MONOTERPENES IN ESSENTIAL OILS

Biosynthesis and Properties

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ABSTRACT

Monoterpenes are compounds found in the essential oils extracted from many plants, including fruits, vegetables, spices and herbs. These compounds contribute to the flavor and aroma of plant from which they are extracted. Monoterpenes are acyclic, monocyclic, or bicyclic C_{10} compounds synthesized by monoterpene synthases using geranyl pyrophosphate (GPP) as substrate. GPP is also the precursor in the synthesis of farnesyl pyrophosphate (FPP) and geranyl-geranyl pyrophosphate (GGPP), two important compounds in cell metabolism of animals, plants and yeast. Monoterpene cyclases produce cyclic monoterpenes through a multistep mechanism involving a universal intermediate, a terpinyl cation which can be transformed to several compounds. Experimental studies, using animal cancer models, have demonstrated that some monoterpenes possess anticarcinogenic properties, acting at different cellular and molecular levels. From these discoveries it seems clear that monoterpenes could be considered as effective, nontoxic dietary antitumorigenic agents that hold promise as a novel class of anticancer drugs.

INTRODUCTION

Essential oils (EO) are mixtures of compounds characterized by their capacity to generate flavor or aroma. Generally EO are obtained from spices, aromatic herbs, fruits or flowers. Many of them are used for seasoning and flavoring food, as basis of perfumes and

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other household items, and in aromatherapy for the treatment of several affections. EO can be extracted from the whole plant or a part of it, and although the method of extraction is very important to yield an essential oil capable of producing "almost as the raw plant" aroma (Moyler, *et al.*, 1994), the plant biological component is the decisive factor to obtain an essential oil with specific organoleptic characteristics (Irving and Adams, 1973). However, the biochemical and genetic aspects involved in the synthesis of different compounds present in EO have been barely studied. It is also important to note that other factors such as climate, soil and growing conditions influence the quality and concentration of components of an essential oil (Müller-Riebau *et al.*, 1997). Thus, to ensure consistency in a formulated product containing natural extracts, it is important to specify the country of origin of a plant material ingredient as well as its botanical name (Moyler, 1994).

As previously mentioned, EO can be extracted using different processes which must result in a minimal chemical change of the compounds present in the oil, in order to maintain its natural aroma. The economy of the process and the yield and recovery of active components are important. Some techniques of interest for extraction of aroma compounds are steam and water destillation, hydrodiffusion, and water infussion as well as use water or steam as solvents. Other methods use alcoholic tinctures, extraction of oleoresins, using organic solvents such as methanol, ethanol, isopropanol, ethyl acetate or acetone (Moyler, 1994). However, the use of non-toxic solvents during the extraction process is an important issue because of regulatory restrictions (Marion *et al.*, 1994). New techniques using supercritical or subcritial CO_2 have been developed with significant advantages compared to the use of organic solvents (Moyler *et al.*, 1994; Meireles and Nikolov, 1994). Methods such as gas- and high-performance liquid chromatography, mass spectrometry and nuclear magnetic resonance have been used to determine the composition of oils, the quantities present in the extracts, as well as the nature of the oils components (Tateo *et al.*, 1994).

Analysis of EO show that, of the different compounds forming them, terpenoids are most abundant and are present either as hemiterpenes, monoterpenes or sesquiterpenes, and as their derivatives like alcohols, esters, acetates, and others. Terpenoids form a unique group in the sense of the range and diversity of compounds they represent. Structural types and their derivatives comprise thousands of compounds, being the vastest group in nature (Connolly and Hill, 1992). In many spices, monoterpenes and their derivatives are by far the most abundant compounds in the EO, being responsible for the characteristic flavor and aroma the plant possesses.

Monoterpenes in their natural environment give different properties to the plant in which they are present. Citral, for example, is an important constituent of the smell of lemon. Thymol is involved in the flavor of mandarin oranges. Other monoterpenes, such as limonene and geranyl are constituents of flower scents and attract plant pollinators. High concentrations of monoterpenes in plants will repel many potential predators, but may attract other animals. Animals use citronellal, citral, and α- and β-pinenes as feeding deterrents and geraniol, geranyl esters, myrcene, and terpinolene as pheromones. Some others, such as 1,8-cineole and camphor, are involved in plant-plant interactions. Some commercially important monoterpenes are menthol, camphor, carvone, thymol, fenchone and α-pinene (Luckner, 1984). Recently application of monoterpenes as anticancer drugs based on the studies showing this effect in animal models, has been demonstrated (Gould, 1995).

In this chapter a short review is presented about some of the main monoterpenes found in essential oils, the biosynthetic reactions involved in their production, and their properties as antimicrobial agents and anticancer compounds.