

The **flagship** magazine for **A-level chemistry**

# Chemistry

Volume 20 Number 2 November 2010

## review



## Fight or flight?

Organic chemistry and hormones

### Plus

Build your own experiment

Improve your calculation skills

Hydrogen bonds that can stop a bullet



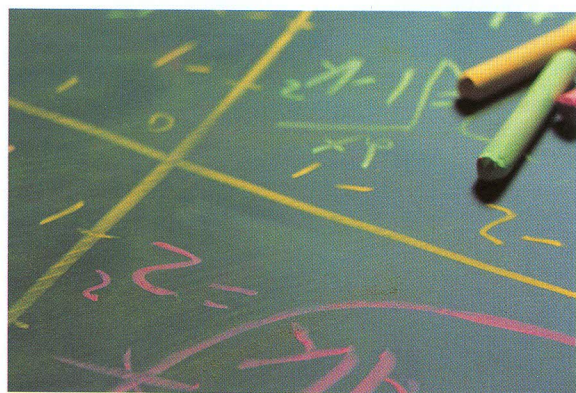
**PHILIP ALLAN**  
UPDATES

[www.philipallan.co.uk/chemistryreview](http://www.philipallan.co.uk/chemistryreview)





## Chemistry in the atmosphere



Improve your calculation  
skills

### UK's leading conference provider...

Philip Allan Updates runs more student and teacher events in more subjects than anyone else. Visit [www.philipallanupdates.co.uk](http://www.philipallanupdates.co.uk) for our latest programme.

## 2 Falling in love

*Joanna Buckley*

## 7 Out of Thin Air

Atmospheric nitrogen

*Tim Harrison and Dudley Shallcross*

## 10 Using nature to preserve fish oil

*Stephen Beckett and Grahame Mackenzie*

## 14 Lab Page

Heating under reflux

*Maria Turkenburg and Isaac Bruce*

## 16 In Pictures

Magnetic marvel

*Ross Jagers*

## 19 Scientists of Substance

Kwilek: creator of Kevlar

*Gill Wroe*

## 24 Focus on Industry

Kevlar and composites

*Allan Clements et al.*

## 29 Answer Back

Calculations

*David Billett*

## 34 Back Page

Science beats food fraud

*Michael Morgan-Williams*



# Using nature to preserve fish oil

## exam links

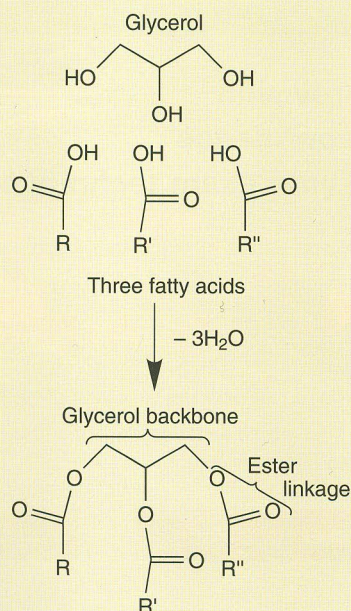
Fish oils are **esters** of fatty acids (**carboxylic acids**) and propane-1,2,3-triol (glycerol). To prevent fish oils from breaking down through processes such as **hydrolysis** and **oxidation** involving **free radicals**, a new process has been developed to encapsulate the oil in microscopic pollen grains.

**R**ecent research has shown that fish oils are particularly beneficial for your health. Unfortunately such oils do not keep very well, they often taste unpleasant and are therefore difficult to add to our normal food. In order to get around

these problems, chemists at the University of Hull have been enclosing (**microencapsulating**) the oil inside the shells of pollen particles. These particles are entirely natural and currently most of them are a waste material that just blows away in the wind.

## Increasing shelf-life

Box 1 explains the structure of the major type of molecule in fish oil, while Box 2 shows how it can change into a form that has a really bad taste. This happens very quickly in fish oils, particularly if there is any oxygen in the presence of light or a slight impurity (such as a metal). One way to help preserve oil is by placing it inside a container, which keeps it away from these two factors. Another is to add a chemical called an **anti-oxidant**, which can delay the breakdown. By filling the pollen particles with the oil, all three of these protective systems are in place. Because the oil is contained within the pollen shell, it becomes a powder that can easily be added to other foods.



R, R' and R'' are carbon-carbon chains of the fatty acid units possessing either single or double bonds, as in EPA (Figure 2)

Figure 1 A triglyceride.

### Box 1 What is an oil?

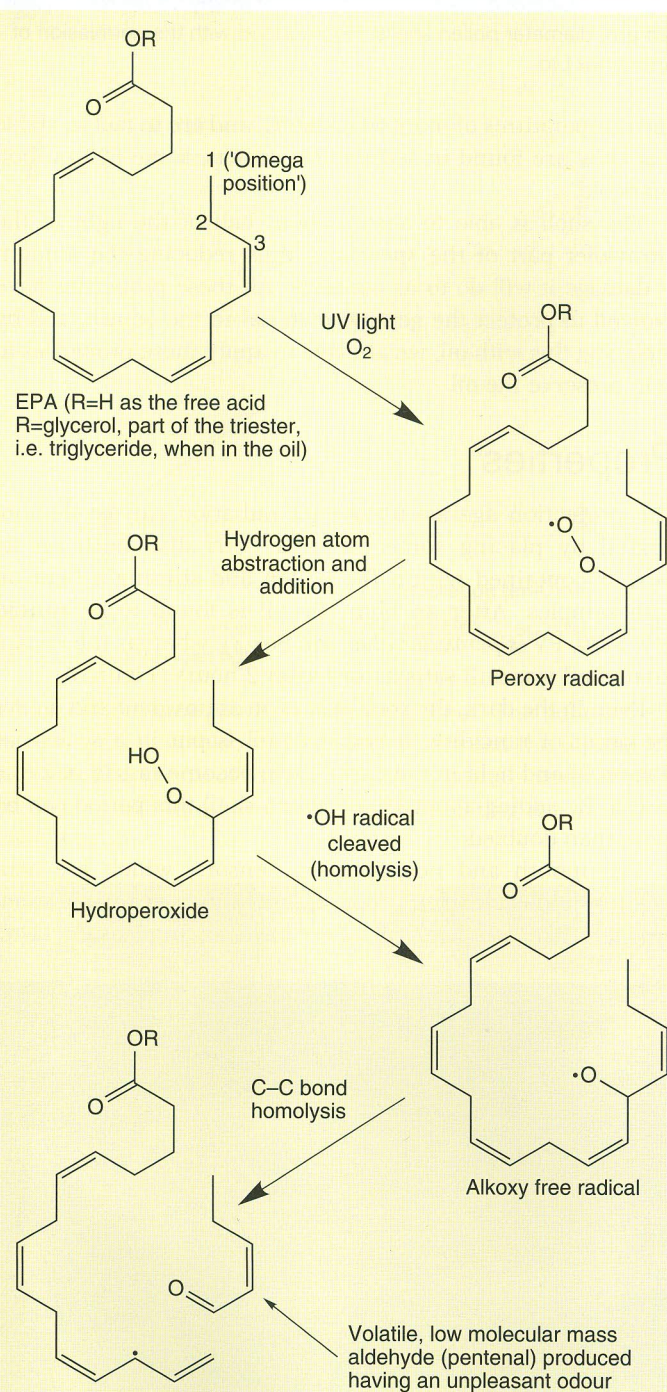
An oil is liquid at room temperature and a fat is a solid that will melt at higher temperatures. However, both are triglycerides (or triacylglycerols) that are composed of a glycerol 'backbone' (propane-1,2,3-triol) molecule, to which three fatty acid molecules are attached by **ester** linkages (Figure 1). A fatty acid is a long-chain carboxylic acid (see CHEMISTRY REVIEW, Vol. 15, No. 1, pp. 28–31). The difference in chemical structure between oils and fats is the number of double bonds in the hydrocarbon chain. A *saturated* fatty acid has no double bonds, whereas an *unsaturated* fatty acid has at least one double bond (we refer to a fatty acid with two or more double bonds as being *polyunsaturated*). The more double bonds in a fat molecule, the lower the melting point. Therefore oils have more double bonds than fats. Note that the chain length of a fatty acid also has an effect on the melting point, with longer chains melting at higher temperatures.



## Box 2 How do fats break down?

There are two major mechanisms, namely **hydrolysis** and oxidation. Hydrolysis, catalysed by either alkalis or **enzymes**, is able to split off fatty acids from the glycerol backbone (Box 1). Small free fatty acids in particular tend to have a really unpalatable taste.

Oxidation affects the free acid or triglyceride, present in an oil or fat. This rancidity involves breakdown of the fatty acid chains, initially at the methylene ( $-\text{CH}_2-$ ) between the double bonds, as shown in Figure 2. This gives several small molecules, mostly aldehydes such as pentenal, that are able to react with the sensors in the mouth, usually giving an unpleasant sensation.



**Figure 2** An example of oxidative rancidity.

## What is pollen?

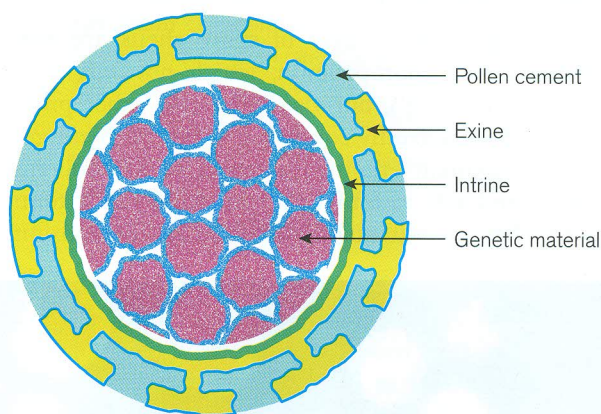
Pollen grains are effectively microcapsules that contain the male reproductive cells of most plants. The cross section of a pollen particle is shown schematically in Figure 3. The pollen is transported by wind or insects to another flower, where it can fertilise the female cells. In order to help the new plant grow it also contains all the nutritious components needed (i.e. fats, proteins and carbohydrates) and so pollen particles are very nutritious. Because of this, bees collect pollen from flowers (see photo on p. 10) to feed the grubs in the hive that will eventually develop into new worker bees. Some of the pollen gets stuck on the bee itself and is deposited on another flower, where it can fertilise this bloom.

Each pollen particle has a size and shape specific to the plant from which it originated. This has led to pollen identification being widely used in forensic science. Figure 4 is an **electron microscope** picture of pollen particles from *Ambrosia trifida* (giant ragweed) and shows how they are all identical.

The size of pollen particles can vary from forget-me-nots (*Myosotis* spp.) with a diameter of about 0.003 mm to squash (*Cucurbita pepo*) at 0.2 mm. The work at the University of Hull has concentrated on pollens with a diameter within the range 0.02 mm to 0.04 mm as these particles are big enough to hold a large proportion of oil and yet small enough not to feel gritty in the mouth if added to food.

## Preparing pollen shells

All the genetic material and pollen cement must be removed from the pollen (Figure 3). This can be carried out by soaking the pollen in an acid such as vinegar (ethanoic acid). This leaves a largely spherical double layered shell. The outer layer, or *exine*, is made of a tough polymer called sporopollenin. The

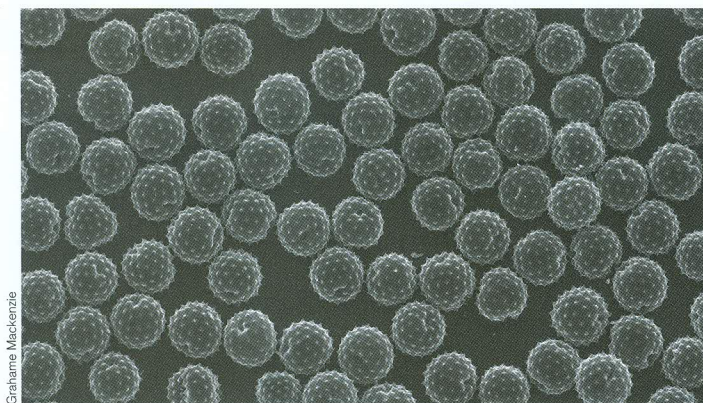


**Figure 3** Schematic diagram of a cross section of a pollen particle.

## did you know?

Sporopollenin, the material from which the outer coat (or exine) of the pollen grain is made, is the most durable, decay-resistant, natural organic polymer known. It seems to be a highly cross-linked biopolymer, but as it is so chemically stable, the precise composition of sporopollenin has not been fully determined because it cannot be degraded suitably by many enzymes or powerful chemical reagents.





**Figure 4** Scanning electron microscope (SEM) picture of 15 micron diameter *Ambrosia trifida* (giant ragweed) pollen. Reproduced with the permission of Sporomex Ltd.

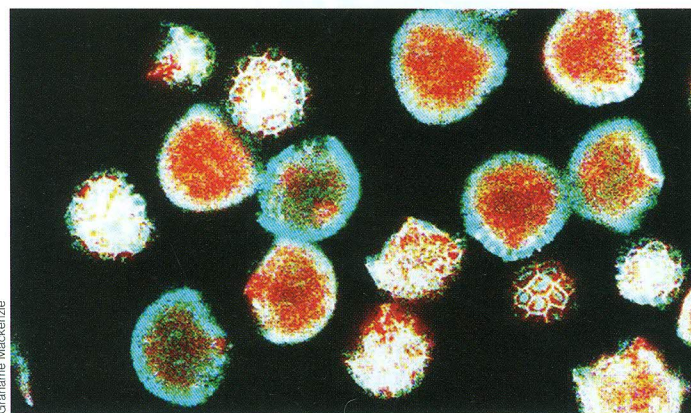
intine is the inner layer and largely composed of cellulose, which can be removed by heating in an alkali solution if required. The **confocal** laser scanning microscope enables cross sections of the particles to be viewed. Figure 5 shows the cross section of complete pollen particles while Figure 6 is a picture of empty pollen shells.

The empty shells can then be dried ready for refilling with the fish oil. The shell itself has very small holes (pores), less than 100 nm in diameter, through it. These can be seen in scanning electron microscope pictures of some pollen particles (Figure 7).

Some of these pores are **lipophilic**, which means that they attract fats, so if the empty pollen shells are put in an oil, the fat slowly enters the space inside the shell. The filling can be sped up by adding a small amount of ethanol to the oil or by placing the mixture inside a vacuum.

## Properties of pollen shells

The tough exine outer layer of spore shells are made of a polymer called sporopollenin, which not only makes it lipophilic ('oil loving'), but also has many other protective properties. Although only composed of carbon, hydrogen and oxygen (approximate empirical formula  $C_3H_5O$ ) pollen shells are elastic and able to remain intact under many tonnes of pressure. They can withstand acidic and alkali environments



**Figure 5** Confocal microscope picture of 25 micron (25  $\mu\text{m}$ ) diameter pollen particles. Reproduced with the permission of Sporomex Ltd.



**Figure 6** Confocal microscope picture of empty 25 micron (25  $\mu\text{m}$ ) diameter pollen shells. Reproduced with the permission of Sporomex Ltd.

and temperatures of more than 250°C, and are in fact so stable that they are found in sedimentary rocks, some 500 million years old.

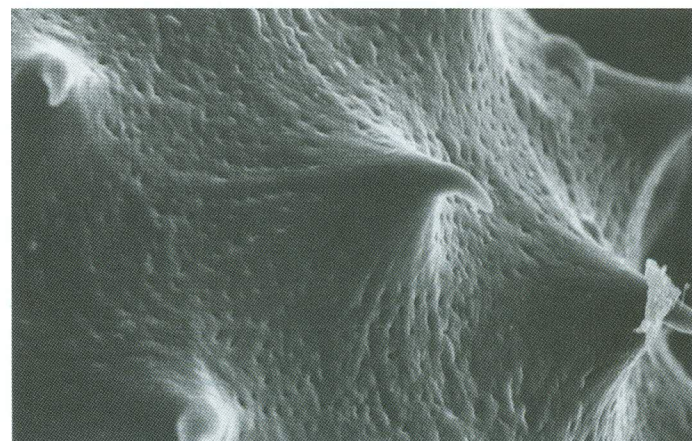
The shell is able to absorb about half of the light in the ultraviolet part of the spectrum, thus reducing the amount of damage it will do to its contents. All these properties have evolved to protect the genetic material in the centre, and by replacing this with oil, we are able to apply these properties to help preserve the oil.

## Properties

The protection against ultraviolet radiation can be demonstrated by placing some oil in a Petri dish both on its own or contained within the pollen and shining a light on both samples. After an hour the oil is found to be **rancid** (PV > 20, PV is *peroxide value*, see Box 3), whereas the encapsulated oil was still satisfactory after 2 hours (Figure 8).

Even in the dark, the shell acts as an antioxidant and delays the onset of rancidity. If cod liver oil is put in a sealed jar (Figure 9) and held in the dark, it will become rancid in 2 to 4 weeks. By adding about 1% of pollen shell this period can be more than doubled.

The mouth and nose contain sensors, which are activated by molecules from food and give us a taste sensation. Products like cod liver oil often have an unpleasant taste,



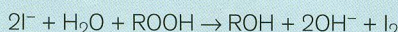
**Figure 7** SEM picture of *Ambrosia trifida* (giant ragweed) pollen particle. Reproduced with the permission of Sporomex Ltd.



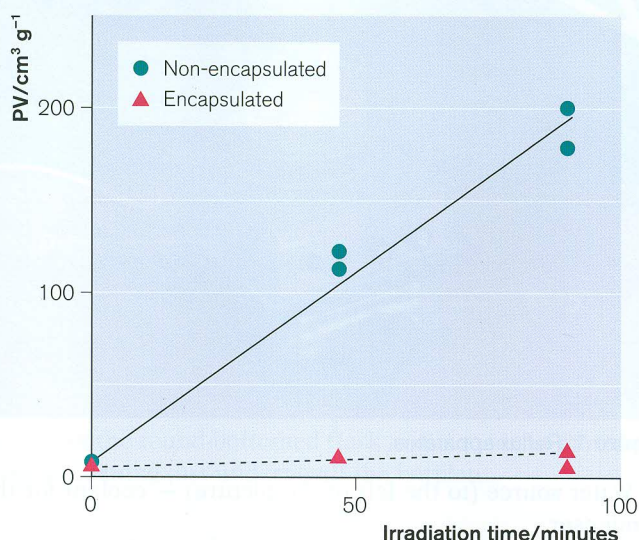
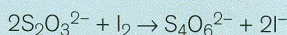
### Box 3 How can chemists measure rancidity?

Many different methods are available, but perhaps the most common is to measure the peroxide value (PV) of a fat or oil (Figure 8).

The peroxide value is determined by measuring the amount of iodine ( $I_2$ ), which is formed by the reaction of the peroxides (i.e. ROOH, formed by rancidity) with iodide ions ( $I^-$ ):



The base produced in this reaction is taken up by ethanoic acid. The iodine ( $I_2$ ) liberated is measured by titrating with sodium thiosulfate ( $Na_2S_2O_3$ ), using starch solution as an indicator (starch and iodine form a blue-black complex).



**Figure 8** Rancidity measurements (PV, see Box 3) against time of exposure to ultraviolet light

which discourages people from eating them. The pollen shells have no taste and also form a barrier between the oil and the sensors. The centre of the shell is able to contain several times its own weight in oil and yet the person eating it is unable to taste it at all.



**Figure 9** Bottles containing oil together with a small amount of pollen shell.

## glossary

**Antioxidant** compounds naturally present or added to oils and fats to inhibit oxidative reactions.

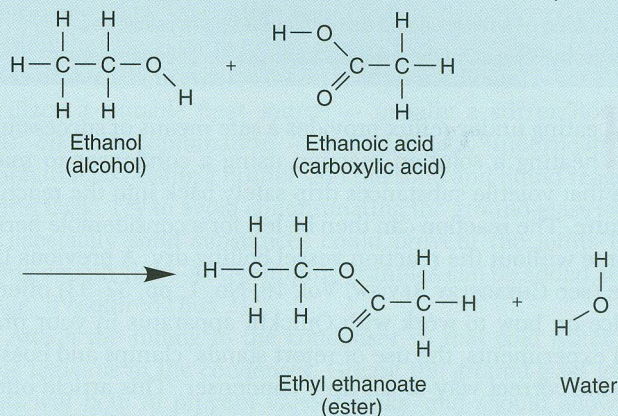
**Confocal microscopy** a technique to get high resolution, sharp images using a scanning laser light to illuminate one point at a time, building up an image that is entirely in focus.

**Electron microscope** uses a beam of electrons rather than a beam of light to view samples at high magnification and high resolution.

**Enzymes** mainly proteins, which are catalysts that increase the rates of chemical reactions but are returned chemically unchanged.

**EPA** eicosapentaenoic acid (see Figure 2, where R=H): it is an important omega-3 essential fatty acid.

**Ester** an ester is formed when an alcohol reacts with a carboxylic acid in a condensation reaction (i.e. water is eliminated). For example:



(For naming of esters, see CHEMISTRY REVIEW, Vol. 19, No. 3, pp. 11–12.)

**Hydrolysis** splitting of a molecule with water catalysed by an acid, base or enzyme.

**Lipophilic** a substance that is easily attracted to oils and fats and repels water.

**Microencapsulation** containing something in a shell so that the total particle size is in the micron range (approximately 1–100  $\mu\text{m}$ , i.e. 0.001–0.1 mm).

**Rancidity** development of off-flavours. This can be due to hydrolysis (in which the fat breaks down into fatty acids and glycerol). In addition, the double bonds in unsaturated fatty acids can be oxidised, often through reactions with radicals or reactions initiated by light (Box 2).

Oils and fats are an important part of our diet, but some, especially fish oils containing essential fatty acids (EFAs, so called because they are not synthesised in the human body) have a positive effect on our health, particularly on the heart and in cancer prevention.

We have shown how nature's method of protecting genetic material of plants can be used to preserve and help you eat fish oils. The same technique can be used to help deliver medicines. Further details about this work can be obtained from [www.sporomex.co.uk](http://www.sporomex.co.uk)

**Stephen Beckett** carried out research into chocolate for 28 years, and is currently the managing director of Sporomex Ltd and an honorary professor at the University of Hull. **Grahame Mackenzie** has researched pollen shells for more than 20 years. He is a reader in bioorganic chemistry at the University of Hull.