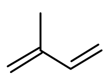
ISOPRENE, TERPENES AND NATURAL ALKENES AND ALKYNES

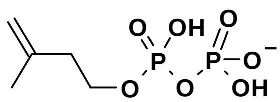
ETHYLENE

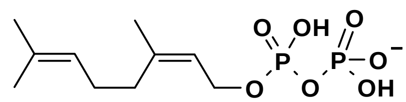
The simplest alkene, ethene, is produced naturally by all higher plants from the amino acid methionine and is a plant growth regulator. It causes trees to lose their leaves and stems to thicken. It is best known for its ability to ripen fruit and is responsible for the accelerated ripening of fruit confined in bags or in the presence of ripe fruits.

ISOPRENE AND TERPENES

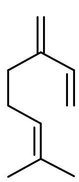
Some of the most interesting naturally occurring compounds originate from 2-methyl-1,3-butadiene, otherwise known as isoprene, in plants; the isoprene itself is synthesized from acetate. Pyrophosphate esters of isoprene are the actual reagents for these construction projects; pyrophosphoric acid is an anhydride of phosphoric acid.

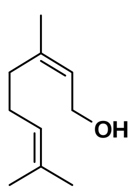

isoprene

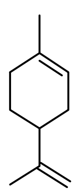

isopentenyl pyrophosphate

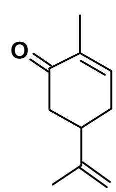

geranyl pyrophosphate ---> ---> squalene

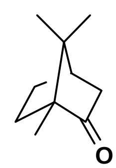
The isoprene units are always linked 1,4 and head-to-tail in terpenes (the preferred addition orientation even in mineral acid), but are often linked further in bizarre ways to produce rings. Oxygen functional groups are often included, as might be expected from hydrolysis of the pyrophosphate linkage. The diversity of compounds produced is amazing, but the pattern of one methyl group every fourth carbon reveals their origin. The simplest, monoterpenes, consist of 2 isoprene units. The stereoisomers of these simplest terpenes provide interesting illustrations of the stereospecificity of odor receptors; for example (+)-(*S*)-carvone is responsible for the odor of caraway and (-)-(*R*)-carvone the odor of spearmint.

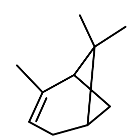

myrcene


geraniol

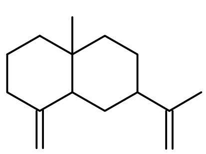

limonene

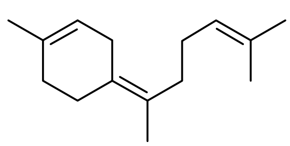

carvone

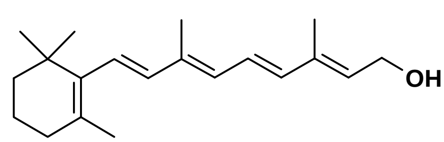

camphor


pinene

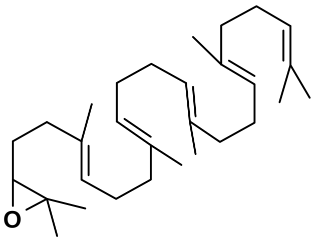
Sesquiterpenes (1.5 terpenes) have 3 isoprene units and diterpenes have 4.


beta-selinine (celery)

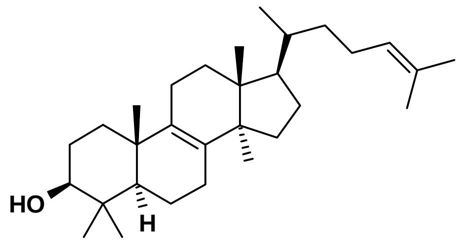

zingiberine (ginger)


Vitamin A

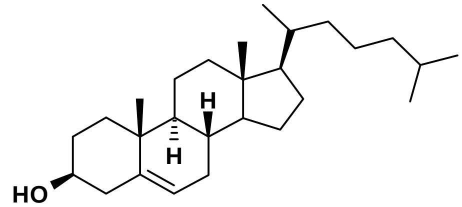
Triterpenes and higher occur in recognizable form but are most notable for their conversion into the steroids. The conversion of squalene into lanosterol is essentially a carbocation alkene polymerization reaction, much of which can be accomplished from the epoxide without any assistance from enzymes. The conversion of lanosterol to cholesterol and its conversion into such compounds as estrogen, progesterone and testosterone is much more complex. Cholesterol is also essential for adjusting the rigidity and permeability of cell membranes; it is commonly found in mammals as a fatty acid ester (polyunsaturated esters are the so-called "good cholesterol").



squalene epoxide



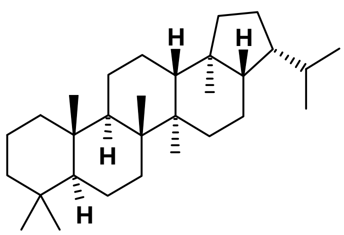
lanosterol



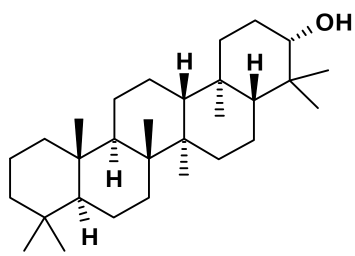
cholesterol

The most common tetraterpenes are the carotenes, such as *beta*-carotene (found in tomatoes, spinach, carrots, which your body cleaves exactly in half to make Vitamin A) and lycopene (tomatoes, carrots)

It was recently discovered that a class of compounds called hopanoids serve similar functions for bacteria as the steroids do for higher plants and animals; they are also made from squalene. Most amazing, the hopanoid skeleton survives in sediments, both marine and terrestrial, and in coal and oil, leaving no doubt as to the biological origin of these hydrocarbons.



hopane



tetrahymanol

ALKYNES

One of the more interesting classes of new anti-cancer drugs is a group of naturally occurring enediynes which cleave DNA. Each has a cyclodec-3-en-1,5-diyne ring tucked into a complex molecule which includes aromatic rings and sugars; a recent synthesis opens the possibility for systematic modification to produce new and better drugs. *In vivo* the endiyne cyclizes to form a benzene ring with two unpaired electrons (a diradical) which then cleaves the DNA.

FURTHER READING

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