PHARMACOGNOSY AND PHYTOCHEMISTRY

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Week 2

Lecture 6

Week 2: Lecture 6: Introduction & Classification of Lipids

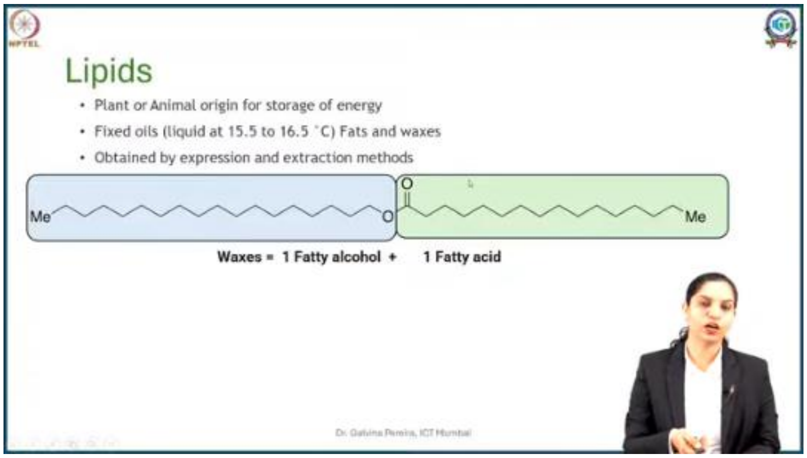
Hello everyone, and welcome to the NPTEL online course on Pharmacognosy and Phytochemistry. This week, we will learn about a very interesting set of compounds that are very lipophilic in nature, or what you can say, oily in nature. These compounds are lipids and volatile oils. So, let's delve into a week full of learning about these oleaginous compounds. Lipids, as the name indicates, are compounds that are lipophilic in nature. That means they are hydrophobic or soluble in organic solvents.

Plants and animals generate lipids. A good example of lipids is fatty acids. So, plants and animals generate fatty acids when they need to store energy. Lipids are primary metabolites, which are generally used by plants and animals to store energy. Now, if you examine lipids, we can divide them into fixed oils, fats, and waxes.

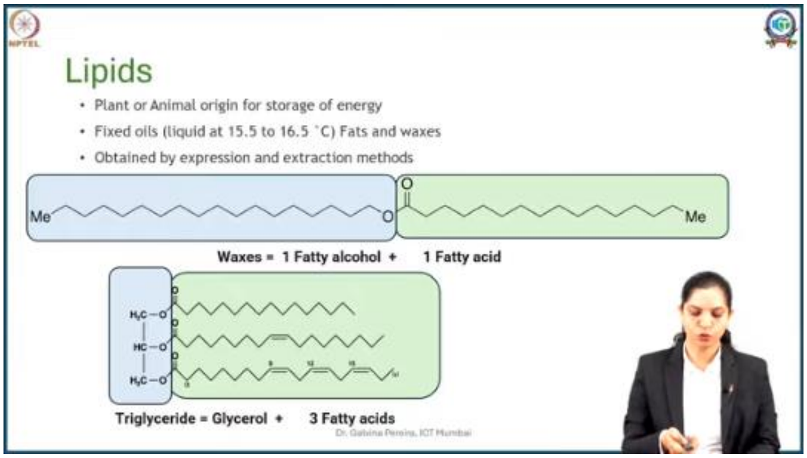
Of these, fixed oils are similar to your cooking oils, such as groundnut oil, and are generally liquids at room temperature. Fats are liquids at room temperature but generally solidify if the temperature drops below 15 degrees Celsius. So, below 15 degrees Celsius, they are solids, whereas waxes remain solid until their congealing point, which is very low. These lipids can be obtained from plants or animals by numerous techniques.

The easiest one is expression. Imagine your groundnuts are crushed and pressed between two extruders to extract the groundnut oil. Or the lipophilic substances can be dissolved in organic solvents such as petrol, hexane, or chloroform to dissolve all the nonpolar compounds. Once they are extracted, these nonpolar solvents can be evaporated. After evaporation, the residual compounds left are all lipophilic compounds.

Among lipophilic compounds, a simple example we can discuss here is waxes. So, what are waxes chemically? Chemically, waxes are esters. Now, if you observe carefully, this is a fatty acid, and this fatty acid is esterified with a long-chain alcohol. So, waxes are nothing but esters.



of long-chain fatty acids with long-chain alcohols, making them relatively high molecular weight and solid at room temperature, whereas oils or fats are not simple esters but are referred to as compounds called triglycerides. Why? Because they form esters not with one hydroxyl group but with three hydroxyl groups. So, three such fatty acids will form esters with three alcohols.



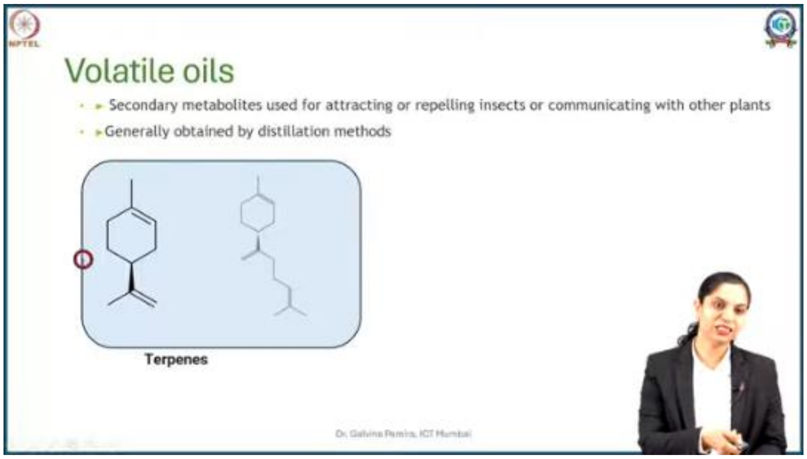
To give you what is called triglycerides. The reason why they are called triglycerides is if you see this moiety, which is highlighted in blue, this is your glycerol. So with every hydroxyl of glycerol conjugating and forming an ester linkage with a fatty acid, sometimes these fatty acids may be similar, sometimes these fatty acids may be dissimilar. So take a molecule of glycerol and take three fatty acids. When they conjugate with each other, they are called triglycerides. So if you see lipids, when it comes to your fixed oils or fats, they are generally triglycerides. Whereas if you see your waxes, they are generally monoester derivatives.

Now, a little different from that are volatile oils. Volatile oils have absolutely nothing to do with fatty acids. In fact, volatile oils are not primary metabolites. That means they are not generated by the plants to store energy. In fact, they are generated by plants and animals for attracting insects or repelling insects.

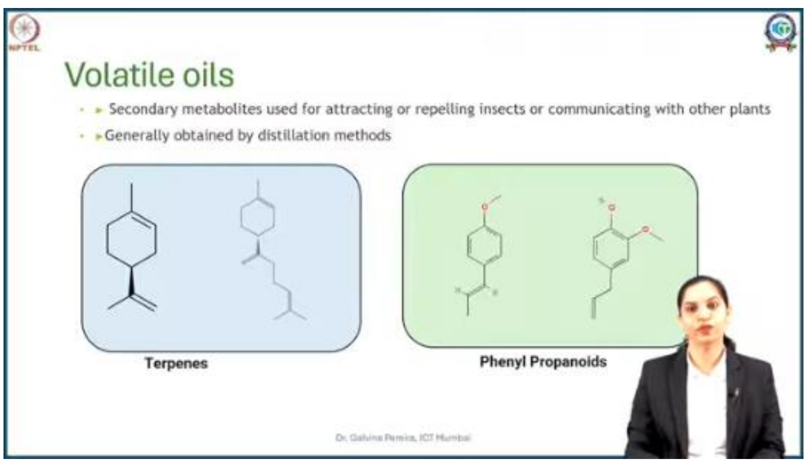
So if you take a whiff of a rose, you get a beautiful aroma. That aroma compound serves the purpose of attracting insects so that it can pollinate. On the other hand, there are certain plants, for example eucalyptus, in some cases the purpose of that is to repel insects. Or in some cases, the plants also secrete these aroma chemicals to communicate with each other. And there's a huge science behind it. The science is called allelopathy. So mutually, they communicate with each other, they show each other their strength, and they show each other they exist.

So these volatile or essential oils, which have a nice aroma, are produced as secondary metabolites in plants. Now, knowing that they are volatile, they are generally not expressed or pressed. They are generally distilled. They are volatile. They have a low boiling point.

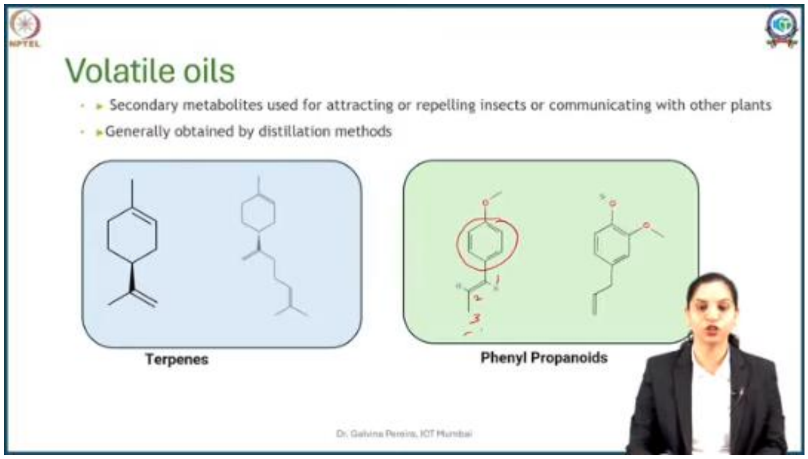
So if you distill them, they easily get collected as distillate, and you can get your pure aroma chemicals distilled out. So a few examples of volatile oils are those that belong to the class of terpenes. Here, I have two examples. If you see this, the first one is limonene, and this occurs in orange peel. And the second molecule, if you can see, is almost similar, but there is an adduct formed out here.



So five more carbons are added to it, and this compound is called bisabolene. So this occurs in the Zingiberaceae family. So you will see them occurring in ginger and so on. The next class of compounds in essential oils are phenylpropanoids. So phenylpropanoids are known for their phenyl ring.



And in addition to that phenyl ring, you will have 1, 2, 3 carbons, often referred to as propane. So the first structure here is the structure of an anethole, which is present in your phenyl. In restaurants, when you go after your meals, you've been served badi sauf or sauf or fennel fruits. These fruits have a nice flavor as well as a good aromatic taste. This is attributed to anethole.



Now, one more compound here is eugenol. This occurs in cloves and is also an example of a phenylpropane derivative. So your volatile oil, rather than containing long-chain fatty acids, contains beautifully small fragrant molecules, which are low molecular weight, belonging to the terpenes and phenylpropanoid class. Now, if I have to differentiate between lipids and volatile oils, the first point is that lipids are primary metabolites. Plants and animals produce them for the purpose of storing energy.

They are energy storage molecules, whereas if you see essential oils or volatile oils, they are secondary metabolites. They have more advanced functions like pollination or defensive roles. Or sometimes, some aroma chemicals are potent enough to kill plants in the vicinity as well. Now, if I talk about lipids, they are generally esters of fatty acids.

If you say you are. Fixed oils, or if you say fats, they are esters of glycerol. Whereas if you say waxes, waxes are esters of monohydric alcohols. Whereas if you see volatile oils, we just saw they are derivatives of terpenes or phenylpropanoids. Now, lipids or oils or fixed oils—if you see groundnut oil, if you see linseed oil, if you see mustard oil—these fixed oils are present in plants to a very large extent, especially if you see the seeds' oil. Seeds are laden with it, so just by pressing them, you can get the oil out. Whereas volatile oils are present in a much smaller percentage.

You know, in some cases, it may be just between 1 to 5 percent. And as a result, when you just press it, it might be difficult to procure essential oils. So lipids can be easily extracted by expression. Volatile oils, you'll have to distill the plant part to get the essence out of it. Now, coming to the next point: needless to say, lipids—because they are high molecular weight compounds and esters of big fatty acids with glycerol—have a very large molecular weight and a very high boiling point.

Whereas essential oils have a very low boiling point and can be distilled out very easily. Lipids can be further divided into fixed oils, which are liquid at room temperature and triglycerides, fats, which are solid below 15.5 degrees Celsius but still triglycerides, and waxes, which are esters of monohydric alcohols.

Essential oils can be categorized into two categories. One is called eleoptene. These are compounds that are liquids at room temperature. Take, for example, rose oil. It's liquid.

Whereas stearoptene are derivatives that are solid at room temperature. Examples include camphor, menthol, or thymol—these are essential yet solid at room temperature. Depending on their physical state, you can classify essential oils or volatile oils as eleoptene and stearoptene derivatives. Now, let us understand the differences between lipids. These are fixed oils, fats, and waxes.

As discussed, compounds like groundnut oil, which are liquids at room temperature, are called fixed oils. Substances that generally solidify below 16.5 degrees Celsius and are triglycerides in nature are referred to as fats. Waxes are esters of monohydric alcohols and are solids at room temperature. A good example of that is beeswax.

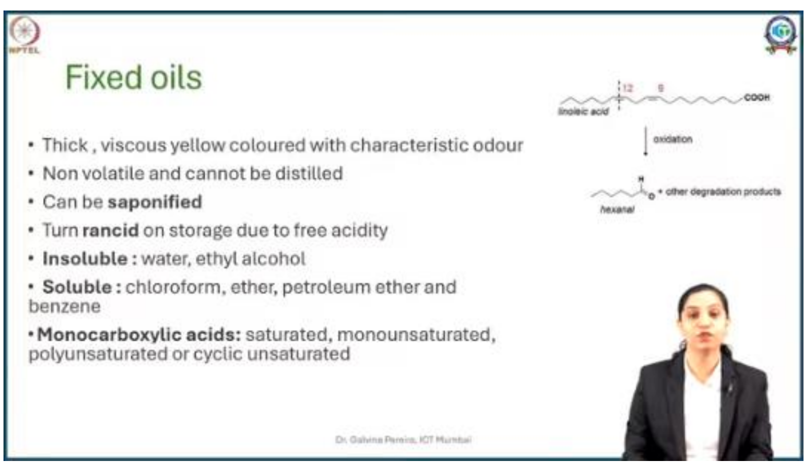
Now if you see esters or fatty acids in nature there are numerous fatty acids which are present ranging from different carbons length. This carbon can be as small as you know C3, C4, propionic, butyric acid and you can go on and on and add more carbons to it. So if you see a range like C12, C14, C16, C18 we refer to as your myristic, lauric, capric or even your stearic acids they form esters with glycerol to give you what are called as fixed oils. The degree of saturation determines their solid nature. So if you have more unsaturation they'll form liquid substances or liquid oils.

The moment there are saturated fatty acids especially saturated long chain fatty acids which are forming esters with glycerol in that case they form solid compounds below 16.5 degrees Celsius and they are referred to as fats. I'll exemplify this with a simple example. If you heard of vegetable ghee or dalda, that's basically a fixed oil and you know fixed oils are liquids at room temperature and they contain a number of unsaturated fatty acids. Suppose if you hydrogenate it, what is going to happen on hydrogenation is all those double bonds are going to get reduced and you are going to get more saturated compounds.

These saturated compounds create solids or these saturated compounds create more ordered structure and become solid and therefore are referred to as fats. So your vegetable ghee or dalda can be referred to as hydrogenated fixed oils or simple fats, which are solids at a temperature below 16.5 degrees Celsius. On the other side, your waxes, because they contain a large carbon fatty acid. Say for example, malic acid or C30, C32 fatty acids.

Now, here the carbon length is relatively large, and there is a huge ordered structure. And as a result, even at room temperature, these compounds remain solids. So they contain a higher ratio of high molecular weight saturated fatty acids compared to your fixed oils and fats. A good example of this is your fixed oil, such as groundnut oil.

A good example of fats is your dalda or vegetable ghee, and a good example of waxes is your beeswax. Now, if you see fixed oils—imagine groundnut oil, sunflower oil, or most of your cooking oils—they are thick and very viscous. slightly yellow to green color. Now, the interesting part is if you see fatty acids or glycerides, they are colorless. This yellow color of the oil actually comes from the pigments present in plants. For example, if you are extracting olive oil, olives are naturally green in color.



So, if you press those olive fruits, you will get green-colored oil because the chlorophyll and lipophilic pigments dissolve in it. Similarly, if you think about coconut oil, it does not have any pigments in it. And as a result, your coconut oil comes out very clear. Whereas, in some cases, seed oils will show pigments, especially from their hulls, contributing to a slight yellowness. Not only are they colored because of these pigments, but in some cases, the lipophilic compounds present also impart a characteristic odor to them.

Now fixed oils because they are not volatile cannot be distilled but you can easily convert them into soap. Now what happens is a classical saponification reaction. So if I am talking about a triglyceride on hydrolysis it will give me back my glycerol plus it will give me back my fatty acids. Now this hydrolysis is generally done in the presence of a base. So what is going to happen here is that hydroxy is generally replaced by alkali.

So you get sodium, salt or fatty acids which we refer to as soaps. In the process this hydroxy also get converted into their corresponding sodium salts and become more water soluble so you get soaps and fixed oils can easily saponify in fact most of your soaps that you use are sodium salts of fatty acids now one more thing is if those fatty acids are unsaturated that is if they contain double bond what is going to happen is they absorb or react with oxygen which is present

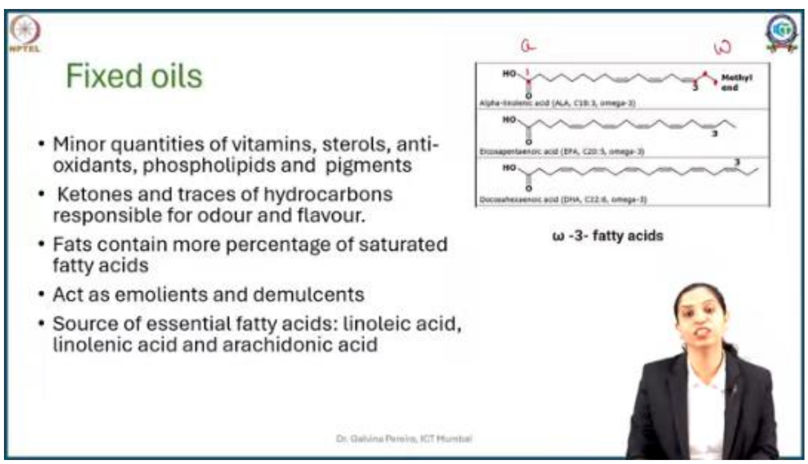
in the air they form what are called as initially peroxides and this peroxides later on cleave to give you aldehyde like derivatives. So a simple example of a cleavage at 12 will give you a hexenal and other degradation products. So if you see certain dry fruits especially your cashew nuts initially they'll have a good flavor but later on they turn rancid. Rancid is nothing but it's an odor and it's a flavor which is developed due to the presence of aldehydes in your drug. That can be your oils, that can be your fixed oils or that can be your oil containing substances such as dry fruits.

Now, if I take oil or cooking oil, you know, it's not going to be soluble in water. So they are highly lipophilic. They are insoluble in water. They are insoluble in alcohol. Bearing one, which is your castor oil, which is slightly soluble in alcohol, but they are happily or readily soluble in organic solvents.

These are your chloroform, ether or your diethyl ether, petroleum ether and benzene. Now, depending upon what makes the triglyceride, you can have saturated, monounsaturated, polyunsaturated fatty acids or cyclic unsaturated fatty acids. So if you see monounsaturated fatty acids, you must have heard of this name called MUFA. Monounsaturated fatty acids are commonly referred to as MUFA whereas polyunsaturated fatty acids are referred to as PUFA. PUFAs are generally considered to be good for your health.

A good example of PUFAs are your omega-3 fatty acids. Now omega-3 fatty acids derive their name from the omega unsaturation. So if you see IUPAC nomenclature, we generally number it from the first carbon. Now in Greek, you call it as your alpha or A. Now let's say the terminal or the last one. It is denoted by a Greek alphabet omega.

So if you start, this is called your omega-1. This is called omega-2, and this is called omega-3. The fatty acid derivatives in which the omega-3 is unsaturated are called omega-3 fatty acids. Now, they are essential for us because our body is unable to produce many of them. So we have to rely exclusively on external sources for their intake.



Now, why do we have to rely on them? Because they are essential components in our body, such as your cellular membrane and neuronal sheath. So if you see your health supplements, you must have heard of or read about EPA, DHA, or ALA. So what is this? This is your ALA, which is alpha-linoleic acid, an 18-carbon omega-3 fatty acid.

Eicosapentaenoic acid is a 20-carbon compound with five double bonds. So, eicosa is a C20 compound with five double bonds, the first one being at omega-3. Apart from that, there is also another important essential fatty acid: docosahexaenoic acid. This is a C22 compound with six unsaturations.

That is why it is hexaenoic acid. And it is also an omega-3. So these three fatty acids are considered essential for us, and they play a vital role in our body. Apart from that, when oils are extracted from plants, they also dissolve numerous lipophilic ingredients. Now, these lipophilic ingredients include vitamins, especially the oil-soluble vitamins, sterols like cholesterol, cytosterols or plant sterols, antioxidant compounds such as carotenes, phospholipids, and pigments such as chlorophyll.

Now, as they are produced, they also deteriorate and give aldehydes, ketones, and other derivatives. Now, these aldehydes, ketones, and other derivatives, which also make their way into the oil, are responsible for the flavor as well as the odor. So if you see fat, fat contains a higher percentage of saturated fatty acids compared to fixed oils. Now, all of these ingredients can be used as emollients. Emollients are substances that can prevent moisture from evaporating.

So especially during the cold, dry season, you'll see your skin turning very harsh or dry. Or very rough—in that case, if you want to prevent the evaporation of oil, you apply an oily layer. We apply creams, and these are referred to as emollients and, in some cases, demulcents. Now, a good source of essential fatty acids: We also have linseed, which provides linoleic acid, linolenic acid, and arachidonic acid. So here are a few.

Apart from that, we can have oils coming from marine sources as well. Now, with a chemical test, you can identify fixed oils by using sodium hydroxide. Now, this is a simple saponification test. So if you take your oil and saponify it with sodium hydroxide, you know you are bound to get soap. Now, this soap is going to be water-soluble.

So when you dissolve copper sulfate in it, which is a nicely water-soluble blue salt, you will see a homogeneous solution. Whereas if it is not a fixed oil—if it is something like a hydrocarbon or something like paraffin—it will not saponify. And as a result, your copper sulfate will form a distinct layer and will not dissolve. Another way to check if your compound is a triglyceride is by converting that glycerol into aldehyde derivatives or even ketone derivatives. For that, what you have to do is take some oil—about 5 drops—add a pinch of sodium hydrogen sulfate, and heat it.

The moment you heat it, it gets converted into acetol or sometimes 3-hydroxypropanol, which is further converted into acrolein. The typical acrolein or glycerin odor, if you detect it, indicates that it contains glycerol and therefore it's a triglyceride. Now, fixed oils can be classified depending upon their nature, especially as oils and fats are divided into drying, semi-drying, and non-drying. Now, if you refer to fats, they are going to be solid. Examples of that are cocoa butter, kokum butter, nutmeg butter, or coconut oil.

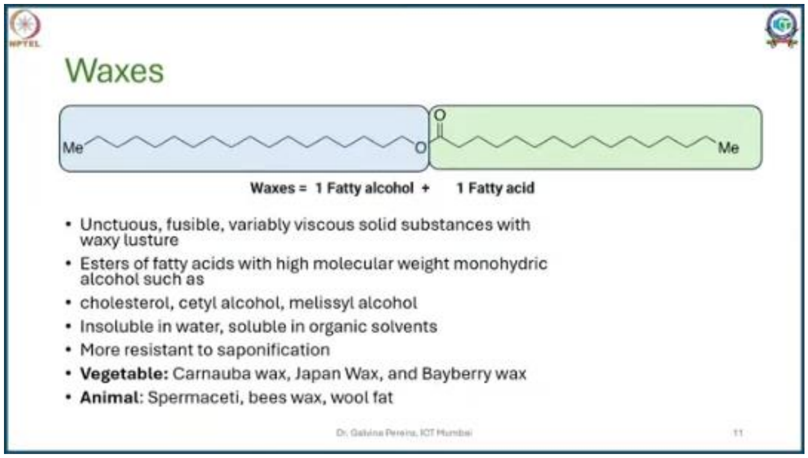
So they are generally solid, you know. They are considered solid at room temperature. Non-drying oils are the oils that will not change in their viscosity. Now, there is an important reason for it. Now, whenever the oils have unsaturation, this unsaturation causes them to oxidize and polymerize.

The moment they oxidize and polymerize, they form a film. So, when they dry and form a film, they are called drying oils. Good examples of drying oils are linseed oil, hemp oil, poppy seed oil, or walnut oil. Semi-drying oils have unsaturated compounds but slightly less. So they don't form a very strong film and do not dry out quickly.

Examples of semi-drying oils are castor oil, mustard oil, sesame oil, rapeseed oil, or cottonseed oil. Non-drying oils contain mostly saturated compounds, but with small chains. As a result, they don't resinify or form a film. Examples of non-drying oils are peanut, almond, croton, or even raspberry oil. Now, if you look at animal sources, you can obtain oils and fats from animals as well.

This includes your marine animals such as your fish. So from fish, if you take the bones, you can get your bone tallow, which are fats. Or if you take your liver—you know, your cod liver or shark liver oil—which is obtained by heating the livers of cod and shark, you can get your whale oil from the skin and parts of a whale. Apart from that, there are certain terrestrial animals which are used for that. So, you know, if you see your lard or mutton, you heat it, you get a good amount of fats which solidify at room temperature. And also some oils, such as your lard oil. So once the lard is solidified, you get a liquid around it.

That's referred to as lard oil. And there's also an animal which gives you neat-foot oil. So these are two sources or animal sources of your fats and oils. Now, comparing or coming to waxes, waxes, as we discussed, are made up of monohydric alcohols conjugated with one fatty acid. They are, you know, unctuous, fusible substances with a waxy luster.



They are high molecular weight, made up of monohydric alcohols. Generally, their constituent is a fatty alcohol or sometimes sterol, such as cholesterol. Fatty acid alcohol can be cetyl alcohol or melissyl alcohol. Fats are completely insoluble in water. They are lighter, less dense, so they float, and they are very resistant to saponification.

Some examples of waxes include carnauba wax, Japan wax, or bayberry wax, and from animals, the waxes that you get are spermaceti, beeswax, or even wool fat. Now, coming to volatile oils, they are very odorous principles. They evaporate when exposed to air or even at room temperature. That's where you have your perfumes. Because they have a nice aroma, they are called essential oils because they represent essences or odorous principles.

They are made up of terpene derivatives or phenylpropane derivatives. They may be the oxygenated derivatives present in various parts of plants. Unlike fixed oils and fats, which rancidify, these actually polymerize to form resinous derivatives. Examples of volatile oils include drugs like eucalyptus oil, which is your Nilgiri oil, and rose oil. So here are a few textbook references to this part of the lipids.

And thank you, everyone, for your patient listening.