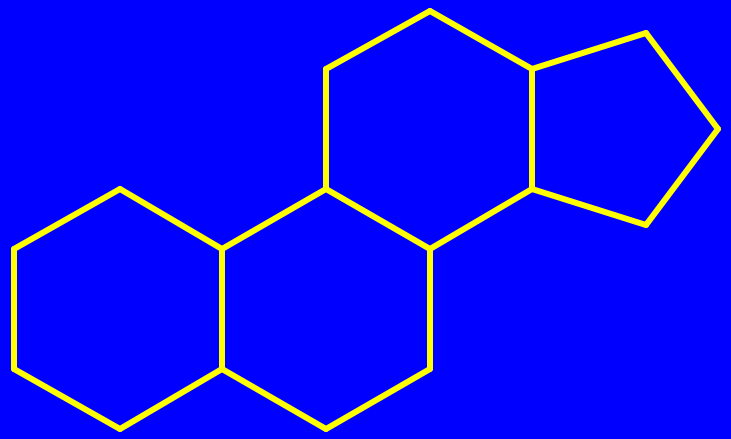
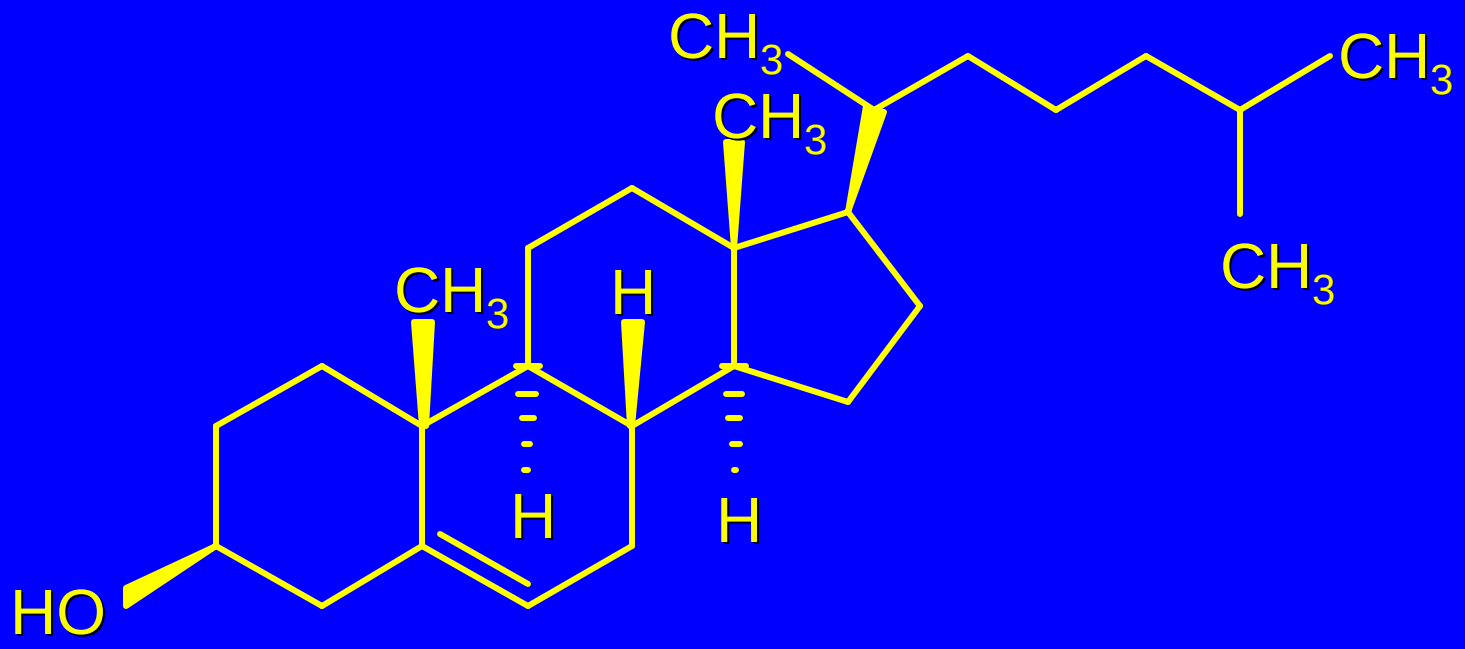
26.11
Steroids: Cholesterol

Structure of Cholesterol



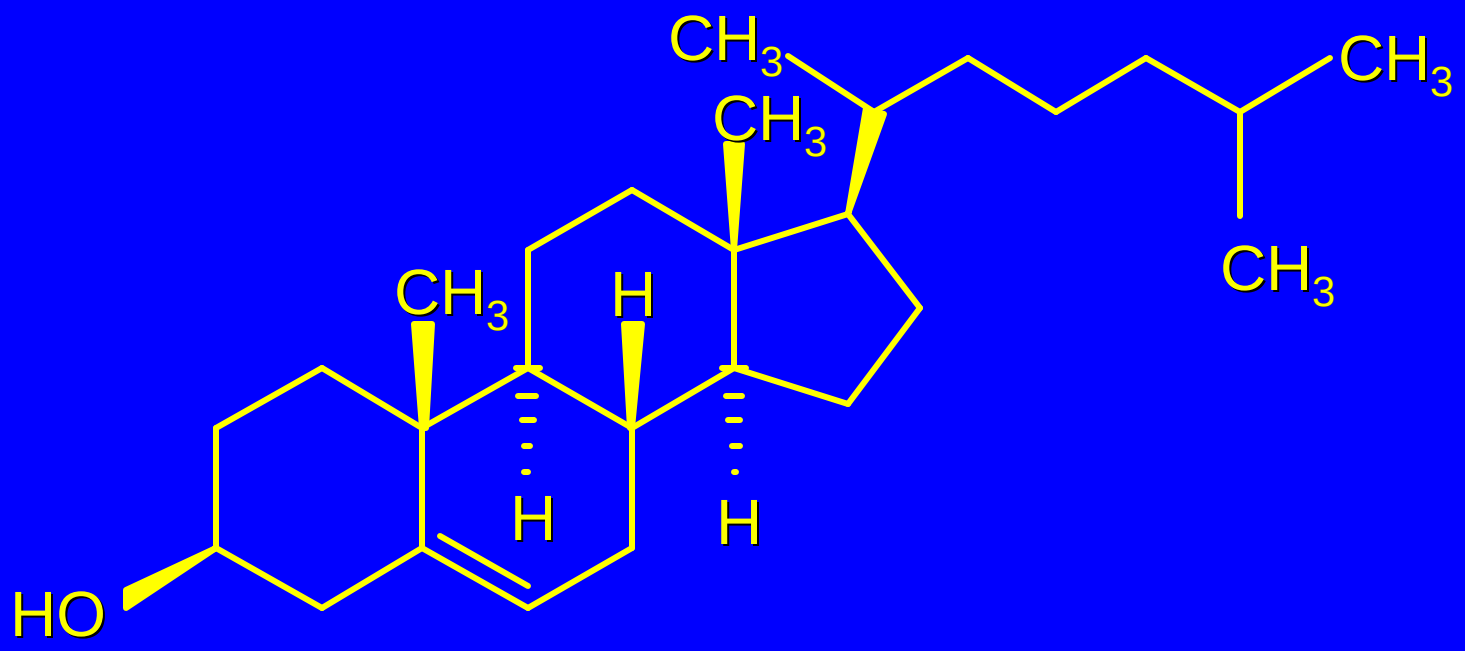
Fundamental framework of steroids is the tetracyclic unit shown.

Structure of Cholesterol



Cholesterol has the fundamental steroid skeleton modified as shown.

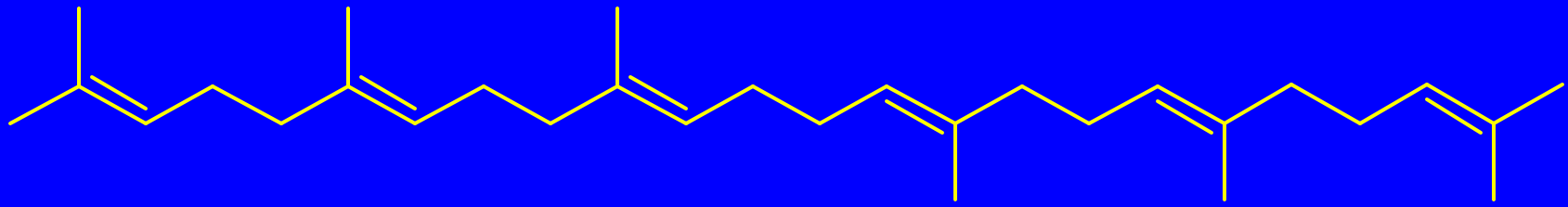
Structure of Cholesterol



Some parts of the cholesterol molecule are isoprenoid. But other parts don't obey the isoprene rule. Also, cholesterol has 27 carbons, which is not a multiple of 5.

Biosynthesis of Cholesterol

Cholesterol is biosynthesized from the triterpene squalene. In the first step, squalene is converted to its 2,3-epoxide.



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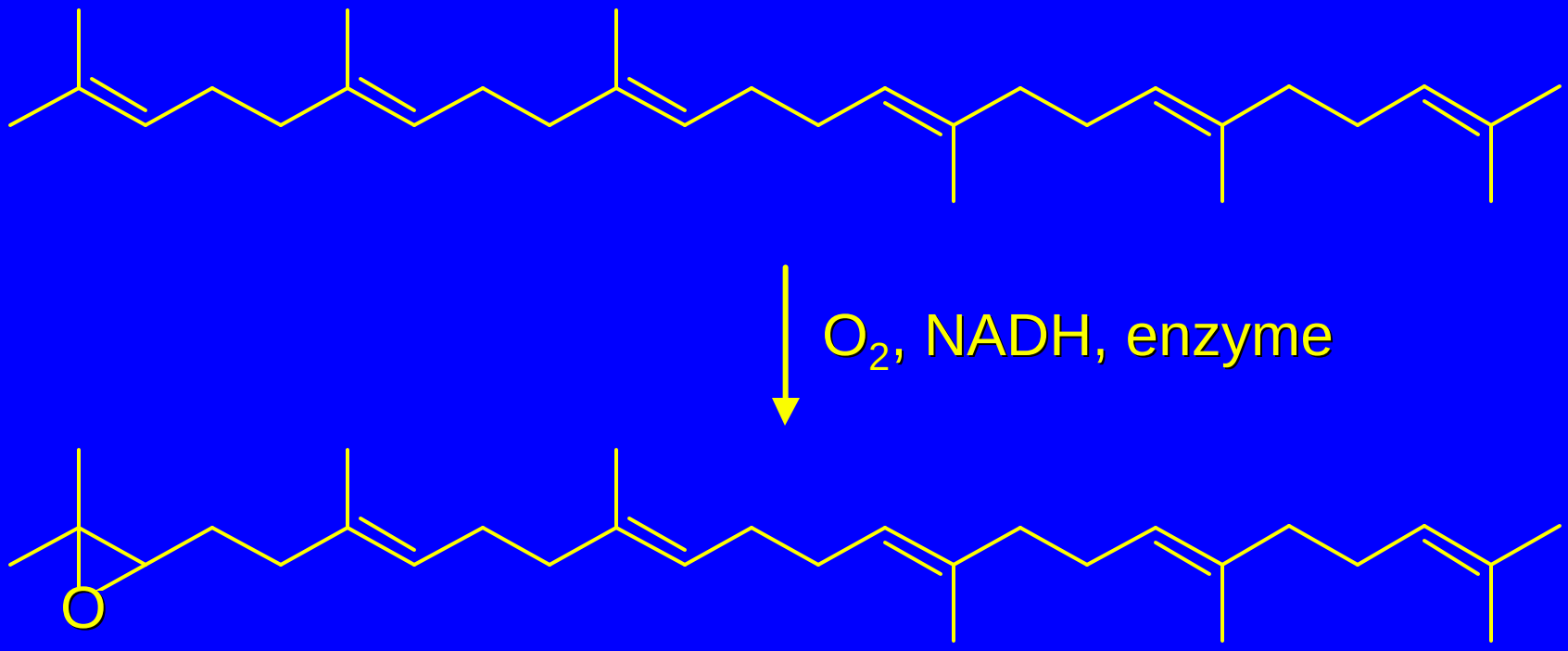
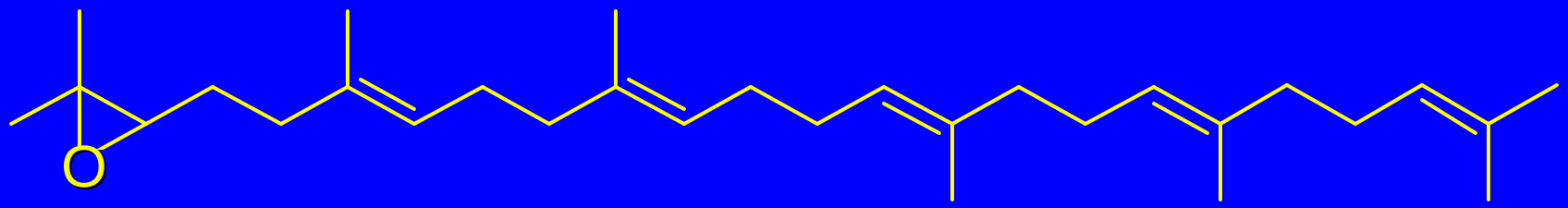
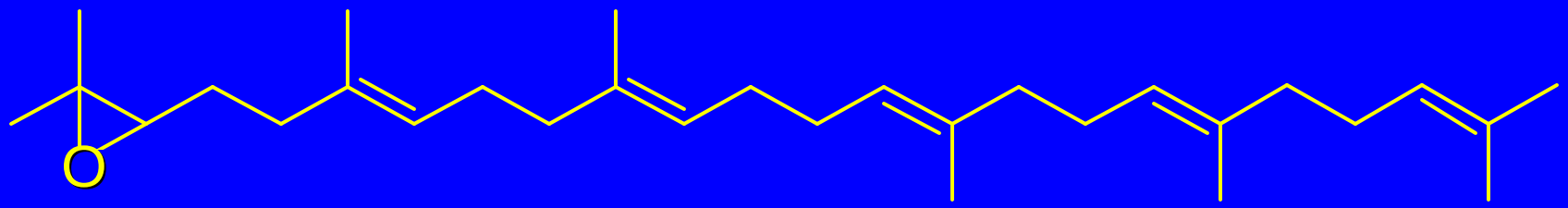


Biosynthesis of Cholesterol



To understand the second step, we need to look at squalene oxide in a different conformation, one that is in a geometry suitable for cyclization.

Biosynthesis of Cholesterol



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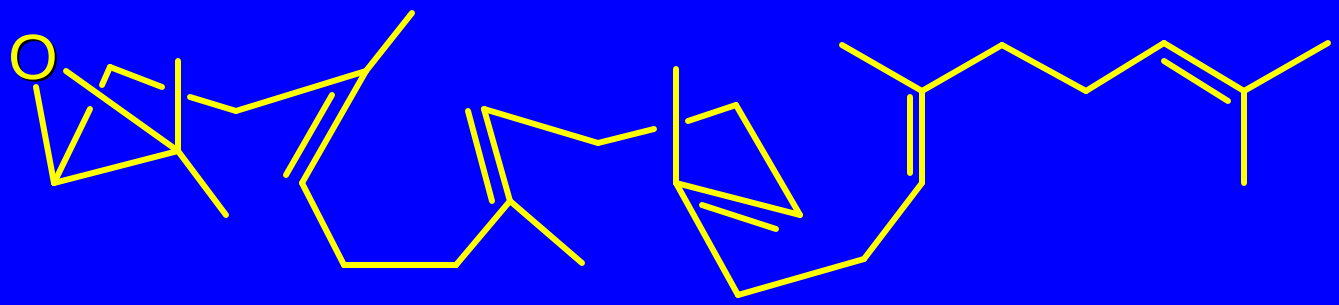
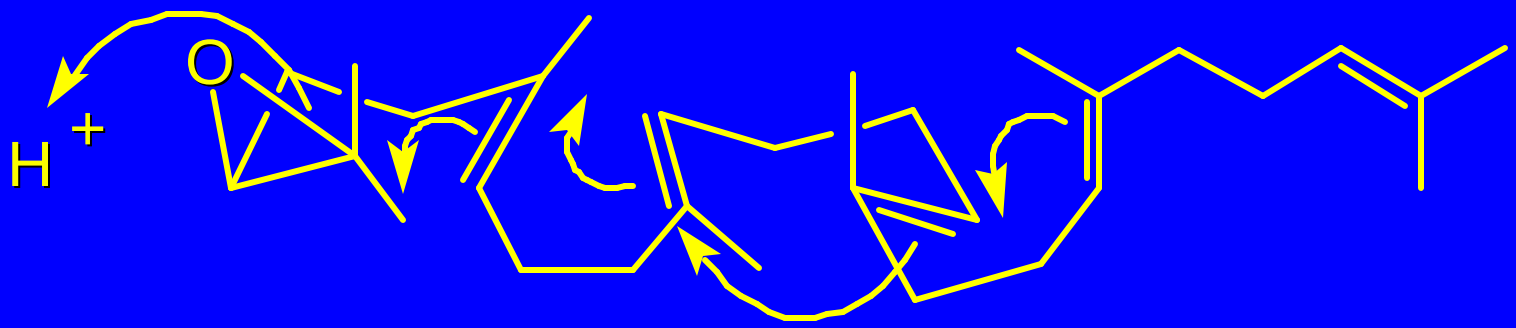
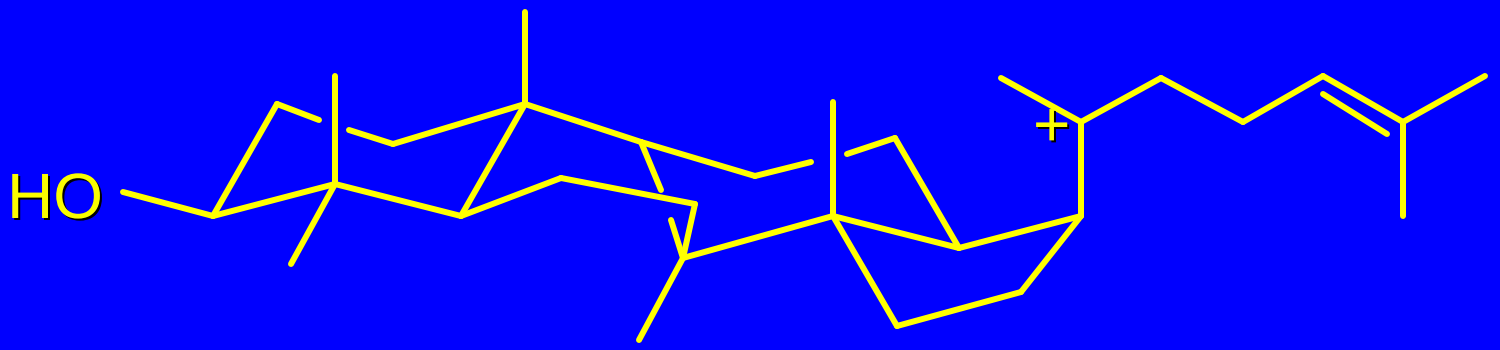


Biosynthesis of Cholesterol

Cyclization is triggered by epoxide ring opening.



Biosynthesis of Cholesterol



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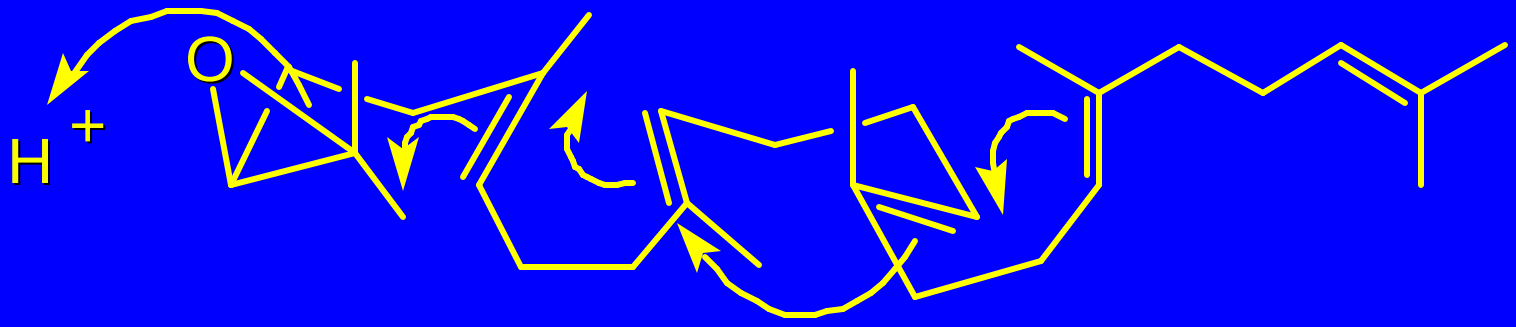
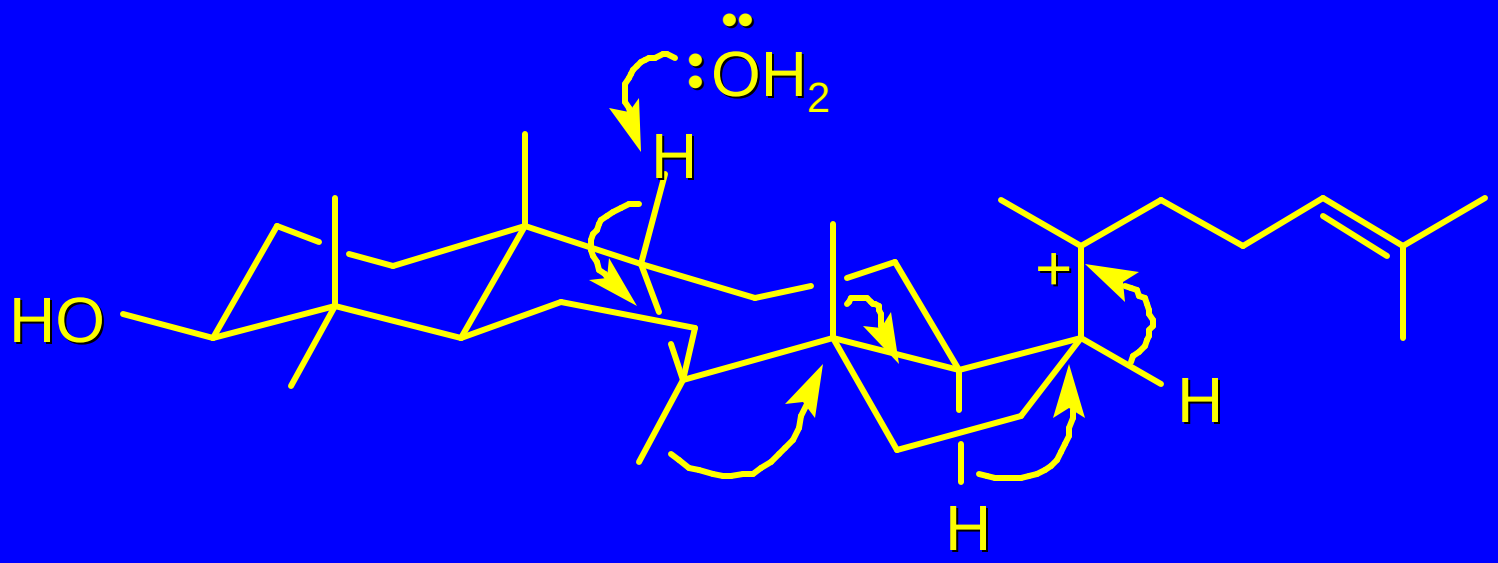
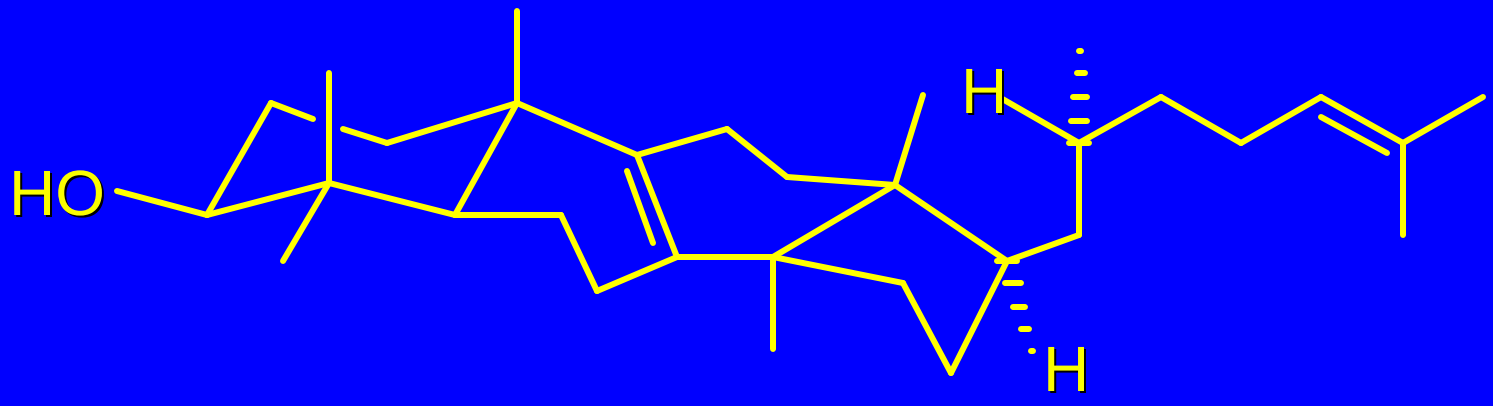


Biosynthesis of Cholesterol

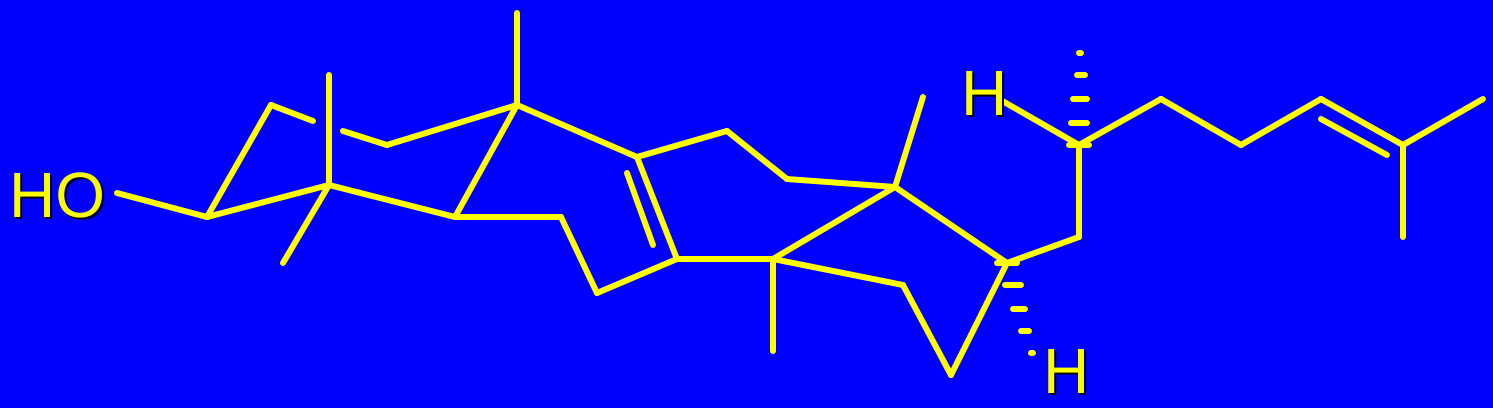


Loss of a proton is accompanied by a series of hydride shifts and methyl migrations.



Biosynthesis of Cholesterol

The product of this rearrangement is a triterpene called lanosterol. A number of enzyme-catalyzed steps follow that convert lanosterol to cholesterol.



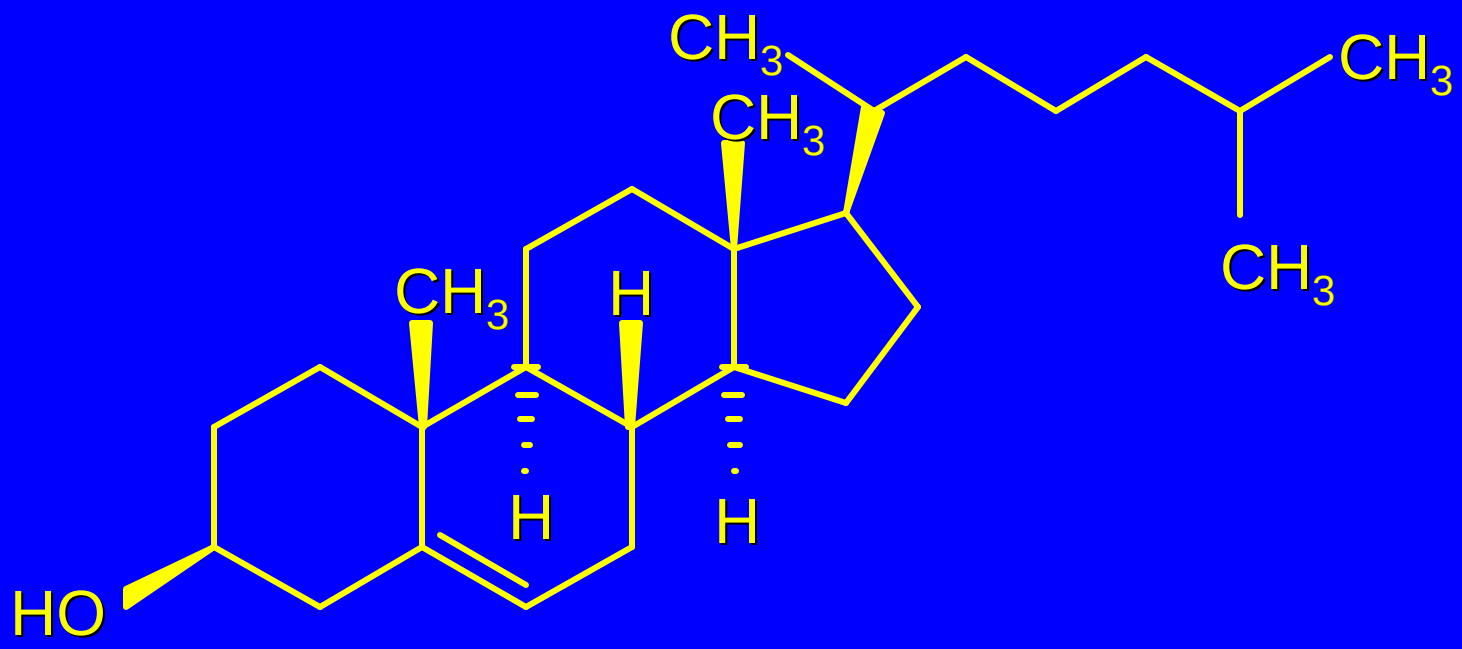
Cholesterol

Cholesterol is the biosynthetic precursor to a large number of important steroids:

- Bile acids
- Vitamin D
- Corticosteroids
- Sex hormones

26.12
Vitamin D

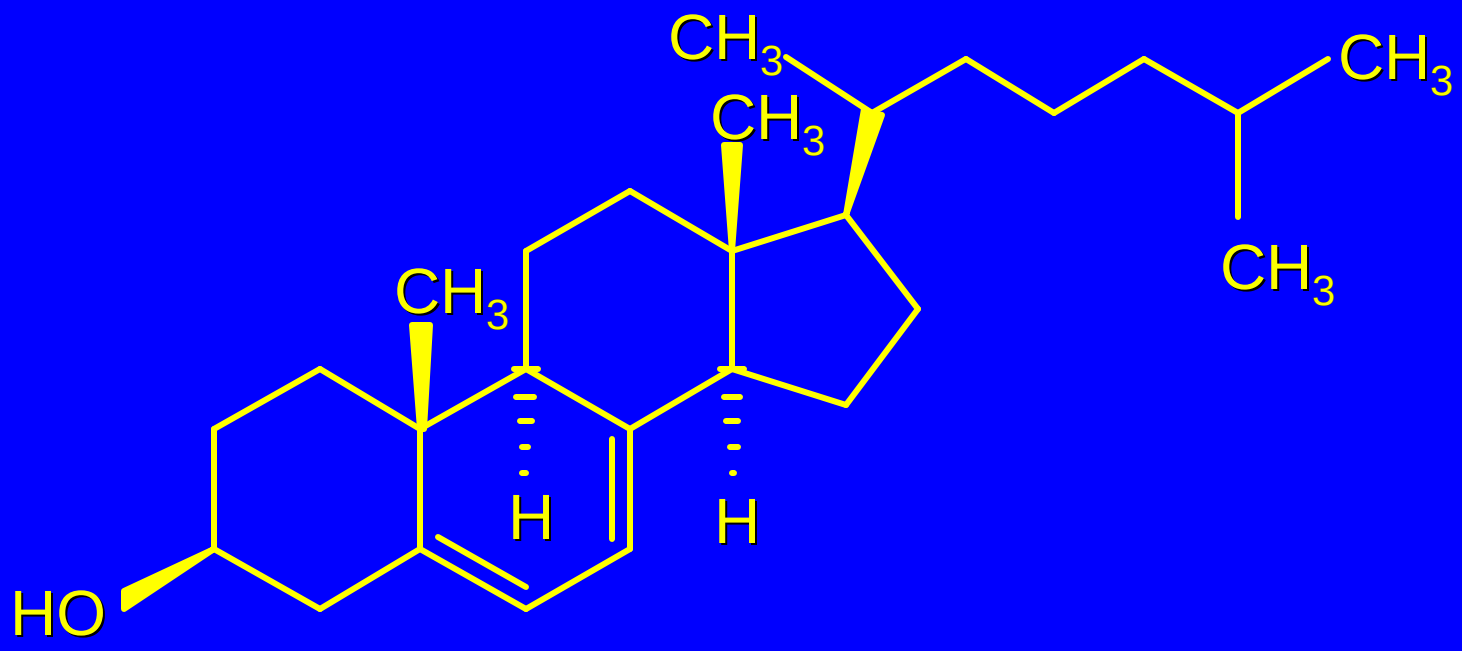
Cholesterol



Cholesterol is the precursor to vitamin D.

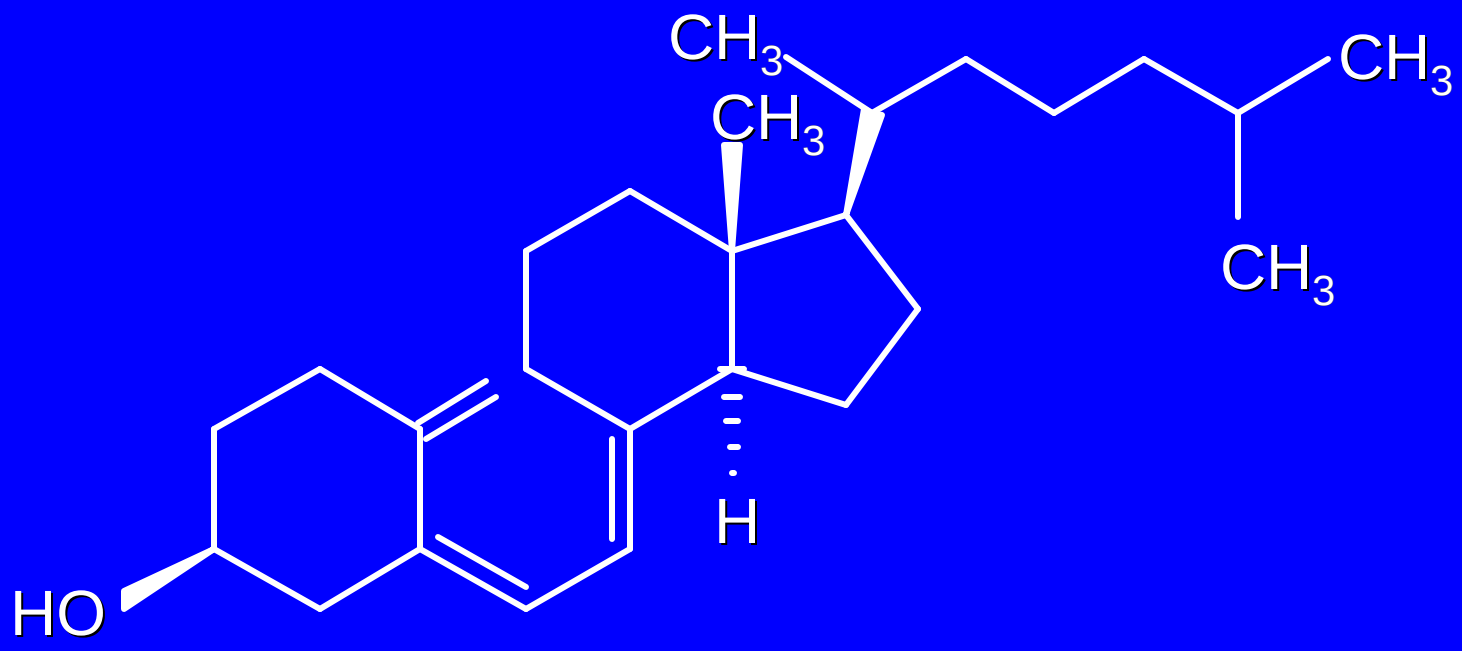
Enzymes dehydrogenate cholesterol to introduce a second double bond in conjugation with the existing one. The product of this reaction is called 7-dehydrocholesterol.

7-Dehydrocholesterol



Sunlight converts 7-dehydrocholesterol on the skin's surface to vitamin D_3.

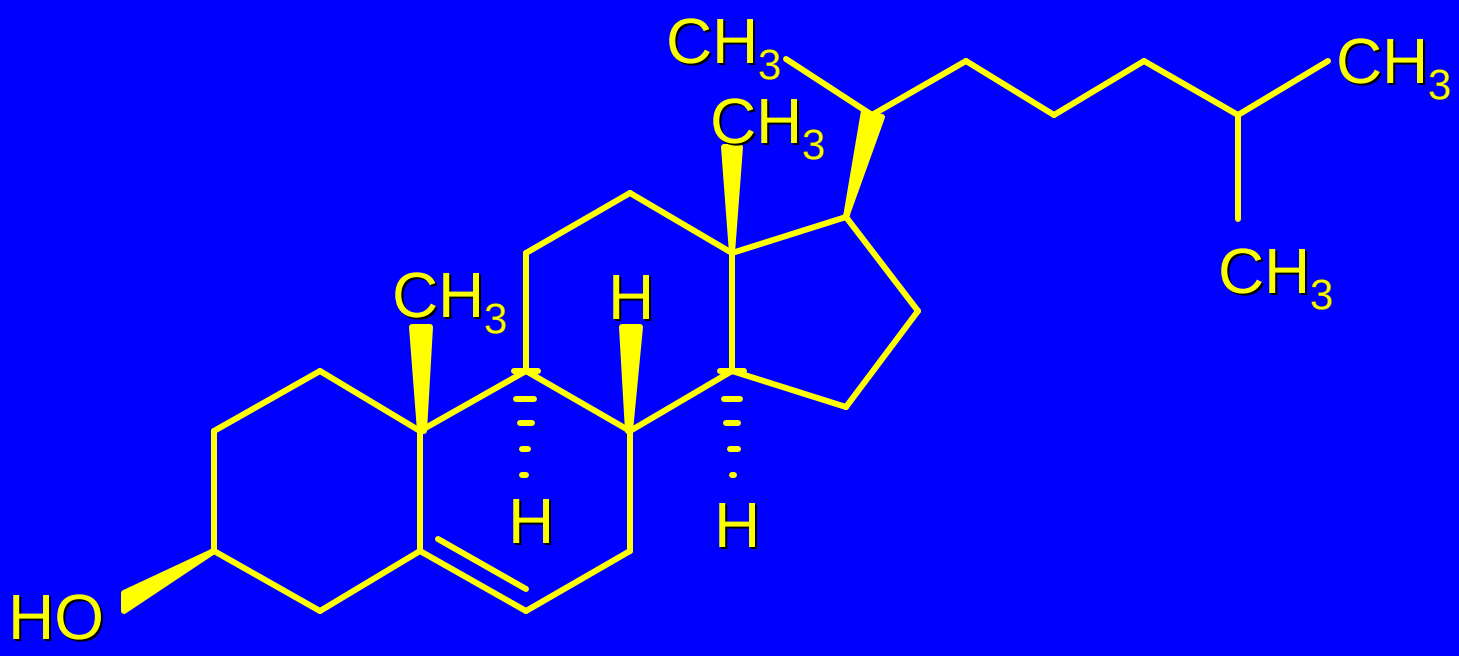
Vitamin D_3



Insufficient sunlight can lead to a deficiency of vitamin D_3, interfering with Ca^{2+} transport and bone development. Rickets can result.

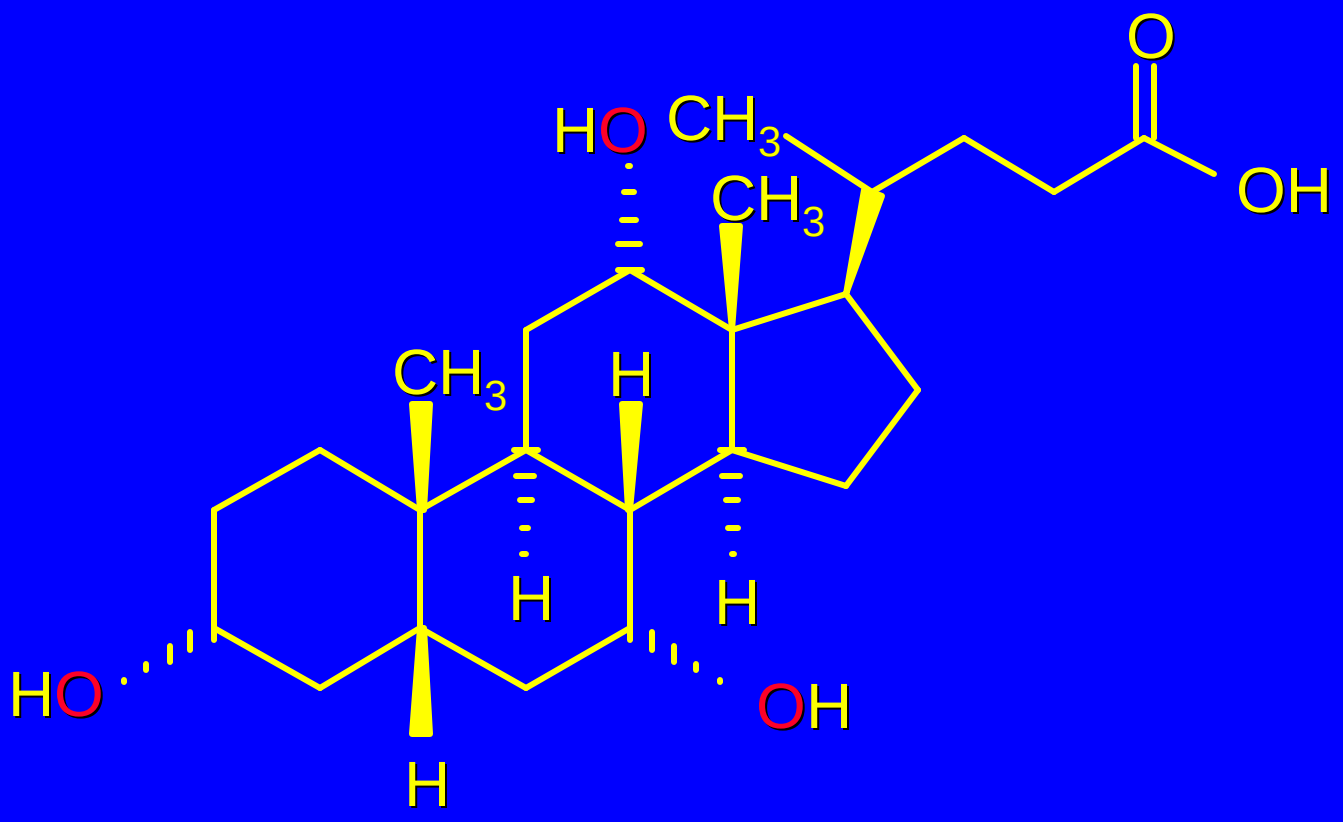
26.13
Bile Acids

Cholesterol



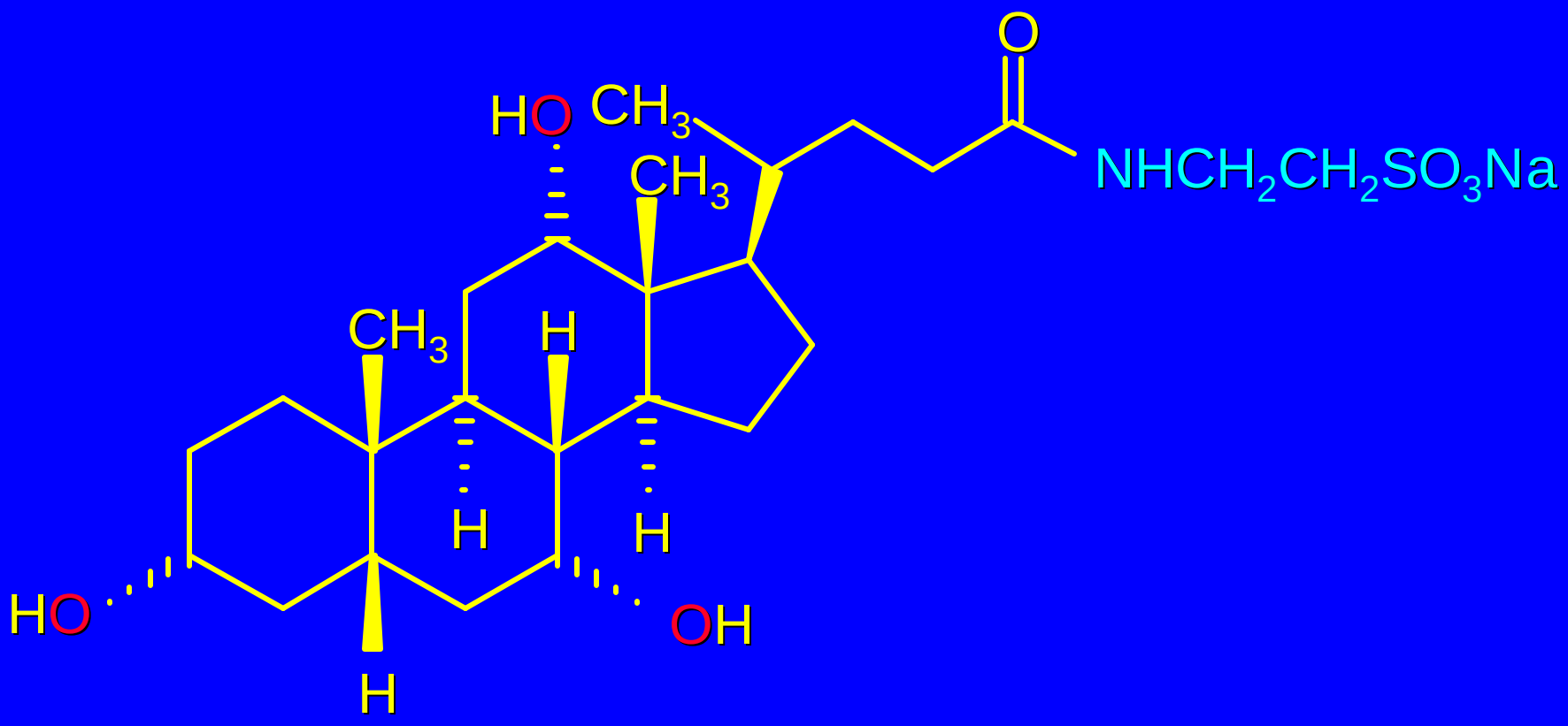
Oxidation in the liver degrades the cholesterol side chain and introduces OH groups at various positions on the steroid skeleton. Cholic acid is the most abundant of the bile acids.

Cholic Acid



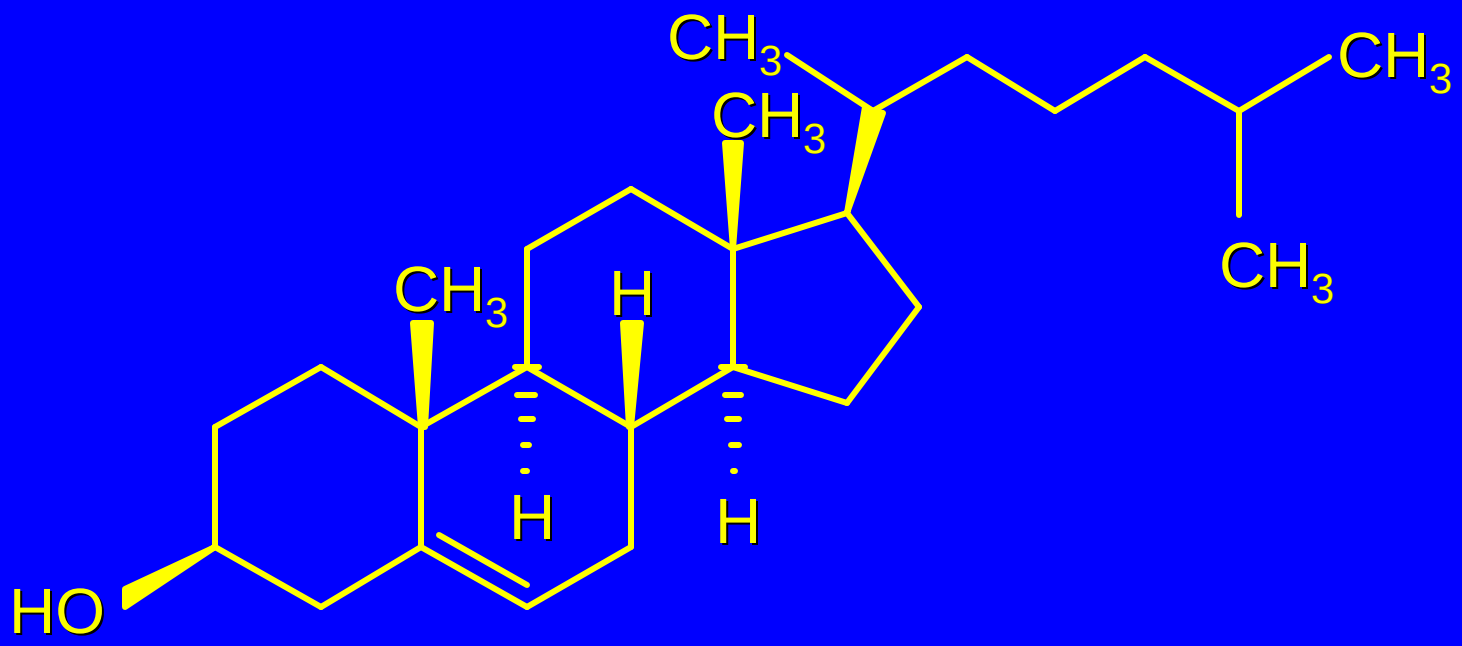
Salts of cholic acid amides (*bile salts*), such as sodium taurocholate, act as emulsifying agents to aid digestion.

Sodium Taurocholate



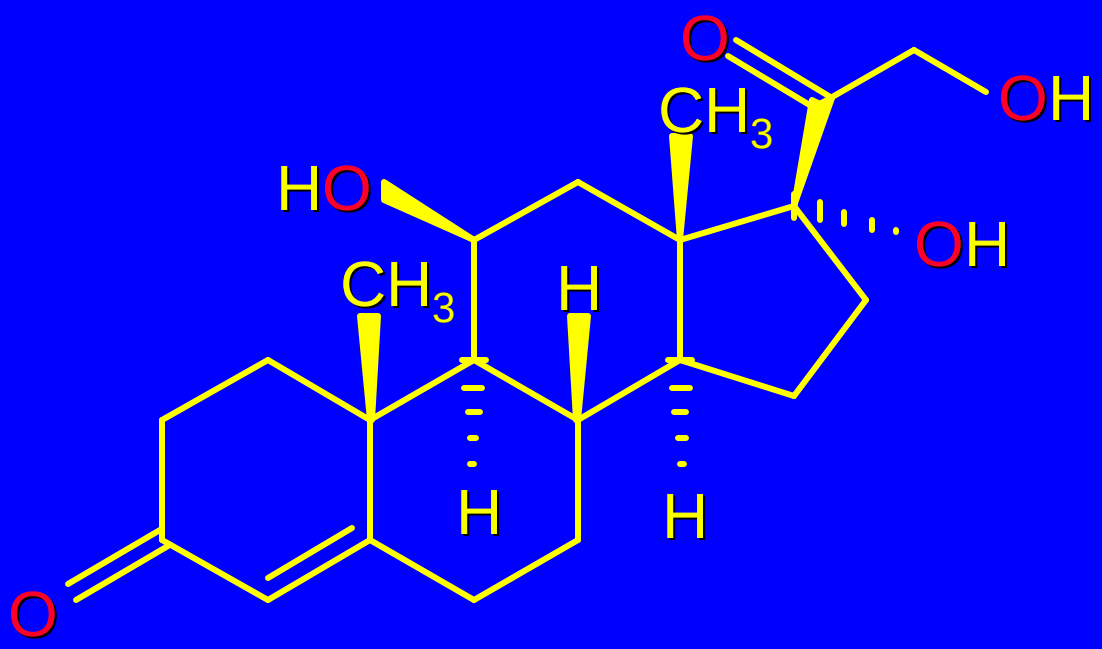
26.14
Corticosteroids

Cholesterol



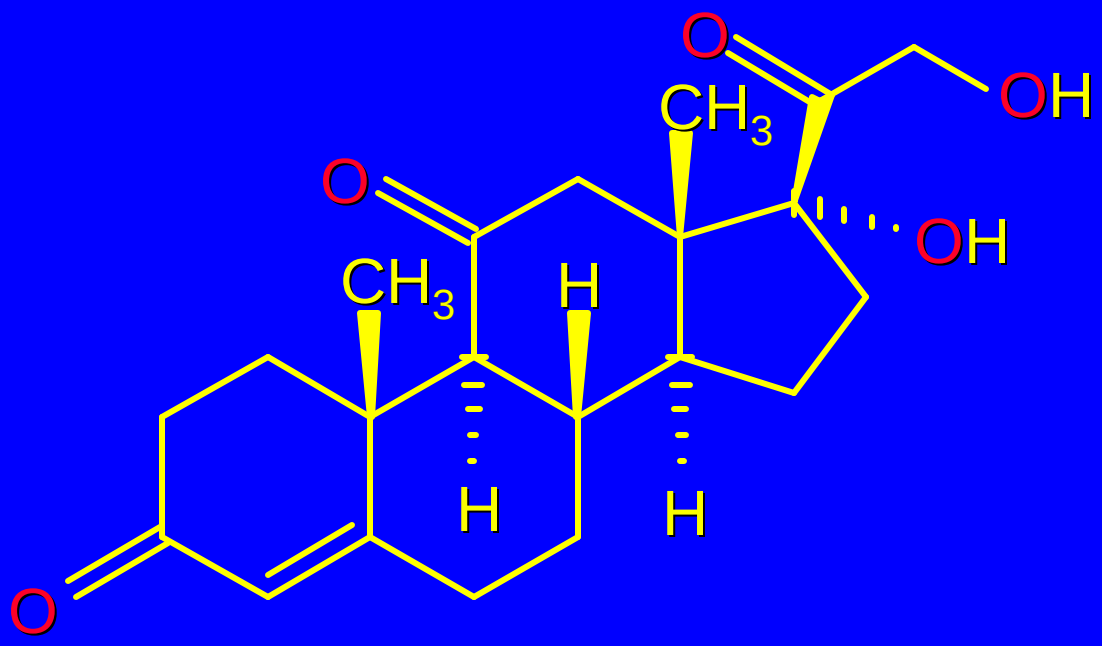
Enzymatic degradation of the side chain and oxidation of various positions on the steroid skeleton convert cholesterol to *corticosteroids*.

Cortisol



Cortisol is the most abundant of the corticosteroids.
Enzyme-catalyzed oxidation of cortisol gives cortisone.

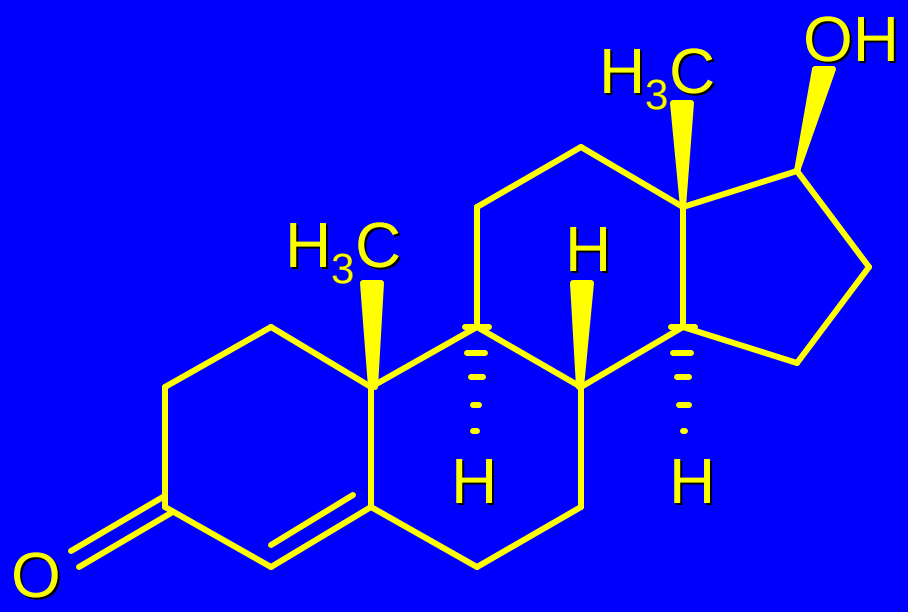
Cortisone



Corticosteroids are involved in maintaining electrolyte levels, in the metabolism of carbohydrates, and in mediating the allergic response.

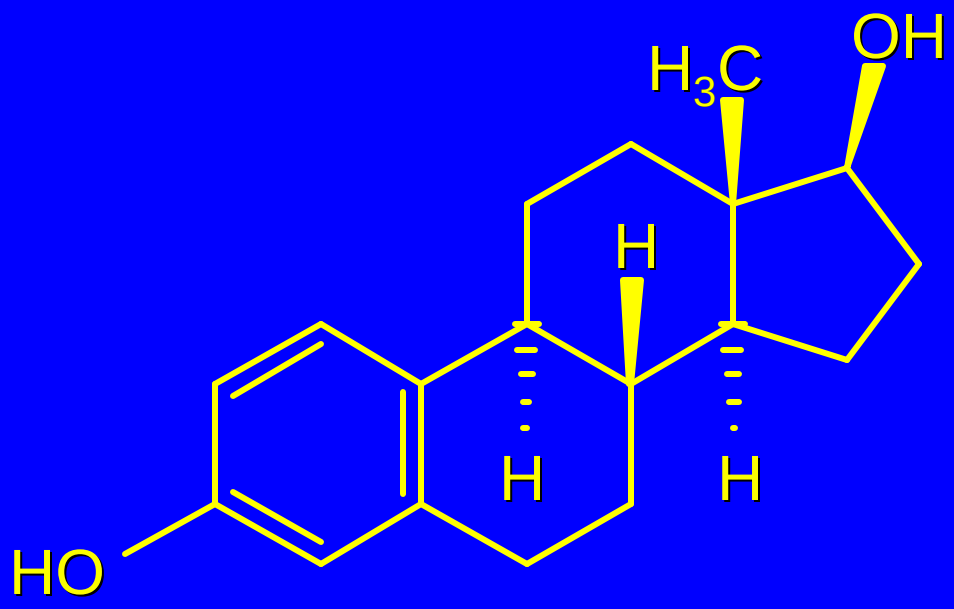
26.15
Sex Hormones

Testosterone



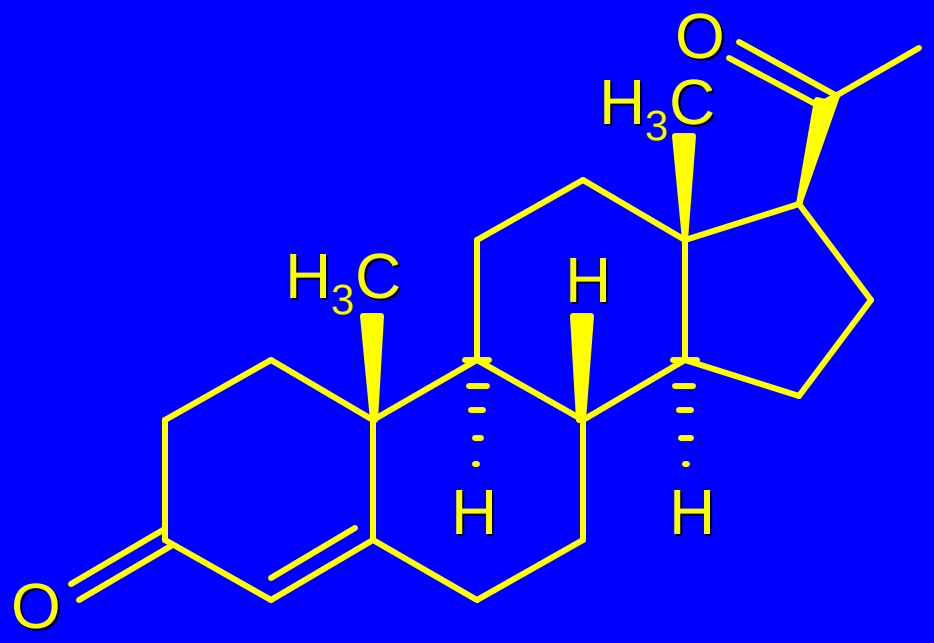
Testosterone is the main male sex hormone.

Estradiol



Estradiol is a female sex hormone involved in regulating the menstrual cycle and in reproduction.

Progesterone



Supresses ovulation during pregnancy.

26.16
Carotenoids

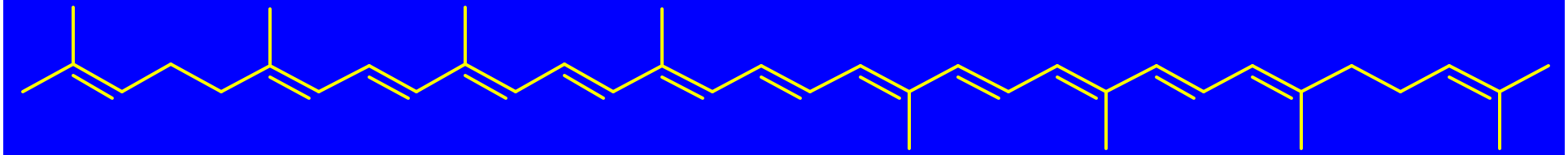
Carotenoids

Carotenoids are naturally occurring pigments.

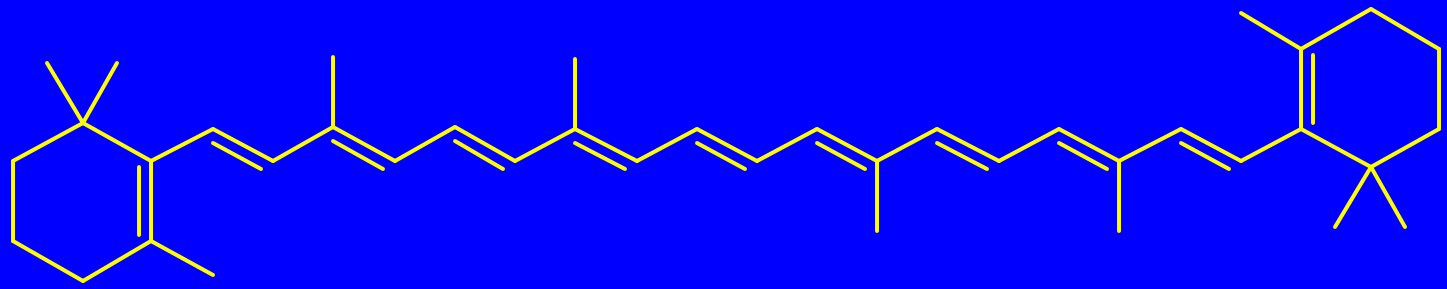
Structurally, carotenoids are tetraterpenes. They have 40 carbons. Two C_{20} units are linked in a tail-to-tail fashion.

Examples are lycopene and β-carotene.

Carotenoids



Lycopene (tomatoes)



β-Carotene (carrots)