PHARMACOGNOSY AND PHYTOCHEMISTRY

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Week 9

Lecture 44

Oleo-resins containing drugs

Hello everyone, and welcome to the NPTEL course on pharmacognosy and phytochemistry. This week, we are learning about a set of compounds called resins. We saw what resins are and the different types of resins. When it comes to examples, we saw resin-containing drugs such as colophony. Then we saw benzoin, which is an example of balsams.

In the previous session, we saw examples of oleo-gum resins. Examples of which included your Guggul, Myrrh and Asafoetida. In this particular session, we will delve into a more interesting set of resinous compounds. The resins we discuss in these sessions are the ones we consume on a day-to-day basis. So the three oleoresin gums we are going to discuss today are ginger,

turmeric, and chillies. So ginger, turmeric, capsicum, or chillies—what they have in common, compared to the previous ones, is that when we discussed oleo-gum resins, we said they are resin combinations containing essential oils, carbohydrates, and resins. Now, these three drugs do not contain the carbohydrate element.

That means they are combination of two moieties and these moieties are your resins and volatile oils. So let's see one by one of all these three and how these oleoresins are therapeutic and beneficial to them. The first case is your ginger. now ginger we all have seen in our kitchen is actually a rhizome now this rhizome may be scraped or unscraped that means the outer cork of it must might have been removed

or it might be intact in india very often we consume fresh ginger and as a result when you buy your ginger from market you will find that it already has its cork But due to a cold condition, some countries it is not possible to cultivate ginger. In such cases, in order to preserve ginger, they often have it decorticated for long term storage and to prevent the nodes from developing into a new plant.

So ginger belongs to a plant called as Zingiber officinale, which comes from the family zingiberaceae. Now the zingiberaceae family members has numerous numerous rhizomes which are very rich or which have been used in culinary such as your galangal, turmeric. But Zingiber officinale is more often referred to as your ginger. So in BP the unbleached ginger is officially the Zingiber officinale

And the plant part of the ginger which is used is the rhizome. Now geographically ginger has been cultivated in most of the tropical to temperate climates. This includes the islands of Jamaica. In African subcontinent we have ginger abundantly being cultivated in India as well as in China. Now when you procure your ginger from these sources.

There are slight differences in the color, in the shape, and in the morphology of these three ginger sources. Not only that, they also differ in pungency. So, there is a good variation or geographical variation even in Zingiber officinale, which has been obtained from different geographical sources. Now, once you cut the ginger, this ginger also comes under the category of

what you call prepared resins. So, when we did our first session on resins, we said you have natural resins, and in some cases, you need to have what are called prepared resins. The reason why we need to have prepared resin is, you know, if you cut ginger with a knife, at no point will the resin exude out.

Now, there is a reason for it. So, I can show you in the diagram. So, this is what you call a microscopic section. So, if you take your ginger, slice it thin, and put it under the microscope, this is what it is going to appear like. Now, if you observe carefully, this is mostly parenchymatous in nature, and

within this parenchymatous nature, if you see these yellow dots, these are the ones which store oleoresin. So, this is an oleoresin cell into which your ginger oleoresin has been accumulated. so if you cut it it is not possible that every time you cut a cell and it's going to leach and as a result, in order to extract this resin out of ginger, it is essential to dry the ginger, powder or pulverize it, and thereafter extract it in a suitable solvent. Now, this suitable solvent can include anything between alcohol

And in some cases or industrially, ginger oleoresin has also been procured by a process called supercritical fluid extraction, where supercritical carbon dioxide is used to extract this from the ginger powder. So if you see ginger, ginger comes under the category of prepared resin, and if you see the combination, it is an oleoresin combination.

So ginger, how do you procure it? So mostly, if you see this ginger, you see numerous bulbs out here, or we often refer to them as fingers. So, these bulbs are often cut off if you want to propagate the plant, and then they are planted during the summer season in good dry soil and then watered. Now, once during the rainy season, they start growing big leaves, and eventually some of them bloom.

After blooming, they start withering off. And it is seen that especially during the winter season, initially the leaves will turn yellow and gradually wither and dry. It is during this time that the stems are carefully cut off, and the rhizomes are dug. Now, during the process of digging, care is taken that the rhizome is not damaged. It is lifted almost in a very intact manner, washed nicely, and then dried in the sun.

Now, in some cases, when you want to preserve your ginger for a longer duration of time. Now, what happens is if you keep these fingers or rhizomes of ginger in a good moist place, you will see they gradually develop stems. We don't want that to happen if you want to store it for culinary purposes. For cultivation, that is fine.

But for culinary use, we don't want it to grow into a new plant. And for this reason, when I want it in commerce for preparation of resins for culinary purpose, what is done is this ginger is taken and boiled. This boiling often renders the ginger sterile and incapable of any further growth. And as a result, you will see the ginger will stay intact.

So it is blanched or boiled. And after boiling, what happens is in some cases you will see the cork comes off. Now in Indian culinary, we take the unboiled naturally obtained ginger which has been dug off. But like I said for commerce, when you want to export it to the colder countries and you don't want it to germinate during the shipment or during the storage period, what you can do is

you take the ginger, boil it or blanch it, gradually remove the peels to ensure that there is no budding or no growth happening in the ginger. Now once this boiling is happened it will tend to deteriorate or ferment and as a result it immediately after boiling it is dried. Now it may be tray dried or it may be dried in sun for a period of 5 to 6 days. in some cases during the boiling because of heating like i said some processes such as you know browning start

because it contains good amount of starch so to you know take care of the color what is done that it is observed that if you reheat it that is reboil it and again redry it maybe two to three times or so you will see that in that case the ginger is more whiter and more aesthetic as compared to a singly boiled ginger

so this is how your ginger is prepared but in addition to it there are numerous other processing methods which includes sun drying so you can directly take your ginger peel it from the cork peel the cork and dry it in ginger and supply it as such in some cases it is dried in oven directly you know in places which are moist or damp throughout the year it is not possible to dry the ginger under sunlight because that dampness will not allow the moisture to evaporate in such cases artificial heat is used and

And the best condition is to heat it in a tray dryer at a temperature not exceeding 60. It is said that 60 is a good temperature. At any point of time if you exceed a temperature over 70 degree Celsius your ginger starts to brown. And as a result, a temperature over 70 degrees Celsius is not desired. Another way of saving ginger, which is often done in Indian households, is to take fresh ginger, wash

it properly, and scrape it with a scraper. So when you scrape it, the peels or the skin are removed, and you need not bleach it thereafter. You just need to keep it in cold conditions.

Nothing will happen to your ginger. Now, when it comes to long-term storage, a few processes like bleaching or liming are done.

Now, what is the bleaching and liming process? Now, after boiling, in some cases, the ginger is soaked in lime water. This gives a good appearance to the ginger. It appears more white and is often referred to as lime ginger.

But if you see the official source, as we discussed, BP, the official ginger is what is referred to as unbleached and unlimed ginger. So that is not used in therapeutics, but it can be used for culinary purposes. So it is used in lime and And in some cases, when you want a container or shipment storage, it is also fumigated.

The fumigation is done mostly with sulfur dioxide gas. So in a very enclosed container space so that the gas stays for a while and permeates inside the ginger. This also prevents the growth of bacteria, fungus, molds on the surface as well as prevents any growth thereafter. So you can lime it, you can bleach it with your sulfur dioxide or you can have a combination of both. That is fumigate it with sulfur dioxide and subsequently dry it, lime it and save it.

Now another additional way in which your ginger is prepared is to extract the oleoresin out of it. So in cases where you don't want the large quantities of raw material to be transported, the main flavoring principles of ginger lie in the resin we just saw those tiny greenish dots inside the ginger so we can extract it by solvents including your ethanol hexane or even like i said supercritical fluid extraction concentrate those extracts and those extracts are directly shipped as your ginger flavor

Now what exactly imparts the flavor of ginger? We will see the chemical composition. Now the oleoresin of ginger contains almost 1-2% essential oil and most of the resinous composition are the mixtures of your phenylpropanoids and their derivatives. So if you see your volatile oils, your volatile oil contains somewhere like your philandrine, especially your beta phellandrene, camphene, cineol, citral, borneol. They contain little bigger compounds which are more fragrant and responsible for the aroma of ginger. This includes your zingiberin, which is the main flavoring principle and aromatic principle of ginger,

bisabolene, farnesene. Then you have your beta sesquiphellandrene or curcumin and other sesquiterpene alcohol, which includes your zingiberol and ginger diol.

So these sesquiterpenes are the main compounds which are responsible for, you know, the aroma as well as flavor changes. your ginger but in addition to that you also have compounds such as gingerols and gingerones ABC, as well as iso-gingerones. So if you see your gingerols here, gingerols are typically phenylpropanoid derivatives. Take for example 6-gingerol. So 6-gingerol is, if I cut it

like this, you will see a phenylpropanoid out here. So this is your phenyl. This is your 1, 2, 3 propane. And now when I cut this, I just start numbering from this carbon. So 1, 2, 3. 4, 5, and 6.

So wherever this hydroxy is, you get the gingerol, and it gets its name from this. So this is an example of 6-gingerol. Again, if you see your 8-gingerol, you have a phenylpropanoid moiety out here, but if you see the hydroxy position, you will see here 1, 2, 3, 4, 5, 6, 7, and 8.

So your hydroxy is at the 8 position. So you have your 8-gingerol. Similarly, you will have your 10-gingerol. You can just do the counting, and you will see it matches. So 6, 8, 10 gingerols.

Now it is seen that this plant, you know, During the stages of its preparation, the gingerols undergo dehydration. That means they lose a water molecule. So imagine they are losing a water molecule like this. So I am losing this HOH, and as a result, it leads to the formation of a double bond out here.

And these compounds are called shagols. So shagols originate from gingerols basically by a dehydration process. Now, in some cases, when you want your ginger for culinary purposes, if you consume it, you know it's extensively pungent and spicy. The spiciness of the ginger can be decreased by removing these compounds.

So, if you see your gingerol, you can destroy your ginger oil by treating or boiling it with 2% potassium hydroxide. Similarly, if you see the same compound, I just break it from here, and you know that is what is called your gingerone. This gingerone is also destroyed

if you use a little concentration or a higher concentration, about 5%, if you take sodium hydroxide and heat it or keep it in prolonged contact with your ginger. The pungency of gingerone also vanishes.

So your ginger oils and gingerones can be treated or kind of inactivated, and the pungency of the ginger can be destroyed by alkalis. And as a result, once the alkali is destroyed, you get a slightly sweet scent and aroma of ginger. Now, where do we use this? So ginger has principally found its application in culinary food, nowadays in medicines, and also interestingly in cosmetics.

Now, if you see your ginger oleoresin, if you just take the concentrated extract you have those sesquiterpenes, ginger oils, and other alcoholic derivatives, the ginger the ginger oleoresin offers much strong, pungent, spicy aroma and flavor. And that is the reason, if you see in culinary industries, when they prepare the flavor concentrates, rather than ginger powder, they use ginger oleoresin.

Not only that, in food whenever you want to add it to drinks such as ginger ale, you cannot add ginger powder. You need to add an extract. In that case, the addition of ginger resin or ginger oleoresin imparts the desired effect without affecting the clarity or consistency. Similarly, you have lozenges which contain ginger and also numerous flavors which

encompass a combination of ginger with other spices. In that case, rather than ginger powder, ginger oleoresin is being used. Now, coming to the pharmacological effects, traditionally and even in modern days, we Indians use ginger for motion sickness. So, you know, to relieve nausea, the feeling of vomiting, this includes morning sickness, motion sickness, or even for cancer patients.

The nausea caused by chemotherapy, ginger or sunt powder as we refer to it, is a very commonly practiced or used remedy in India for this kind of condition. In addition to that, consuming ginger provides your body with a good amount of anti-inflammatory and antioxidant principles, which are beneficial in numerous inflammatory diseases like bowel disease, and also arthritis, as well as numerous wound-healing actions, have been attributed to the consumption of ginger in our diet.

Now moving on to the next resin. The next resin is a very spicy one, and that's your capsicum. Now, capsicum—there are numerous, numerous species of capsicum in the world, but the capsicum we discuss here is your Capsicum minimum or Capsicum annum, which is your common kitchen chili. Now, this consists of dried ripe fruits of Capsicum minimum or Capsicum annum, and it's a Solanaceae family member.

We often saw your Solanaceae family as the one containing alkaloids. So, this is also a Solanaceae family member, and this also contains alkaloids, which ones we'll discuss shortly. Now, chillies are grown throughout the world. They are preferred and loved by people for their tangy, spicy flavor that they impart. The level of spiciness varies geographically and depends upon the species of chillies.

Now, the most famous chillies come from regions such as America, India, Japan, Mexico, Sri Lanka, and to a certain extent, China. Now, if you see Capsicum minimum or Capsicum annum, that is our common kitchen chili. If you slit it, you will see that this chili has an outer coating and an inner soft, whitish, membranous dissepiment. Now, this dissepiment divides the fruit into two compartments, and you will

find small kidney-shaped or what are called reniform seeds attached to it. I have kept an image of the seeds of chillies for it. So, you will see they are nice kidney-shaped, and if you see carefully, the seeds are slightly translucent, and you can see the inner spiral-shaped embryo inside them. So, they are flattened and show a coiled embryo in them.

Now, coming to the composition, the intense pungency of the chilli is attributed to alkaloids. Like I said, it's a Solanaceae family member. So, it is bound to have alkaloids. And in this case, it has amide alkaloids. So, similar to your piperine, this is also an amide derivative, but this is much, much more pungent.

So, Your capsaicin is one of the most pungent principles, and in your Capsicum annuum, it is present to the extent of 0.5%. Now, that is responsible for spiciness. The color of chilli comes from a set of pigments which belong to the carotenoid class. A good example of a carotenoid pigment which is present in your chilli is your capsanthin

Now, in addition to capsaicin, you also have other pigments such as capsorubin. Then you have your cryptocapsin. In some cases, your capsaicin, cryptocapsin, and cryptoxanthin are often found intertwined and complexed with each other or polymerized with each other. You have your beta-cryptoxanthin.

Then you have your epoxides, which include your capsaicin epoxides. The yellowness is imparted by zeaxanthin, and in addition to that, you also have beta-carotene. So many carotenoid pigments are present, and as a result, you will see your chillies become intensely red or deep blood to ruby red in color as they dry. In some cases, some chillies have so much of this carotenoid that they appear blackish in coloration.

So, one important attribute of chillies is pungency, and pungency is measured by what is called SHU, that is, your Scoville Heat Units. Now, Scoville Heat Unit is one good measure used in the food industry to check how pungent a particular food is. food product is not necessary chilli but any food product is so what is done is that food product and kind of disperse it in a sugar alcohol or sugar water mixture, and then

you see how many times you have to dilute one part of that food so that after dilution, I should not be able to perceive any heat. or spiciness. So, if I am no longer able to detect the heat or spiciness, that dilution is counted as SHU. I will give you an example.

Now, in India, we have a spicy chilli often referred to as King Chilli or Bhut Jholokia. Now, this chilli is what is called about a crore of SHU. A crore of SHU means you have to take one gram of it and smear it in this many ml. That is one crore ml.

You can put it in that much. And after that, you will not perceive. But if you take the pure active principle, that is capsaicin, it is almost 16 crore SHU. So imagine the spiciness or pungency of capsaicin. The spiciest chili known in the world so far is the Carolina Reaper, which is found in the US subcontinent.

And that has about, you know, like, 1 crore about 40 lakh. SHU or intensity now it is seen that if you want to quantify it the earlier method is they use a panel of 5. So if 5 people tell you at this dilution, I am not able to detect the heat or spiciness, that was what SHU was. But in modern days, methods such as HPLC are now available.

What is done is we know capsaicin is 16 crore SHU. Then I will quantify in terms of its content, my chili contains how much. So if my chili contains, say, you know, 5% SHU, I multiply that and get my SHU units directly. The pungency is now calculated based on your SHU. so not only the pungency the color of your chilies is also standardized

So spice traders saw that globally, different chili varieties gave you different colors. There was a need to standardize it, and that's where you came across a standard called the ASTA value, which is the American Spice Traders Association value, and that uses, you know, like a color index method. So that is an ASTA method 20 is to 1. Now what is done is you take your chili, 1 gram, and dissolve or extract it in acetone and

see the absorbance at 460 nanometers. Now when you see the absorbance at 460 nanometers, your ASTA value is calculated as absorbance into 164 into, you know, like your UV correction factor. referred to as ic and then how much grams of chili you have taken that is the weight of chili so often referred to as your concentration. So it is absorbance by concentration into 164 into your IC. So

typically, your paprika has an ASTA value, that is the redness value of. 65 to 180 but if you see the oleoresin like I said that's going to be more concentrated and this is also a prepared resin that has a value between 500 to 3500 Asta units. Now coming to its applications, chilli because of its spiciness is used in pepper sprays which have been used in self-defense, crowd control

and you know it possesses so much of eye irritation so that if that spray goes on your face, your face is almost numb, watering, painful and your eyes become temporarily blind. If you use this resin, this is a part of most of your ketchups. So your ketchups are mostly hot and sweet or spicy ketchups such as your Tabasco sauce. They kind of use or add resins to it.

Not only that, the purified compounds that is your capsaicin and capsaicin, that is the alkaloid as well as the carotenoids have different different applications in coloring as well as in the pharmaceutical industry. Capsicin in pharmaceutical industry is used in pain management. You use lot of those balms that is pain balms and you will see many of them will have capsicin as an ingredient.

So this is useful in management of your neuropathic pain, your muscle pain. It is also used in management of your arthritis. It is used to improve your digestion. It is said that your consumption of chilli gives you warmth and this warmth is beneficial for digestion and to boost metabolism.

now the last oleoresin containing drug that we refer to is your turmeric now this is a very common kitchen condiment and spice known for its brilliant bright yellowness or yellow color we often refer to as haldi and it's obtained from the rhizomes of curcuma longa often referred to as your curcuma domestica this is also zingiberacae family member like your ginger and it has less spiciness as compared to your ginger but it's more aromatic

as well as the medicinal effects of its compounds are much much full as compared to your ginger so turmeric is cultivated in maharashtra especially you know like erode or sangli districts or even in tamilnadu it is cultivated throughout the India but these are the two chief principal producers and suppliers for turmeric in India now like your ginger this is also oleoresin so you can see it is there in your oleoresin cells so turmeric again is extensively a oleoresin containing drug where the pigment that is the oleoresin is localized in oleoresin cell

It is starchy and as a result you can see here there are numerous bluish color starch grains which have been stained with iodine. And you can see this yellow color oleoresin cells which contain your yellow pigments. So what are these yellow pigments? So yellow pigments are what are referred to as your curcuminoid derivatives. We'll see little bit about it shortly.

So if you see turmeric, turmeric is a plant again cultivated. Mostly what is done is the fingers of it are cut in a manner very similar to that of your ginger and cultivated in the summer season. Very likely it is in the same like annual plant. It will start blooming and once the leaves are turned yellow or dried in color, you can dig up the rhizomes.

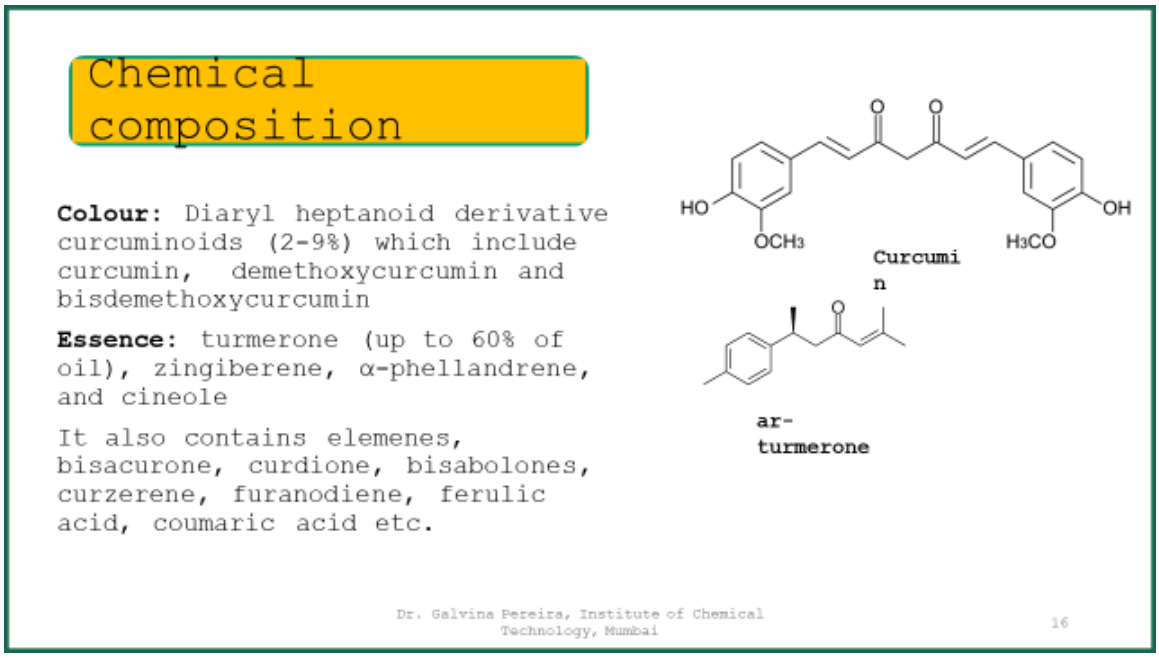
Again, these rhizomes are carefully pruned. They are nicely washed to take care of any extraneous matter and similar to ginger to prevent any growth or nodes from appearing. During the storage time they are subjected to curing. This curing involves boiling.

and in some cases peeling. So this turmeric is exposed to a repeated cycle of heating, boiling and cooling and subsequently drying till it acquires a stiff stone like or very hard consistency. This is what is referred to as prepared rhizomes. Now, these prepared rhizomes also contain little black spots or imperfections, and those are removed by polishing.

Now, chemically, what we discuss is that they contain compounds or pigments. The yellow pigments of turmeric are due to what are called diphenyl heptanoid derivatives, referred to as curcuminoids. So, these curcuminoids are somewhere between 2 to 9 percent in your Curcuma domestica or Curcuma longa. But if you see other varieties like your Lakadong one, you get almost 12 percent or 9 to 12 percent of this. So,

In your Curcuma longa, you have your curcuminoids, which are a mixture of three pigments. The principal one, the main one, which makes up about 80% of this resin, is what is referred to as your curcumin. Now, this curcumin is again... what you refer to as a very symmetric dimer if you observe carefully, and this, when you remove one methoxy out of it, you call it your demethoxy curcumin.

Remove another methoxy out of it, and you get what is called bis-dimethoxy curcumin. So, out of the curcuminoids, your curcumin is the major one, consisting of almost 80 to 85 percent in some cases. Then you have your dimethoxy, which is a minor one, about 7 to 9 percent. Then you have your bis-dimethoxy, which is the smallest or present in the least amount. Now when you are taking curcuma or your haldi, the aroma of it is due to a presence of compound which is your arturmerone. So arturmerone is... Again, a terpenoidal derivative and this is your sesquiterpenoidal derivative. And if you see your turmeric oil, your A-turmerone makes up almost 60% of your essential oil. In addition to that, you also have your alpha and beta-turmerone.



This only changes from here. So, the degree of unsaturation changes and you get your alpha and beta-turmerone. In addition to that, you have your gingivirin, phellandrene, cineole. It also contains numerous other aromatic principles, which include your bisacurone. You have your curidione.

You have your bisabolenes, curzerene. You have your furanodine, ferulic acid, and coumeric acid. Now, coming to the applications of this. Turmeric is, you know, a very strong adjuvant in cancer therapy, so much so that even pills, medicines, or extracts of turmeric have been prescribed for patients undergoing cancer therapy.

This includes or this shows turmeric has beneficial effects in patients suffering from colon cancer, lung cancer, or even breast cancer. It also takes care of your inflammation and as a result it's prescribed in your inflammatory bowel disease. Traditionally it is known as antimicrobial agents, wound healing. It is used in cosmetics and also in our religious Hindu religious ceremony for skin brightening purposes.

Now one derivative of curcumin is Which is also called as tetrahydrocurcumin. Now curcumin when you use in cosmetics imparts a little yellow stain. In order to get rid of it, the double bond of it has been saturated. So imagine if you kind of saturate these bonds.

remove this you get what is called as tetrahydro curcumin and this tetrahydro curcumin is colorless it has little less in terms of the therapeutic qualities as compared to curcumin but nonetheless has no staining properties so in addition to less uh Color, it has enhanced solubility, stability and bioavailability compared to your curcumin. And yes, it has a potent antioxidant, anti-inflammatory and it can be used for skin healing purposes.

So here are a few references if you wish to know more about this set of compounds. And thank you everyone for your patient listening. Thank you.