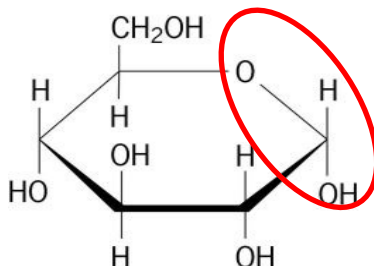


to form an 'internal' hemi-acetal. Which particular carbon atom depends on the bond lengths and angles, the **C-5 atom** is appropriate.

Reducing group

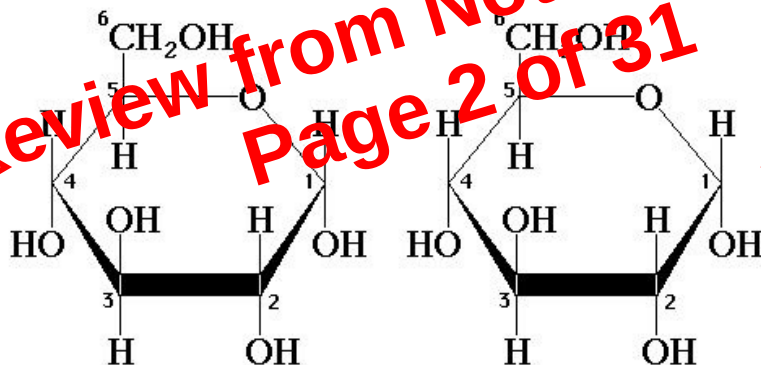


You will see that the fact of ring closure introduces a new asymmetric carbon atom at C-1. There are therefore 2 forms of D-Glucose called α (alpha) and β (beta) respectively. These are both forms of glucose (i.e. they are the same sugar) but the difference is important.

Other ring structures are found in fructose and the **five-carbon** sugars of ribose and deoxyribose.

The hydroxyl group on C1 is special, being 'hemi-acetal' its capable of condensing with another alcohol (hydroxyl) group to form a full acetal. If the group is another sugar, then polymerisation is possible. The simplest polymer is a **dimer**. Thus, two molecules of glucose may condense to form the **disaccharide** maltose.

Non-reducing end



Reducing end

The hydroxyl group on the C1, on the right, is a reducing (hemi-acetal) and can condense with another to lengthen the chain length more or less indefinitely. In such a chain, the end with the "free" -OH on the C1 is called the "reducing end". The other end (C4) is called the "non-reducing end".

A chain comprising up to eight molecules of a monosaccharide is called an oligosaccharide.

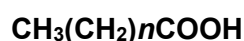
Branching is introduced into straight amylose chains by the creation of α 1-6 links, as found in isomaltose.

Most lipids contain, or are derived from fatty acids and they perform many important biological functions:

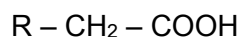
1. Triacylglycerol's (triglycerides): a fuel store of the body (fat).
2. Phospholipids: crucial constituents of biological membranes.
3. Steroids: cholesterol and bile function
4. Eicosanoids: Metabolised from lipids, including prostaglandins: signalling molecules within cells.

Upon hydrolysis, fats and oils yield fatty (aliphatic) acids and glycerol. Since a fat is ionically 'neutral' the hydrolysis products must have been derived from an ester (i.e. of glycerol).

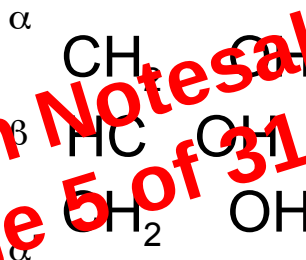
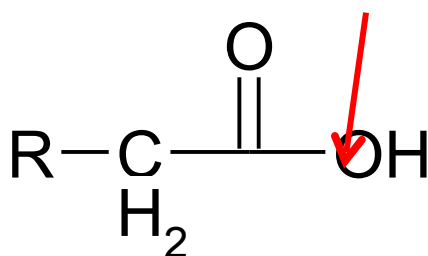
Fatty acids (a homologue of acids: acetic, ethanoic) are characterised by an alkyl chain with a terminal carboxyl group. Usually have an even number of carbon atoms.



The hydrophobic side chain is typically depicted by 'R':

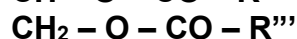
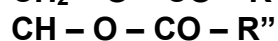
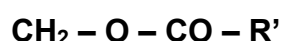


Fatty acids are esterified to glycerol to make a fat.



A triacylglycerol (fat or oil) may thus be

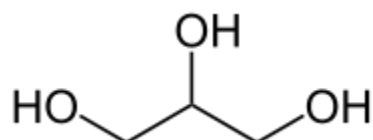
depicted as:



R', R'' and R''' may be the same or different fatty acid (usually an even number).

Saturated:

Since glycerol is a simple molecule:

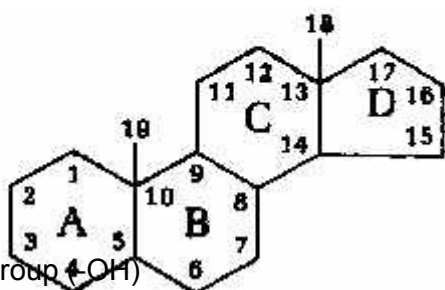


And is common to all fats, the variation between fats is due to variation in the fatty acids. The most commonly occurring ones are simple, saturated and unbranched:



Saponification means the hydrolysis of the fatty acids using NaOH giving the products free glycerol and the sodium salt of the fatty acid (e.g. sodium stearate – “soap”) hence saponification – “soap making”.

The structure of steroids is based on the three ringed compound perhydrocyclopentanophenothrene.



Hydroxyl group (OH)

There are dozens, if not hundreds of derivatives based on this structure, the most widespread of which is **cholesterol**.

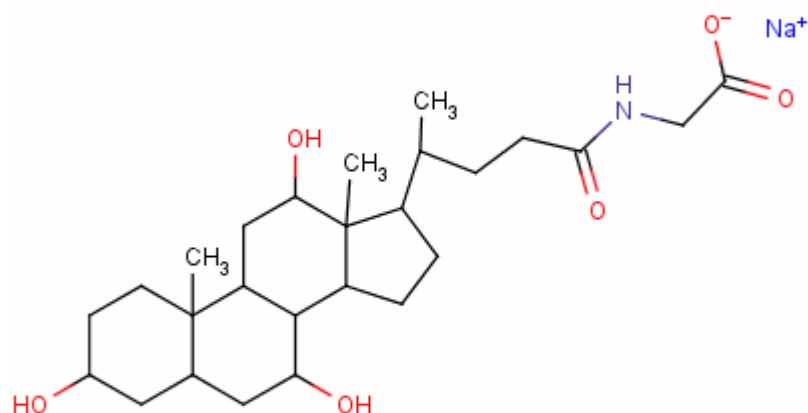
The properties of cholesterol depend on the properties of the functional groups:

1. The –OH may be esterified, reduced or chlorinated.
2. The double bond may be hydrogenated, brominated etc.
3. The side chain may be modified or substituted.

In vivo, cholesterol is not especially active. It tends to accumulate as gallstones or clogging coronary arteries. However, its derivatives are important.

The ring structure of cholesterol cannot be metabolised to CO₂ and H₂O in humans. Excretion is via the liver and gallbladder into the intestine as bile acids. To convert to a **bile acid** (salt) the cholesterol is metabolised with a carboxyl group –COOH, cholic acid). This group is esterified, usually with one of two amino acids (reacting with the amino group or glycine or taurine) to form a peptide link.

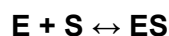
Glycocholate:



The sodium salts of these form sodium glycocholate and sodium taurocholate, respectively.

Enzymes differ from inorganic catalysts:

- They are more specific. Normally catalysing a single reaction
- One to one. One molecule of enzyme reacts with one molecule of substrate reversibly. To form an enzyme-substrate complex.



The presence of an enzyme is detected by the reaction it catalyses and its activity is defined as the rate of *velocity*, V , of the reaction.

There are 2 specific measures of activity:

- Activity – is the simplest rate of the reaction measure in terms of mass of substrate converted per unit time. Usually $\mu\text{mol min}^{-1}$. **An enzyme unit is the amount of enzyme that will catalyse the conversion of $1\mu\text{mol}$ of substrate in 1 minute.**
- Specific activity – is a measure of purity: *activity (product formed) per mg of enzyme present.*

E.g.

An incubation mixture containing 0.1cm^3 of enzyme preparation (removed from a stock bottle containing 10cm^3) was found to convert $30\mu\text{mol}$ of substrate in 10 minutes. *How many units are there in the stock? What is the activity?*

$30\mu\text{mol}$ converted to one minute is therefore $30/10 = 3\mu\text{mol min}^{-1}$

Therefore there were 3 units in the incubation mixture supplied a 0.1cm^3 . In the 10cm^3 of original enzyme there are 300 units.

Basic procedures:

The reaction is to be measured. It takes place in an incubation mixture. This normally comprises of:

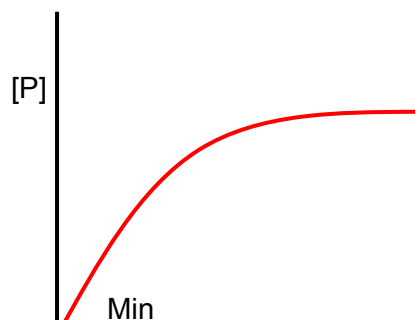
- A solute
- A substrate
- A buffer (an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid)

Plus any coenzymes (e.g. NAD^+) that may be required.

The enzyme is normally added last, and this starts the reaction time = 0 (time zero).

E.g.

A sample (aliquot) of the incubate is removed at regular timed intervals (e.g. 1 min) and the amount of substrate (or product) is assayed. A time plot is constructed – it's easier to think in terms of a product produced. The plot will look something like this:



Why does the curve flatten out?

- a) The enzyme might be being used up.
- b) Enzyme might be becoming inactivated.

- **2 carbon atoms (as CO₂) (NOTE the input was from 2C's from the acetyl)**

Energy powerhouse:

- Acetyl CoA is generated from the oxidative decarboxylation of pyruvate
- Under aerobic conditions, the reactions of this process, citric acid cycle, take place in the mitochondria of eukaryotes. In contrast with those of glycolysis that take place in the cytoplasm.

Step 1:

The reaction is catalysed by **citrate synthase**

Step 2:

The reaction is catalysed by **aconitase**

Step 3:

The oxidative decarboxylation of **isocitrate** is catalysed by **isocitrate dehydrogenase**. The first of 4 oxidative reactions.

This oxidation generates the first high transfer potential electron carrier, NADH, in the cycle

Step 4:

A further decarboxylation generates **succinyl CoA** from **α-ketoglutarate**, catalysed by α-ketoglutarate dehydrogenase complex.

Step 5:

The reaction is catalysed by **α-succinyl CoA synthase**.

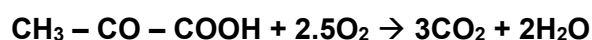
Step 6 and 7:

The final stages of the cycle are reactions of 4C compounds and constitute the final stages of the citric acid cycle: regeneration and oxidation.

Succinate is oxidised to **fumarate** by **succinate dehydrogenase**. **Malate** is oxidised to form **oxaloacetate**, catalysed by **malate dehydrogenase**.

Stoichiometry:

The balance equation for the complete oxidation of pyruvate (last stage of glycolysis) to CO₂ and H₂O in the citric acid cycle is:



C=3 H=4 O=8

C=3 H=4 O=8

Can we account for the items in this equation?

- First CO₂
 - There are 3 decarboxylation reactions (pyruvate, isocitrate, α-ketoglutarate) therefore CO₂ balances.
- Second O₂
 - 2.5 molecules of O₂ represent five atoms of oxygen there are 5 oxidation steps:
 - Oxidative decarboxylation of pyruvate (NAD⁺)