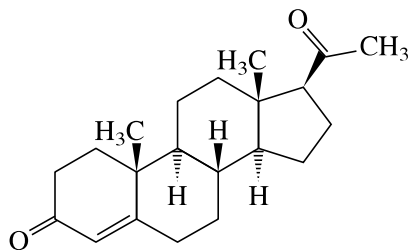
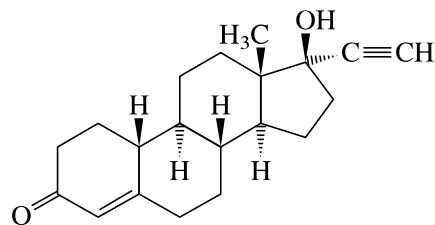


the menstrual cycle and during pregnancy. Synthetic substances, such as *norethindrone*, have been developed that are superior to progesterone when taken orally to “turn off” ovulation. By inducing temporary infertility, they form the basis of most oral contraceptive agents.



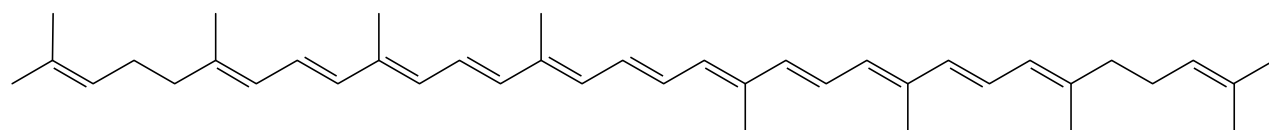
Progesterone



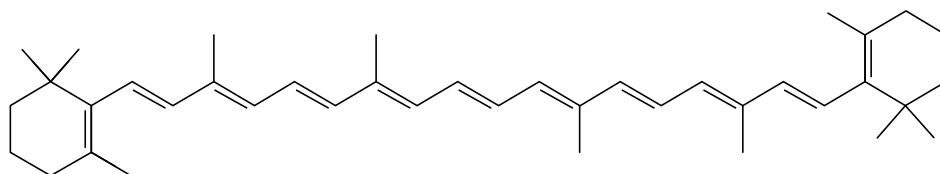
Norethindrone

26.16 CAROTENOIDS

Carotenoids are natural pigments characterized by a tail-to-tail linkage between two C_{20} units and an extended conjugated system of double bonds. They are the most widely distributed of the substances that give color to our world and occur in flowers, fruits, plants, insects, and animals. It has been estimated that biosynthesis from acetate produces approximately a hundred million tons of carotenoids per year. The most familiar carotenoids are lycopene and β -carotene, pigments found in numerous plants and easily isolable from ripe tomatoes and carrots, respectively.



Lycopene

 β -Carotene

Carotenoids absorb visible light (Section 13.19) and dissipate its energy as heat, thereby protecting the organism from any potentially harmful effects associated with sunlight-induced photochemistry. They are also indirectly involved in the chemistry of vision, owing to the fact that β -carotene is the biosynthetic precursor of vitamin A, also known as retinol, a key substance in the visual process.

The structural chemistry of the visual process, beginning with β -carotene, was described in the boxed essay entitled “Imines in Biological Chemistry” in Chapter 17.

26.17 SUMMARY

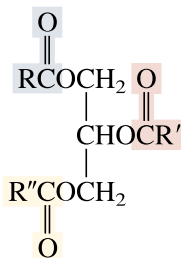
Section 26.1 Chemists and biochemists find it convenient to divide the principal organic substances present in cells into four main groups: *carbohydrates*, *proteins*, *nucleic acids*, and **lipids**. Structural differences separate carbohydrates from proteins, and both of these are structurally distinct from nucleic acids. Lipids, on the other hand, are characterized by a *physical*

property, their solubility in nonpolar solvents, rather than by their structure. In this chapter we have examined lipid molecules that share a common biosynthetic origin in that all their carbons are derived from acetic acid (acetate). The form in which acetate occurs in many of these processes is a thioester called acetyl coenzyme A.



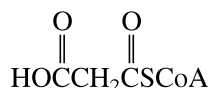
Abbreviation for acetyl coenzyme A
(for complete structure, see Figure 26.1)

Section 26.2 Acetyl coenzyme A is the biosynthetic precursor to the **fatty acids**, which most often occur naturally as esters. **Fats** and **oils** are glycerol esters of long-chain carboxylic acids. Typically, these chains are unbranched and contain even numbers of carbon atoms.



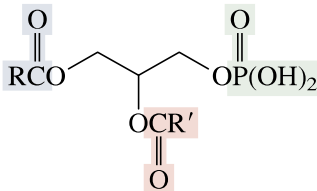
Triacylglycerol
(R, R', and R'' may be the same or different)

Section 26.3 The biosynthesis of fatty acids follows the pathway outlined in Figure 26.3. Malonyl coenzyme A is a key intermediate.



Malonyl coenzyme A

Section 26.4 **Phospholipids** are intermediates in the biosynthesis of triacylglycerols from fatty acids and are the principal constituents of cell membranes.

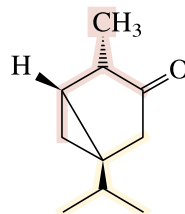


A phospholipid

Section 26.5 **Waxes** are mixtures of substances that usually contain esters of fatty acids and long-chain alcohols.

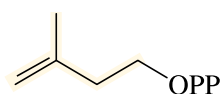
Section 26.6 A group of compounds called **prostaglandins** are powerful regulators of biochemical processes. They are biosynthesized from C₂₀ fatty acids. The structures of two representative prostaglandins are shown in Figure 26.5.

Section 26.7 **Terpenes** are said to have structures that follow the isoprene rule in that they can be viewed as collections of isoprene units.



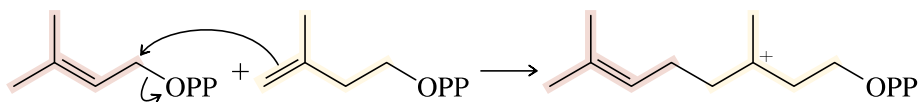
β -Thujone: a toxic monoterpene present in absinthe

Section 26.8 Terpenes and related *isoprenoid* compounds are biosynthesized from *isopentenyl pyrophosphate*.

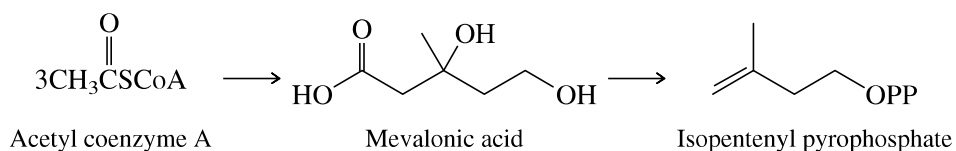


Isopentenyl pyrophosphate is the “biological isoprene unit.”

Section 26.9 Carbon–carbon bond formation between isoprene units can be understood on the basis of nucleophilic attack of the π electrons of a double bond on a carbocation or an allylic carbon that bears a pyrophosphate leaving group.



Section 26.10 The biosynthesis of isopentenyl pyrophosphate begins with acetate and proceeds by way of *mevalonic acid*.



Section 26.11 The triterpene *squalene* is the biosynthetic precursor to cholesterol by the pathway shown in Figure 26.10.

Sections 26.12–26.15 Most of the steroids in animals are formed by biological transformations of cholesterol.

