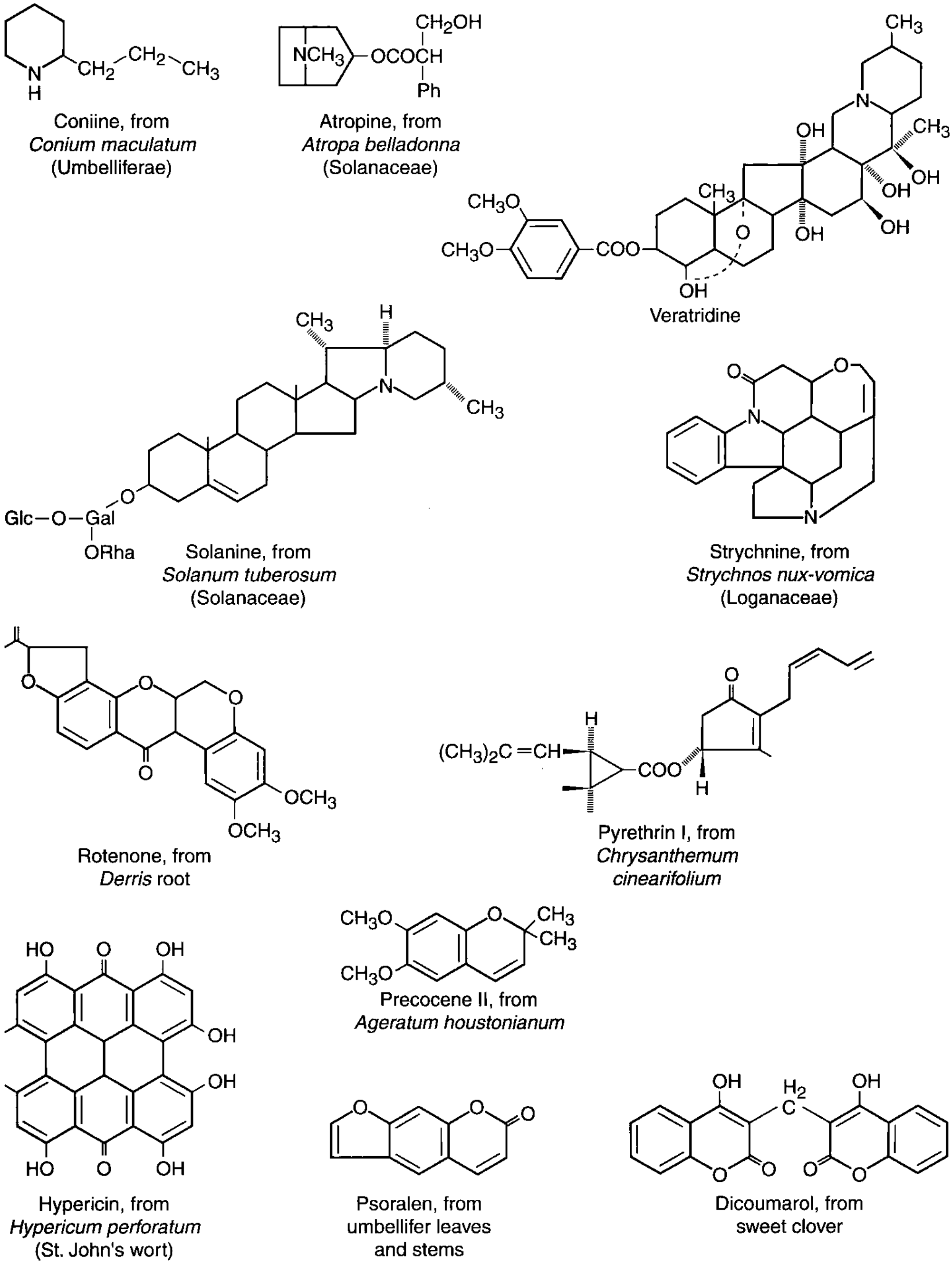

FIGURE 1.1 *Some toxins produced by plants.*

dichlorodiphenyltrichloroethane). The highly successful synthetic pyrethroid insecticides were modelled on natural pyrethrins.