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This chapter explains the definitions and classification of terpenoids. It also describes where and why terpenoids occur in nature and how they are extracted from natural sources.

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This chapter includes a brief introduction to the processes used in biogenesis. It explains how nature constructs the basic 5-carbon building blocks used for terpenoid biogenesis and how these hemi-terpenoid units are connected together to form chains of 10, 15, 20, *etc.* carbon atoms. It includes a brief overview of how these chains can be cyclised and modified to produce the staggering array of terpenoids which are present in nature.

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This chapter gives a short introduction to the methods of structural determination adopted before spectroscopy came into existence. Confirmation of proposed structures by synthesis provides an introduction to synthetic strategy. Myrcene and citral are used as examples of these disciplines and the chemistry of linalool and terpineol serve as a gentle introduction to carbocation chemistry.

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These two key monocyclic monoterpeneoids provide an excellent illustration of isomerism: structural, geometrical and stereoisomerism. The chapter demonstrates the importance of isomeric purity in biological processes involving molecular recognition, the interaction of different

forms of isomerism and the implications of stereochemistry for synthesis.

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Chapter 5 Bicyclic Monoterpenoids

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The chemistry of pinanes, camphanes and bornanes introduces the subject of carbocation chemistry. The basic principles governing the reactivity of carbocations and the factors which determine the selectivity of processes involving them, are therefore to be covered in detail in this chapter. The dramatic changes in chemical structure which can result from simple cation rearrangements are illustrated in these relatively easy to visualise molecules.

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Sandalwood and cedarwood constituents demonstrate the increasing complexity of carbocation reactions as the molecular size increases from 10 to 15 carbon atoms. In addition, Cedarwood chemistry demonstrates how changes to conditions can radically affect the outcome of carbocation reactions. Total synthesis of sandalwood materials introduces the Wittig reaction as a means of delivering geometric selectivity in synthesis. At this point, a revision of the basics of carbanion chemistry including the stereochemistry of the aldol reaction is appropriate. Examples from the chemistry of cedrene and selinene remind us that nothing can be taken for granted in terpenoid chemistry.

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Vetiver, patchouli, *Pinus longifolia*, cloves and hops provide us with examples of further increases in complexity in rearrangements, including the santonin rearrangement, and the corresponding increase in the challenges of total synthesis. The vetivones take us back to the use of degradation as a tool for structural elucidation and then, through the attendant need for total synthesis, forward to the sheer elegance of Stork's synthesis of β -vetivone. Longifolene shows how the course of a reaction can be dramatically changed by the presence of a strategically placed neighbouring atom.

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Nature is never static and this is demonstrated by chemical degradation of higher terpenoids in organisms and in the environment. The emphasis will be on the degradations which yield desirable products such as ambergris, the ionones, damascones, irones and theaspirones. The use of carotenoid derived pigments in vision introduces us to receptor proteins and the senses by which we perceive the universe around us.

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Chapter 9 Commercial Production of Terpenoids 269

In this chapter, the two main reasons for organic synthesis are compared and contrasted. In previous chapters, synthesis was a tool for structural elucidation and the key driving force was the unambiguous nature of the product's structure. Similar thinking is necessary for discovery chemistry. However, for commercial production, the key factors are safety, cost and security. Effluent, including unwanted by-products, is given prominence as part of the cost factor. For complex structures related to natural products, the most cost-efficient and secure starting materials might well be other natural products and this introduces the issue of sustainability. The often complex interplay between all of these parameters is illustrated through appropriate examples.

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Chapter 10 Discovery and Design of Novel Molecules**309**

The basic underlying principles of discovery chemistry are the same as those in discovery of novel molecules for all applications including pharmaceuticals, flavour ingredients, adhesives, lubricants and so on. The first part of the chapter outlines these basic principles and so should serve as an introduction for any area of discovery chemistry. The second part of the chapter uses fragrance ingredients as an example of the discovery process.

Perfumery is a blend of science and art. The language and artistic elements of perfumery will be discussed together with the technical aspects of commercial perfumery. The role of structure/property correlations (QSPRs) in the discovery of new ingredients will be covered. This will lead on through discussion of the scope and limitations of QSPRs to a summary of the current state of knowledge of the process of olfaction. The contribution of discovery chemistry to the history of perfumery is outlined and illustrated by specific examples.

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