PHARMACOGNOSY AND PHYTOCHEMISTRY

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Week 9

Lecture 41

Introduction to Resins

Hello everyone, Namaste, and welcome to Week 9 of the NPTEL course in Pharmacognosy and Phytochemistry. This week, we are going to learn about a new set of compounds called resins. So, what are resins? Resins are solid to semi-solid, amorphous, complex compounds secreted by plants and, in some cases, animals.

Earlier, when we learned about drugs of natural origin, we studied that drugs could be classified as organized and unorganized. Under unorganized drugs, we had gums, mucilages, and, if you recall, we also had latexes and resins. So today, let's delve deeper into what exactly resins are. Resins cannot be defined by any chemical formula because they have complex origins, but they are principally thought to be terpenoidal in nature. They are generally obtained as exudates. When you make an incision on a plant, what oozes out is similar to gums, but gums are carbohydrates. Compared to gums, resins have a more lipophilic nature and greater complexity in their structural attributes.

Resins do not occur in their pure form. When they ooze out, they often combine with other plant metabolites to form what are called resin combinations. Resins such as frankincense, which you may know for its beautiful aroma, or myrrh, are examples. Now if you see them this sink in water that means they have a specific gravity which is higher than water.

But if you take an example of resin such as copal, copal is little lighter than water. So all in all most of the resins are heavier than water but if you take into account even those which are lighter than the water on an average their specific gravity ranges somewhere between 0.9 to 1.25. Now what is their role in plant?

Now there are many theories to plants but the clear role of resins in plant is unspecified. In some cases where it is produced out of injury it is said that that is basically to deter insects from entering into the plants and to give some protection from weather, from water and from desiccation. Now in some cases resins have also proved to be compounds or combinations that can kind of seclude or isolate or even kind of take care of toxic metabolites which are present inside the plants or near the vicinity of the plants which might be attached to the plants and as a result in order to prevent it from entering the plant the plant might secrete such a resinous substances. A good example of resin is your frankincense. Now you might also come across dhoop that is your mir.

Those are also substances which are classified as resins. Now how are the resins biosynthesized? Having said that resins are not clearly defined but majorly terpenaceous in nature. Most of them occur by your terpenoidal pathways. Now we have seen in your terpenoidal pathways.

There were two pathways which were involved. So we have resins which are biosynthesized either by the acetate mevalonate pathway, which includes IPP and DMAPP, that is isopentenyl pyrophosphate and dimethylallyl pyrophosphate. Similarly, the same metabolites are also produced by the xylulose 5-phosphate pathway, which is the methyl erythritol pathway.

Now, apart from that, you might have certain resins, such as turmeric resins or in some cases ginger resins. These compounds are slightly different from what you call isoprenoids. So diagenesis is not part of the terpenoid pathway. Diagenesis is a phenylpropanoid pathway, often referred to as the shikimic acid pathway.

Apart from that, you will also find some resins which are biosynthesized via the acetate malonate pathway, in which the fatty acid chain is involved and linked with other compounds. Now, where are these resins located? In plants and animals, you might find resins located in different places. Now, let me give you an example.

In some plants, such as asafoetida (commonly known as hing, which is used in cooking dal), the resin is found in ducts. In that case, it is found in ducts. This plant has specialized ducts or cavities where the resin is stored. These ducts and cavities, depending on how they are formed, are classified into two types.

One is called schizogenous, and the second is called schizolysigenous. Now you can just imagine your schizogenous as your group of cells. So if I have to draw it imagine I have a cluster of cell. For ease I am just putting about 5 or 6 cells. So let's say I am putting 5 cells.

Over a period of time as the plant ages or matures what happens that this gaps between the cell increases and this leads to formation of cavity. So the same 6 cells will now be unified. But what has happened is you got a cavity in between. This cavity is what is called as a serogenesis cavity.

Now, in some cases, what happens is this goes a step ahead. So after schizogeny, there is lysogeny. That means this cells are going to break up. And as the cells break or sacrifice, you will see a more wider duct. So what happens in this case is schizogeny often happens.

And after that, lysogeny includes. Now, I'm just putting a little more cells here. For convenience, so some of the internal cells get ruptured. So I don't see a complete cell, I might see some ruptured cells, some intact cells, some cell walls are broken

and after that in the next layer the cells are completely intact. So the inner layer, the lysis of the cell has happened and that is why they are called as your schizolyslgenous cells or often referred to as your schizolyslgenous cavity. So schizogeny is when your cells go apart. Schizolyslgenous is when they go apart and after that the cells often sacrifice themselves

or break to create a much wider duct as compared to your schizogeny. So what happens in your asafoetida is your resin is stored in both schizogenous as well as schizolyslgenous cavities. Now in some cases such as ginger or in cases of blood root what happens here is the cells are already there and they are located as a normal physiological resin. So if you see the parenchymatous cells in ginger, so I am just putting it like random.

Now in some cases what will happen is one of the cell gets converted into a resinous cell. So you will see that inside this cell there is a nice resin filled in. So such resinous cells occur in ginger. They also occur in blood root where the underground parts of this plant contain a deep red resin. So when you cut it, this resin kind of is seen and often when you touch it, you will see that your hand turns a little reddish because of the blood root. Whereas in ginger, when you see a section, you can see the cells very clearly as a greenish yellow color cell containing it. And that is the cell or the resin inside it, which is responsible for containing compounds that give pungency to the ginger. So your ginger resin has to be extracted. It's not there in the pipe.

It's there inside the cell. Now, in some cases, it can be there in the elements of hardwood. So your tree trunk has what is called the outer, brighter sapwood and the inner, darker wood, which we call heartwood. So in some cases, like your guaiacum, it occurs that this resin is located inside it. So the only way you can get this resin is by sacrificing the tree trunk.

Take the heartwood, and in some cases, what is done is this heartwood is heated on fire. What happens during the process of incineration is the whole trunk, before it gets incinerated, the resins inside the heartwood kind of melt and ooze out. You might have seen it numerous times when you see wood near the chulha. The internal components start boiling and coming out.

So in a similar manner, your guaiacum comes out of the heartwood of this plant. Now, it might be located in certain glands, and this is a very common occurrence in cannabis. So if you've seen or if you know cannabis drugs such as your charis ganja they come in from drug called as your hemp or often referred to as cannabis. Now the medicinal part or what you call it as the hallucinogenic part of cannabis is actually

the top floral part and if you see it carefully it has numerous numerous glandular trichomes. This glandular trichomes secrete a resin and this resin is full of hallucinogens. Similarly, sometimes what happens that the glands might be located internally. This happens in the case of male fern. Now, not only are glands located in plant kingdom,

you might see certain glands which are secreting resins in the animal kingdom as well. One such case is your lac incend, that is your lacifer lacca. Now, this lacifer lacca has glands which keep on secreting a resinous substance. Now this is for its own protection and as you can see here in the diagram what the insect does is it eats or it kind of takes in the sap of this plant.

It feasts on the sap of this plant and in the process converts the sap of this plant into a resinous material. Now this resinous material is deposited by the insect in its vicinity to protect itself and to protect its neighbors and eventually they fuse to form a big colony. So you can see here while the other branches are empty specifically most of these insects have kind of latched themselves on this particular branch

and the resin that they have secreted is forming one continuous a resinous layer on this branch. Now this resinous layer we remove it for preparing bangles and also for preparing lac base dyes. Now sometimes your resins may be formed as a result of fossilization. A good example of that is your Shilajit which often occurs in the deep crevices

present in the rock where your fungus minerals are kind of localized and they resinify over a period of time. Now this is a good source of minerals as well as your fulvic acid which is good for your health. Now, coming to properties of resins, if you see properties of resins, like I said, in terms of their structure, majority of the resins are isoprene derivatives. Now, this isoprene derivatives polymerize and are secreted out.

Once they are secreted out, they get oxygenated and this oxygenation kinds of brings in cross-linking. And they are often called as oxidative deterioration products. So they kind of resinify, they kind of cross link and more the oxidation occurs, they darken. So they form a polymeric masses that is very difficult to crystallize. So they'll always occur as amorphous translucent mass.

But this mass is very soft initially as it dries and the moisture content becomes less and less the resinous parts or the resins or what you call it as the tears of this plant become little harder. Now this you can take it and gently heat it. You will see as you heat it this mass melts and fuses together. Now this fused mass if you heat it further or if you incinerate it you will see a smoky flame.

This results because it is now rich in carbons. Isoprenes are rich in carbons. Your oxygen is involved in the flaming process but because of a very rich carbon content and a polymeric nature most of your resins give what is called as a smoky flame.

Not only that if you dissolve the resin in a solvent and then apply it they form a thin film. This thin film as the dehydration occurs or as the solvent gets removed out of it more and more cross linking happen and the film hardens on the surface. You can liken it to the example of your turpentine. So initially when you apply the varnish, it is nice and liquid.

But as more and more layers coming in, the cross-linking sets in and the volatiles evaporate. You will find a very smooth, transparent to translucent rigid film. Your resins do precisely that. Now because of their polymeric nature they are very difficult to dissolve. So if you take water because they are hydrocarbons and there are lot of carbons in it they are not soluble in water.

At the same time because gradually they become oxygenated over a period of time they do not dissolve in extremely lipophilic solvents like your petroleum ether or benzene. A good solvent for them would be in a mid polar range. Something like your alcohol, chloroform, ether or even acetone can dissolve them much better than the extremely polar or extremely non polar solvents.

Now many of these resins even after application or even during the storage the oxidation doesn't subside. It keeps on reacting with the atmospheric oxygen and gradually darkens over a period of time. This is called as aging. So more is the age of your resin more darker it will appear. And in some cases where you have acidic resins,

if you just treat them with caustic alkalis like your sodium hydroxide or potassium hydroxide, you might even yield soaps. Now coming to classifications, the resins can be classified based on their chemical nature. Now based on the chemical nature meaning based on the functionalities they possess. Now resins have diverse chemical nature so majority of them have been classified based on the functionality and the way they react.

So if you take the first case the first case is of resin acids or often referred to as your resinolic acids. Now here is an example of abietic acid. Now this is one of the molecule which is present in your rosin or often referred to as your colophony or pine resin. You will see that this is molecule is chiefly terpenoidal in nature and it has oxygenated to form a acid in this case abietic acid. Similarly, in your myrrh, you will find your commiphoric acid, which is discussed lac, which is produced by your lac insect and that contains alleuritic acid. All of them are also used in perfumeries as a fixative. Now, apart from that, you might have resin alcohols. Imagine in case of acid, now you might have compounds which are high molecular weight. And in that case, the end part or a functionality such as hydroxy has been attached to them.

A good example of that is your benzoresinol, which is present in your benzoin or storesinol, which is present in your storax. Apart from that, you might have phenolic groups present on it. Now, phenolic groups, if we saw in your chapter on tannins, many phenolic compounds or basically polyphenolic compounds are abundantly found in plants, and in plants, tannins occur very frequently. And in plants, tannins occur very frequently or abundantly as protective molecules.

So what happens in the process is this process of resinification: the resin acids or these resins may often bind to tannic compounds or tannin compounds and form what are called resinotannols. A good example of resinotannols is Peru resinotannol. which is there in your peru balsam ,tolu resinotannol which is there in your tolu balsam

and siaresinotannol which is there in your siaresin Now, you might sometimes have bigger compounds, take for example ester resins. In this case, what happens is your compounds form ester linkages, take for example derivatives such as your cinnamic acid, benzoic acid. And this cinnamic acid, benzoic acid may form esters with benzoil alcohol, ethanol,

or any other compounds such as your ferrule alcohol and so on. In that case, they are called your ester resins. So ester resins come from esterification, generally by a phenylpropanoidal compound such as your cinnamic acid with other alcohols such as ethanol, benzoil alcohol, or your ferrule alcohol. In some cases, instead of alcohols, your sugar alcohols may be attached.

In that case, they are called your glycoresins. A good example of glycoresin is right in front of you, and that is your scammonin. So you see here in your scammonin, numerous sugar molecules are present, and they are attached by ester linkage to your compounds. And this compounds, if you see, it's more like a fatty acid derivative forming ether as well as ester linkages.

But what is focus of us is your ester linkages have been formed with alcohols. And these alcohols are contributed by sugars. In that case, you call it as your glycoresin. So you'll find it in Jalap, you'll find in your convolvulaceae family and so on. You might find in other members also wherein the sugars are very rich.

So the last class of resin based on their chemical nature is resins. Now resins is something which is just a polymerized long chain resin which is neither affected by acids nor affected by alkalis. It is just a big robust mass which is you know more or less neutral and but insoluble in most of the solvents and generally polymerized. Now they are devoid of any functional group and mostly hydrocarbon in nature.

And as a result, they are not categorized in any of the previous class. So if the any of the previous class doesn't describe your resin and it is very polymeric and insoluble, neither showing acidic or basic trait, it's possibly going to be characterized as your resins. Now type of resins is depending upon their nature and occurrence. You could chiefly classify your resins into three types.

One is what is referred to as your physiological resin. Sometimes it is also called your normal resin. Now we saw plants such as Asafoetida or we saw plants such as Pine. So what happens in them is they already have what is called your resinous ducts. Physiologically located in that, and what the plant does is it secretes the compounds inside the resin duct.

So as the plant grows, this resin duct is full of compounds, so anytime you cut this resin duct, you will get a resinous compound oozing out. And those are called normal or physiological resins. Now, in some cases, what is done to increase the amount of resin in such plants, such as your pine, is they are deliberately injured.

It is said that injury increases the amount of resin. But without injury, the plant as such has what is called preformed resins in them. Now, the second one is what is called pathological resin or often referred to as abnormal resin. So, what happens in abnormal resin is the resin is not present in the plant. But anytime the plant senses a stress or plant senses an injury, it is going to prepare this as a protective mechanism.

So take for example your balsams. Balsams are compounds which are rich in balsamic acids and balsamic acids are nothing but your cinnamic and benzoic acid. Why is the plant going to synthesize this? Because the plant knows that if I synthesize acidic compound, there is a good chance that I can kill the bacteria.

I'll give you a good example. If you are from your food industry or pharmaceutical or even from cosmetic industry, you know very good preservative which goes in your food, pharma and cosmetic industry is sodium benzoate. What is sodium benzoate that eventually in a little acidic condition it will get converted into benzoic acid. So benzoic acid is a very good preservative.

It kills microorganisms and this is precisely that. Balsams is your benzoic and cinnamic acid. And the tree, whenever it senses infection or injury, it produces it to ward off any infections on itself. Now, going to the third case, the third case is prepared resins. Now, we just saw that in certain instances like your ginger or in some cases when we did lignans, if you remember, podophyllum resins. So podophyllum or ginger or even your turmeric, when you cut this, you will see that when you cut a raw turmeric, that yellow color gets transferred to your hand. But if you want to remove it, it is very difficult because they are not located inside any ducts. So giving incision will not ooze them by gravity.

You need to extract them. So what is done is maybe a turmeric powder or podophyllum powder or your ginger powder is taken and then it is extracted with a solvent in which your resin is dissolved. The beautiful solvent for this would be your alcohol for the reason I said you cannot have extensively polar because of the carbon count and

you cannot have extensively nonpolar because of the oxygens which are present in it. So you take a mid polar solvent such as alcohol and extract it. Now all your resin is solubilized in alcohol but one property of resins we know that they are not going to be water soluble. But alcohol is water miscible. So if you take this alcoholic layer, you kind of concentrate it and then pour it in water.

Alcohol is going to mix in water. There are some compounds which came in in alcohol, which are polar. They are going to dissolve in water, but your resins are going to remain insoluble. So when you pour this alcoholic extract in water, it kind of precipitates the resin.

Now, this precipitated resin is collected and that is how you get in market what are called as prepared resins.

Now, they might be further fractionated or washed, purified and then dried eventually to get rid of the solvent. So, this is how your most of the resins or prepared resins are obtained from for the market purpose. Now one more class is when you see your resin combinations. Now, in some cases, resins occur as pure, but in some cases, they might come along or exude along with other compounds. When they exude along with other compounds, they are called resin combinations.

So, plain resin is where your hydrocarbon or isoprene derivatives in the form of acids or alcohols occur as such. Now, in some cases, you get what are called oleoresins. So, what are oleoresins? Oleoresins are when, in addition to your resin, you also get what is called essential oil. A good example of that is your pine resin, where you know your pine has a typical aroma, a turpentine-like aroma.

So, when you cut or make incisions on the tree, you will get your resins, which are rich in acids, but also you will get your pine aroma principles like your pinene, turpentine, and so on. So this has your volatile oil plus your resins and is referred to as your oleoresins. In some cases, gummosis happens, and as a result, your resins come out along or in combination with gums. In that case, you call it gum resins.

And, most abundantly, you might see what are called oleogum resins. So, this is a combination which has oil, Especially your essential oil. This has your gum, that is, your carbohydrate, and a resinous compound. So it's a combination which initially comes out as a whitish emulsion because it has water.

It has your oil and it has your gum which acts as your emulsifying agent as well. So this whole combination of oleogum resin comes in as an emulsion but as the water content goes on drying, the moisture content decreases, they become more and more opaque. So resin combinations you can have oleoresins, you can have gum resins, you can have oleogum resins and in some cases when you are rich when you have resins which is rich in balsamic acids which is your benzoic acid and cinnamic acid in that case those type of resins are referred to as balsams. So for classification purposes since they are not combined with anything we are putting them under the resins class. Now, where do you apply those resins? What are applications of resins? Now, resins have numerous, numerous medical applications.

To take for example, if you take something like a turmeric, it's antiseptic, anti-inflammatory. If you take something like your podophyllum, we just saw your podophyllum, which is used in treatment of cancer. You will see your wound healing activity. If you see resins such as your guggul, used in weight loss your asafoetida or hing is used to treat or take care of your digestive issues

not only that apart from the medicinal uses your resins are also used for non-medicinal uses this includes all your resinous applications where you want films or when you want a dry layer of Which is more water impermeable to be formed. So take for example varnishes, lacquers, adhesives. Now, because of their high molecular weight or polymeric nature, they are used as fixatives.

They are used as perfuming agents, especially the oleoresin ones. Frankincense is used in perfumes and incense. They are also used in cosmetics for creating a film or layer, especially in eye care products, eyelash or eyebrow products. You will see that when you want a film to be formed, you can use a resin to support it.

They have been used for waterproof floor coating because they also provide you insulation and in some cases they have been used to bind explosives in fireworks form a very stiff, hard, water-repellent layer. Earlier, you know, chewing gums—especially natural chewing gums—were made from the sapodilla tree. So, this is still used in some populations,

but more or less nowadays, chewing gums are all synthetic resins. However, natural chewing gum comes from the sapodilla tree. This is also used for flavoring liquor. Traditionally, in Egyptian civilization, resins were used for applying or sticking bandages to mummies or in the process of mummification.

So, this is a brief introduction to resins, and subsequently, we will cover different examples of resins. So, thank you, everyone. There are a few references if you wish to learn more about resins and their properties. Happy learning. Thank you.