# TERPENES

The terpenes are a chemically and functionally diverse group of molecules with nearly 15,000 structures known, terpenoids are probably the largest and most diverse class of organic compounds found in plants.

The unifying feature of terpenes is that they are generally lipophilic polymers based on the simple 5-carbon unit 2-methyl-1, 3-butadiene, or **isoprene**, which is derived via either the mevalonic acid pathway or the MEP pathway.

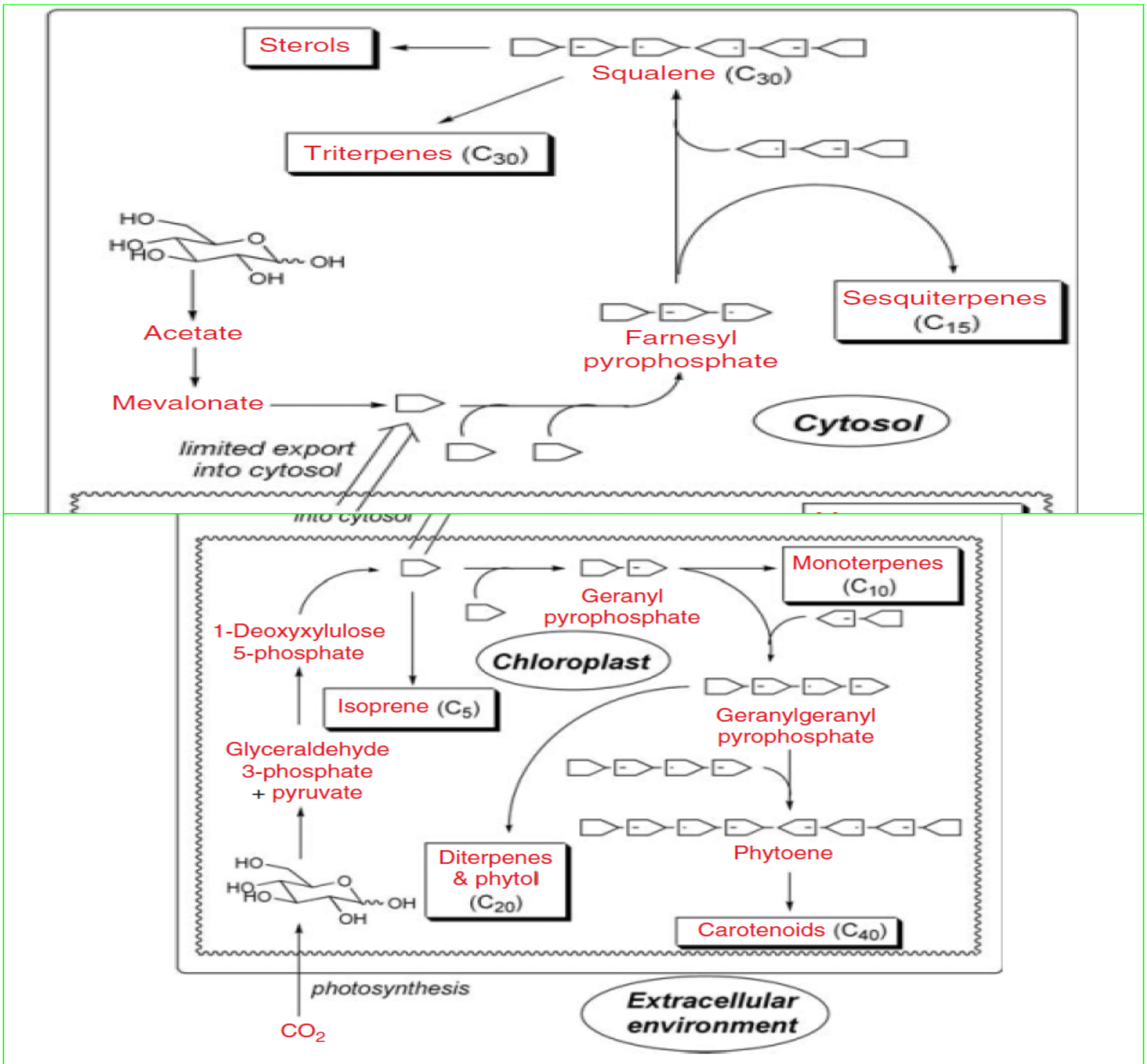
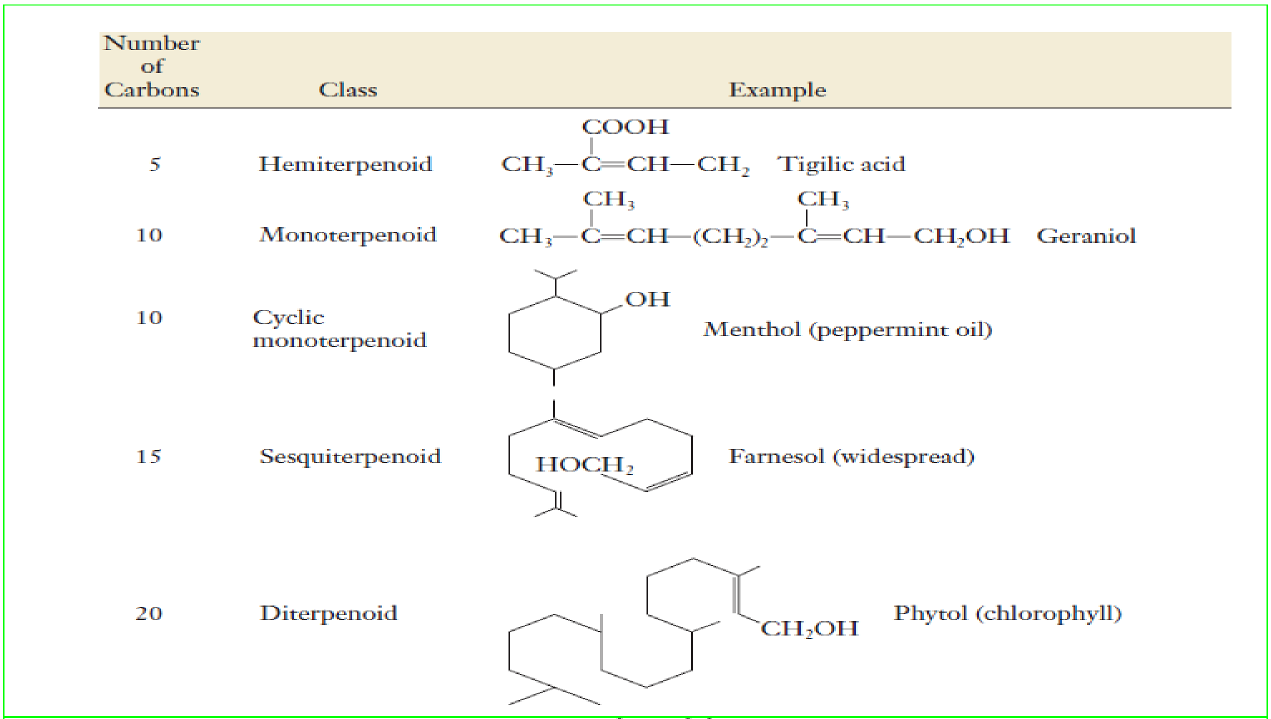
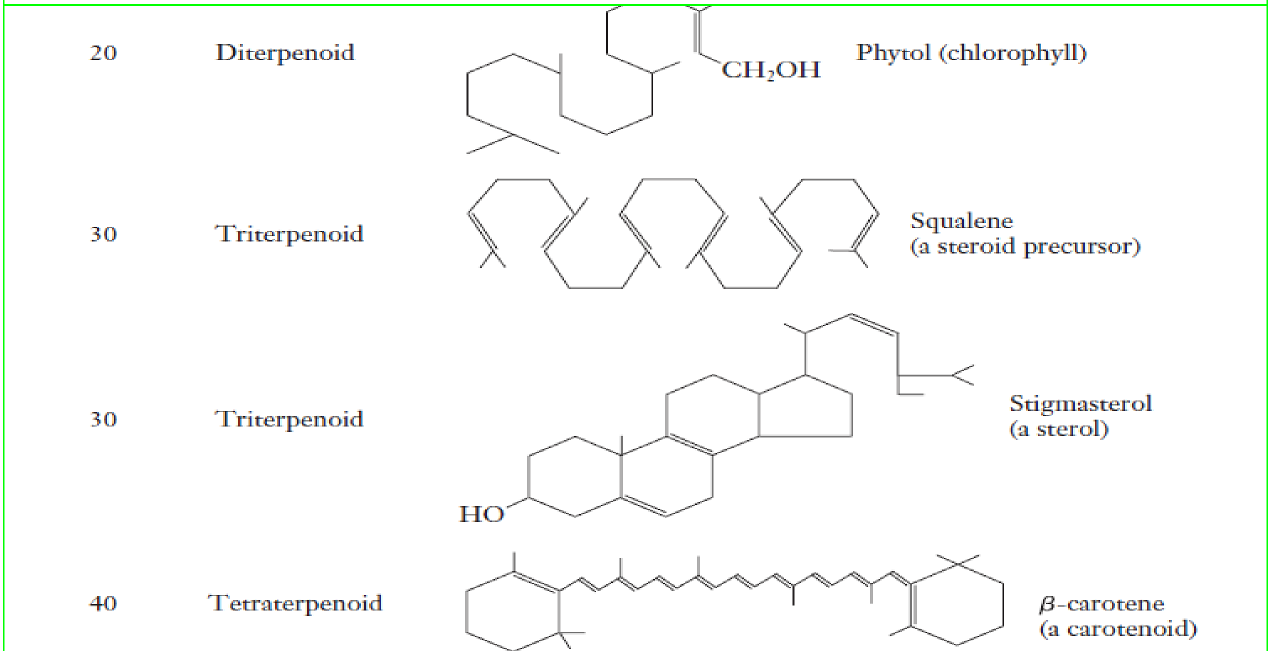



**Figure 3.2** Schematic representation of terpene biosynthesis in higher plant cells. Blocks represent 5-carbon isoprenyl units (IPP or DMAPP).

Terpenes can be grouped into several classes, based on the number of carbon atoms.



| Number of Carbons | Class | Example |
|---|---|---|
| 5 | Hemiterpenoid | $CH_3-C(COOH)=CH-CH_3$ Tigilic acid |
| 10 | Monoterpenoid | $CH_3-C(CH_3)=CH-(CH_2)_2-C(CH_3)=CH-CH_2OH$ Geraniol |
| 10 | Cyclic monoterpenoid | OH Menthol (peppermint oil) |
| 15 | Sesquiterpenoid | $HOCH_2$ Farnesol (widespread) |
| 20 | Diterpenoid | $CH_2OH$ Phytol (chlorophyll) |



| | | |
|---|---|---|
| 20 | Diterpenoid | $CH_2OH$ Phytol (chlorophyll) |
| 30 | Triterpenoid | Squalene (a steroid precursor) |
| 30 | Triterpenoid | HO Stigmasterol (a sterol) |
| 40 | Tetraterpenoid | β-carotene (a carotenoid) |

FIGURE 27.2 Terpenoids are classified according to the number of carbon atoms in the basic skeleton.

This large chemical diversity arises from the number of basic units in the chain and the various ways in which they are assembled.

Formation of cyclic structures, addition of oxygen-containing functions, and conjugation with sugars or other molecules all add to the possible complexity.

The name terpenoid derives from the fact that the first compounds in the group were isolated from turpentine (Ger. *terpentin*), an essential oil (chiefly pinene) distilled from the resins of several coniferous trees.

The terpene family includes hormones (gibberellins and abscisic acid): the carotenoid pigments (carotene and xanthophyll); sterols (e.g., ergosterol, sitosterol, cholesterol) and sterol derivatives (e.g., cardiac glycosides); latex (the basis for natural rubber); and many of the essential oils that give plants their distinctive odours and flavours.

Cytokinin hormones and chlorophyll, although not terpenes per se, do contain terpenoid side chains. It is apparent from this list that many terpenes have significant commercial value as well as important physiological roles. Many terpenes and terpene derivatives may be considered primary metabolites.

The hormones abscisic acid and gibberellin, the carotenoid and chlorophyll pigments, and sterols (steroid alcohols) all play significant roles in plant growth and development. The vast majority of terpenes, however, are secondary metabolites, many of which appear to act as toxins or feeding deterrents to herbivorous insects.

## Terpenes are constituents of essential oils

Many plants, such as citrus, mint, *Eucalyptus*, and various herbs (thyme) produce complex mixtures of alcohols, aldehydes, ketones, and terpenoids, known generally as **essential oils** (essence, as in perfume).

Essential oils are responsible for the characteristic odours and flavours of these plants but they are also known to have insect-repellant properties. The terpenes and terpene derivatives found in essential oils are predominantly hemi-,mono-, and sesquiterpenes, which can be moderately to highly volatile.

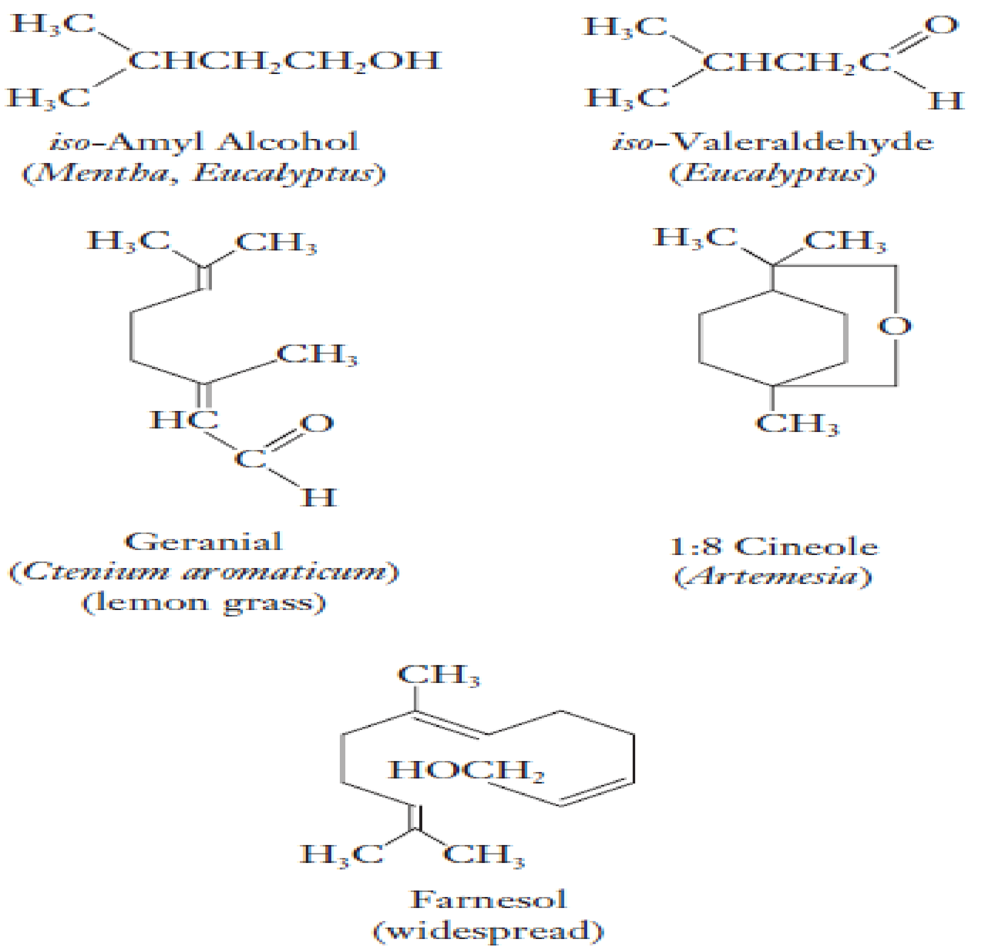



**FIGURE 27.3** **Representative terpenes that commonly occur in essential oils include: hemiterpenes (*iso*amyl alcohol, *iso*valeraldehyde), monoterpenes (geranial, cineole), and the sesquiterpene, farnesol.**

The resins of certain conifers, for example, also accumulate mixtures of terpenes, including the monoterpenes, α- and β-pinene, and myrcene.

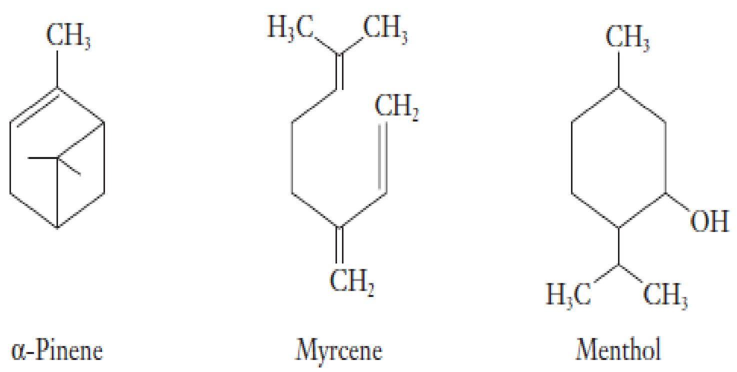
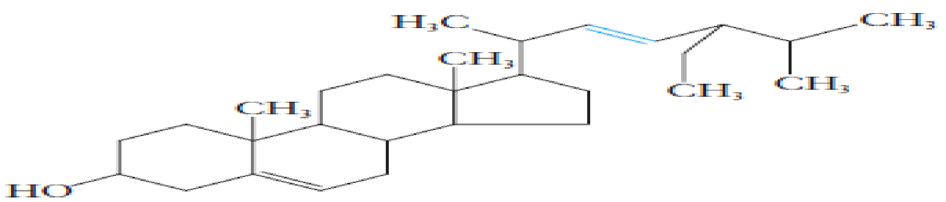



FIGURE 27.5 Pinene, myrcene, and menthol are monoterpenes. Pinene and myrcene are found in the resins of some conifers. Menthol is the principal constituent of the essential oil of peppermint (*Mentha piperta*). Pinene also has insecticidal properties.

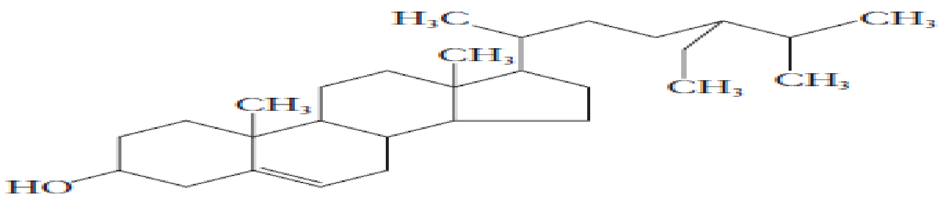
## Steroids and sterols are tetracyclic triterpenoids

Steroids and sterols are synthesized from the acyclic triterpene squalene, although they generally are modified and have fewer than 30 carbon atoms. Steroids with an alcohol group, which is the case with practically all plant steroids, are known as **sterols**.

The most abundant sterols in higher plants are stigmasterol and sitosterol.




Stigmasterol




Sitosterol

FIGURE 27.6 Stigmasterol and sitosterol differ only in the presence or absence of a double bond (highlighted). These are the two most abundant plant sterols.

Which often make up more than 70 percent of the total sterols. However, plants also contain a large number of the more than 150 other sterols known to occur in nature.

Plant sterols include cholesterol which, although widespread in occurrence, is present in only trace quantities. The extremely low level of cholesterol allows plant oils to be marketed as ‘‘cholesterol-free.’’

## Polyterpenes include the carotenoid pigments and natural rubber

Larger terpenes include the tetraterpenes (40-carbon) and the polyterpenes. The principal tetraterpenes are the carotenoid family of pigments. The only important isoprene derivatives with a greater molecular mass than the tetraterpenes are **rubber** and **gutta**.

Rubber is a polymer consisting of up to 15,000 isopentenyl units. The polymer may be linear, as shown in figure or cross-linked into more complex configurations.

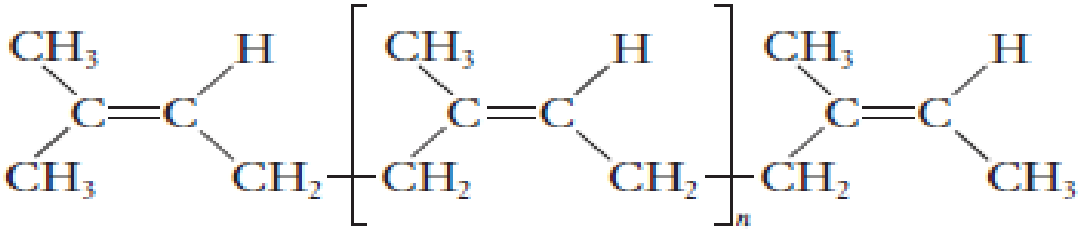


**FIGURE 27.7 Rubber is a linear polymer of isoprene units where the value of *n* may range from a few hundred to several thousand.**

The only difference between rubber and gutta is the configuration of the double bonds. In rubber the double bonds are all cis configurations, while in gutta the double bonds are all trans.

In the plant, rubber occurs as small particles suspended in a milky-white emulsion called latex. Latex production is widespread in plants, with estimates ranging from a few hundred to several thousand species that produce latex in some form. Latex contains about 30 to 40 percent rubber and 50 percent water.

The balance is a complex mixture of resins, terpenes, proteins, and sugars. In most plants, latex is produced in the phloem, accumulating in a series of long, interconnected vessels called **laticifers**. The best-known source of gutta is a desert shrub, *Parthenium argentatum*, which grows in northern Mexico and southwestern United States. *Parthenium* (commonly known as guayule) may contain as much as 20 percent latex by weight, which is stored not in laticifers but in the vacuoles of stem and root cells. Guayule was at one time a significant commercial source of gutta for use in rubber products.

However, while a single rubber tree, if properly tapped, can continue to produce for up to 30 years, guayule plants must be harvested (and, of course, replanted) annually.

Finally, there is a connection between terpenes and air pollution. Many of the essential oils, especially hemiterpenes, monoterpenes, and sesquiterpenes, are highly volatile and are given off in large quantities by plants, particularly during warm weather. Known generally as **volatile organic carbon** (**VOC**), these natural emissions from plants contribute to the formation of haze and cloud, and are involved in the formation of toxic tropospheric ozone.