Natural Dyes

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Lecture No. # 26

Today's lecture is dedicated to a **v**ery special class of natural dyes that is anthocyanin; and anthocyanins, let me tell you have been the largest source of various colors, it is not that anthocyanins are only red in color or blue, but they vary from red to orange to blue's to violet; and this variety of range of color comes from the very fact that anthocyanin dyes can form acidic salts or basic salts and that is because of their beautiful structure.

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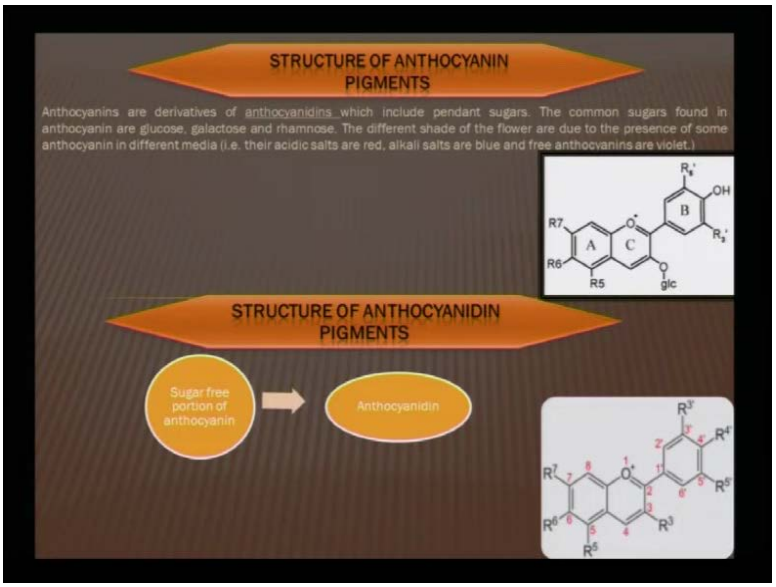

Let us try to look at this slide, where you see that the A, B, C rings are connected and there is a sugar pendant hanging OGLC; now this OGLC represents the sugar moiety and this sugar could be glucose, galactose or rhamnose; it could be other sugars also, but predominately, these are the three sugars that are naturally present along with cyanin-anthocyanin. And when these include the pendant sugar, the anthocyanidins are then called as anthocyanins.

So, if now we try to look at this particular structure, there could be a possibility of R 1, R 2, R 3, and apart from that, there could be R prime, R prime prime and so on. And you see that counting of the ring is done from the oxygen, that is the heteroatom. So, if one is the position of the oxygen in the C ring then, it is counted from clockwise 1, 2, 3, 4, so it has a three substitution, it has a five substitution, it can have a six substitution, it can have a seven substitution, and apart from that, it can have the substitution in the B ring, which could be 3 prime, 4 prime, 5 prime.

Now, these are groups, also can be methyl or hydroxyl are many other such functionalities, which make a huge variety of anthocyanin or anthocyanin dyes. So, looking at this structure, can these dyes be used for natural dyeing was a natural question; and because they have such bright colors and as you may recall, there was a myth about natural dyes that they are very dull and pastel and that is why they did get popularized; that was primarily, because six or seven dyes that were being used from ancient times belong to either indigoid dyes of livened dyes or anthroquinine dyes, but anthocyanin dyes were not explode; for this simple reason that people did not know, how to use them, how to extract them, how to preserve the color, what is the p H sensitivity and so on and so forth. So, we did a lot of extensive work on anthocyanin dyes, and we showed that this particular dye, which was partly used in food industry for some purpose, can also be used for textile dyeing.

And it is with this point in mind that we designed this particular lecture, based on the fact that this particular pigment can be a very good source of natural dye. So, if I have to talk about this natural dyeing of cotton with hibiscus, using hibiscus as a source of anthocyanin; hibiscus is a flower, which is popularly seen everywhere, gudhal ka phool and it is bright red in color. So, it has a very bright attractive color and therefore, we thought, and it is abundantly available.

One very important factor for natural dyeing is that the source should be renewable, and the source should be abundantly available; and it is with that in mind, that we design lecture number 26 based on the fact that, it should now come to your knowledge, that apart from indigoid dyes, anthroquinine dyes and flavonoid dyes, there is a major, major class of dyes, which is called anthocyanin or anthocynanidine dyes, which have beautiful structural situation, as what I showed you in the previous slide, and because of the variation, in the functionality in and position of the functional group on the A, B, C ring,

it is possible to have a variety of naturally occurring anthocyanin. So, the anthocyanin that were present in the hibiscus flower, we will take a look of how was it kind of introduced to dyeing, how what are the procedural details of natural dyeing with hibiscus, are there any modification, how it is extracted and so on and so forth.

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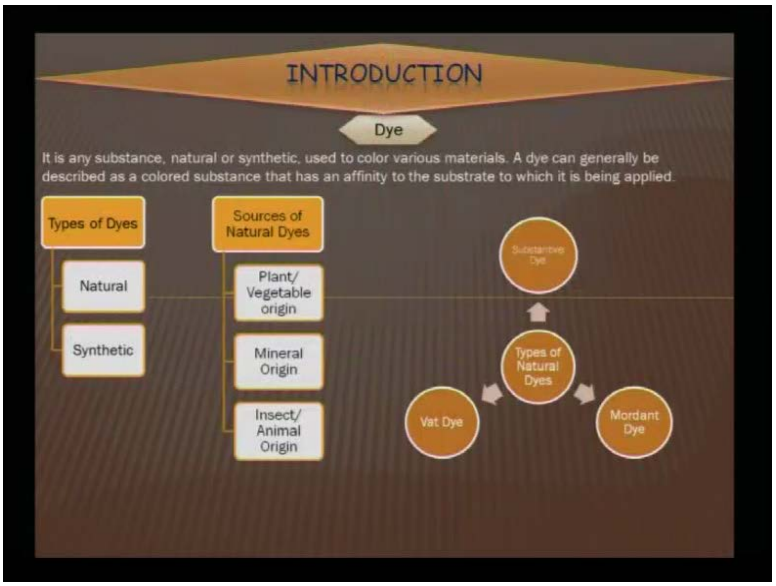

Now, when we try to just look at an overview of dyes, we know that dyes could be a source from natural as well as synthetic, and from the natural source, we have to look for plant origin dyes, mineral origin dyes or animal origin dyes. We have all studied this, but this is just like a recapitulation of natural dyeing, because just a couple of lecture back, we were doing some synthetic dyes. So, I am trying to give you an overview of synthetic dyes and their dyeing procedure, I am also trying to give you an overview of natural dyes, modern dyes and so on and so forth; and among the natural dyes, which which are the dye are most variable.

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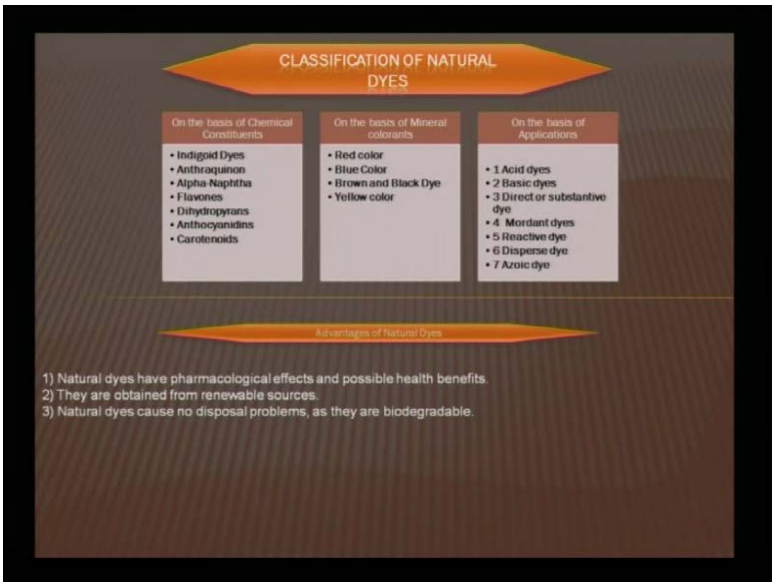

When we try to look at different classes of natural dyes, I was telling you that we have discussed mainly the indigo, vat dyeing, we have discussed you know, alizarin and many other anthroquinine dyes, but we have not into the too much of details of the anthrocyanin. So, I thought that we should spend one or two lecture, just trying to understand, because this is a huge class of natural dye, which can be functionalized or which can be used for natural dying; different colors as what I said, they are acid base or pH sensitive, so reds can be obtained, blues can be obtained, even violets can be obtained. If we keep this dye under the very acidic conditions, say something like 5.5 p H then it would give red color; if we keep it for 9, it will give something like, you know blues, but if they are kept neutral some of them are even dark violet color. So, this is the kind of phenomenal number of shades can be generated from the same dye.

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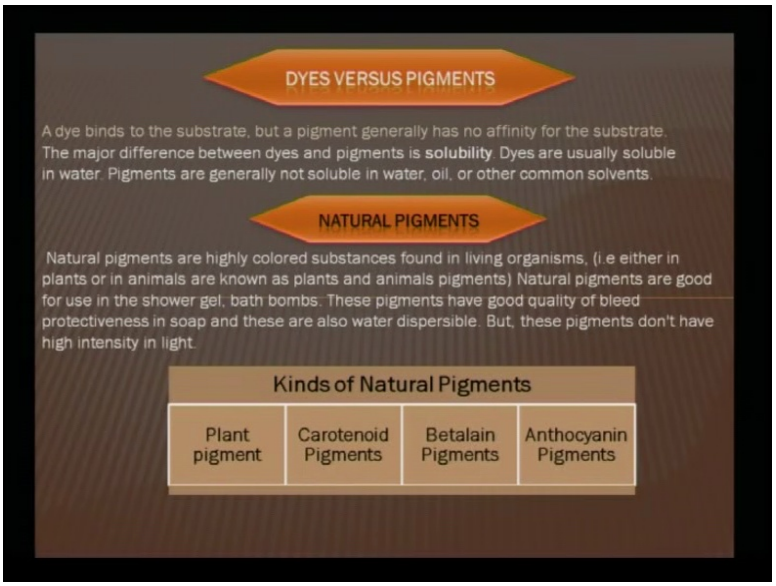

Now, when we try to look at the different types of dyes and the natural pigments, you know the one major class of pigment as I mentioned is of course, carotenoids; we will discuss that also in detail some other time; there is second class, which is detail in betalain and third one is anthocyanin. So, it is this particular natural dye, which we will be talking more and the dyeing procedure that needs to be followed in case of natural dyeing with anthocyanin.

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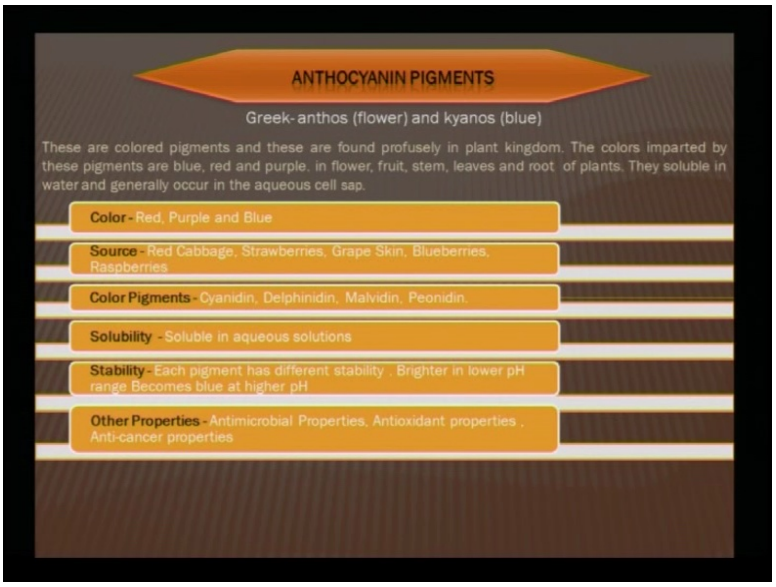

Now, when we try to, you know look at various situations with the anthocyanin, the information is that these are color pigments that are found profusely in plant kingdom. So, this is probably one of the largest occurring natural dye in nature, the color imparted by these pigments are blue, red, purple in flowers, stems, leaves, roots and of the plants; they are soluble in water, generally occur in aqueous cell sap. So, you see, it has all the requisites of being a good dye; first thing it is water soluble, it is abundantly available, it is brightly colored; now the question is, does it adhere to the fabric? Because it has so many OH groups in the A, B, C, D ring, it is possible that it has a good chelation property as well.

So, colors that obtained from anthocyanin could be ranging from red, purple and blue. So, even we are doing anthroquinone dyes, we were only concentrating on the reds or the orange; when we were doing indigoid dyes, we were only concentrating on the blues, but here is a variety, and that is the reason, why I thought, I should spend some time, teaching you about the anthocyanin dyes. Sources could be red cabbage, strawberries, grapes skin, blue berries, raspberries; you see I mean, you can think of any kind of color in nature; in the flowers, various varieties of flowers that have very brightly colored, you know colors like red, blue and violet; and you can close your eyes and imagine that this has to be anthocyanin.

Apart from anthocyanin, there could be associated dyes as well from from the carotenoid series or from the flavonoid series, but the major one will be anthocyanin; color pigment is cyanadine, delphinidin, malvidin, feondin; these are some of the structures and structural difference in cyanadine and malvidin or cyanadine in delphinidin or cyanadine in or feondin is simply the R groups around the A B series, that is all the difference and that creates difference in the coloration.

They are soluble in water, and each pigment is stable, has its own different stability bright in low pH, ranging range becomes blue at high pH and that is what I have mentioned that you know, they have this uniqueness of pH sensitivity; and some of these anthocyanin dyes have been found to have antimicrobial properties, anti cancer properties, and of course, they are anti oxidants; and that is why you know brightly colored fruits are recommended; we say do not eat green grapes, but eat the purple grapes or the dark graphs, that because it has lot of anti oxidants. So, it has its own medicinal values as well as the dyeing properties are absolutely adaptable and apt for the

or the prerequisite that is required for a dye to be a suitable dye, is all found in the this anthocyanin dyes.

Now this is the structure I had initially shown you, but I wanted to correlate the structure and therefore, I was trying to start the lecture with this particular slide; now when this hydrolysis of the sugar is done, that time it will be called as anthocyanadine; but when the sugar is also hanging as a pendant as in shown in the above structure, you will see that it it is called anthocyanin. So, it is just the nomenclature, but nevertheless, it is the composition of these aromatic rings with the oxygen and the R groups being of OH or different types of functional group, which are very good adherent to the fabric and also help in metal chelating.

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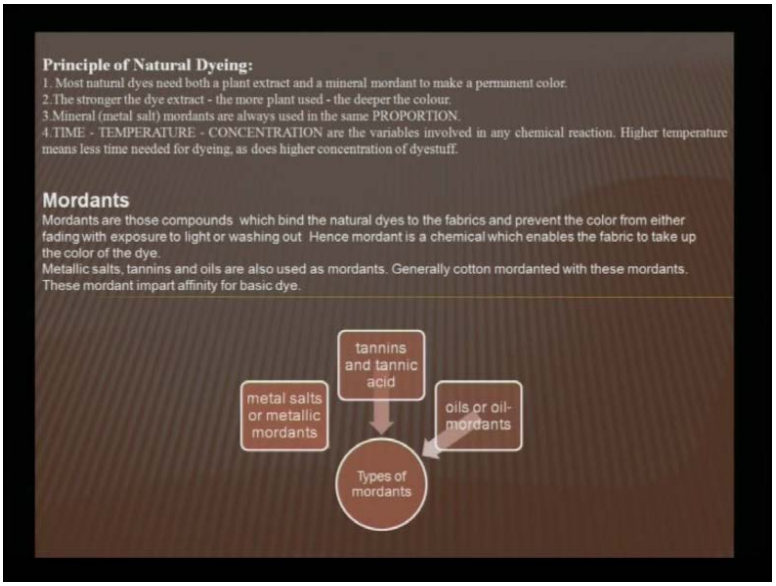

Now, when we try to look at various types of mordanting, we now come to the natural dyeing procedure; we know that for natural dyes, it is important to have modenting step done. Most natural dyes need both a plant extract and mineral mordant to make a permanent color; the stronger the dye extract, the more plant used, the deeper will be the color; mineral or the mordant salts are always use in the same proportion that is varying from 1 to 4 percent, but keeping in mind that copper and chromium should be used as minimal as possible time, temperature, concentration are variables in involved in any chemical reaction. High temperature means, less time needed for dying, as doses of higher concentration of dye stuff will always make good dying; these are certain you

know, presumptions that can be seen whether they are valid for anthocyanin or not; but the popular mordants that are used, we have discussed time and again that metal mordants are the once, which are used.

And here is a dye, with appropriate appendages to attach to the metal salt. So, what happens? The metal salt acts as a bridging edge, on one side is the dye, and the other side is the fabric. So, that is how it acts as a bridging head to connect the dye the fabric and the mordant. So, even it is like a connecting device, you can think in your mind.

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Therefore, now we come to the various possibilities of mordanting, we all know this and we are repeating this several times, in case of natural dyeing, because these possibilities are only acceptable or valid for natural dying. We can either do a pre mordanting of the fabric or we can do simultaneously, is simultaneous mordanting where dying and mordant are done simultaneously or we can have a meta mordanting step that is the post mordanting step. So, meta mordanting is equal in to simultaneous mordanting, and sorry about that, but post mordanting is also possible.

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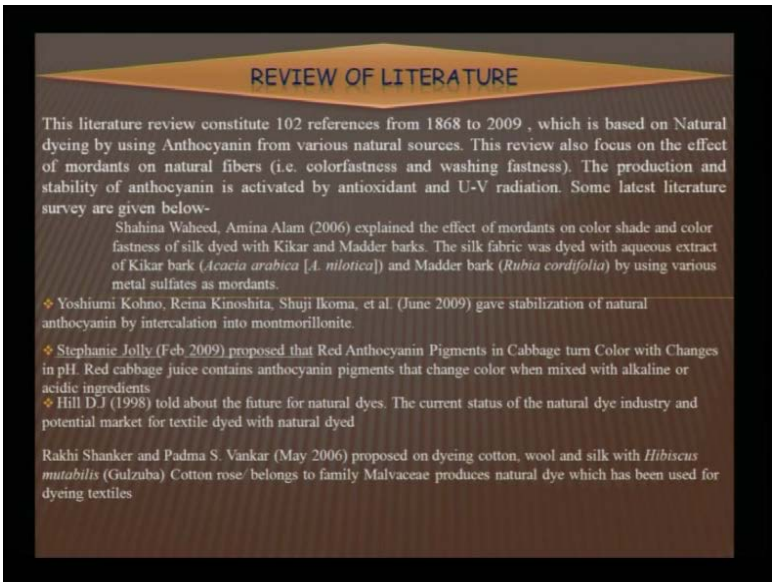

Now, when we try to look at the literature, then we try to see whether people have actually, use this or not, because we were claiming that we were the first one to popularize it, they they this literature, if we constitutes of more than you know, hundred reviews, which were published between 1868 to 2009 and it says that yes, some people did try to use mordants, anthocyanin dyes with natural fibers, but somehow this stability of the anthocyanin a you know, was not established properly while dying with these, and they used it in combination with some other natural dyes; and many a times, it was you know, like misleading whether we can really use the red anthocyanin from the cabbage to change the or to use it, because it know it is very pH sensitive. So, if suppose the dyeing is carried out at different pH, it will give different color and hue color mix a lot of difference. So, this kind of standardization was not available that was for sure.

So, we try to explore in to the details of standardization of the dye. We had spent one full lecture on the effect of standardization; see if we do not standardize these new, newly screened dyes, then one cannot establish or cannot say for sure that this dye will give this color; therefore, it is important that this particular class of dye needs to be standardize.

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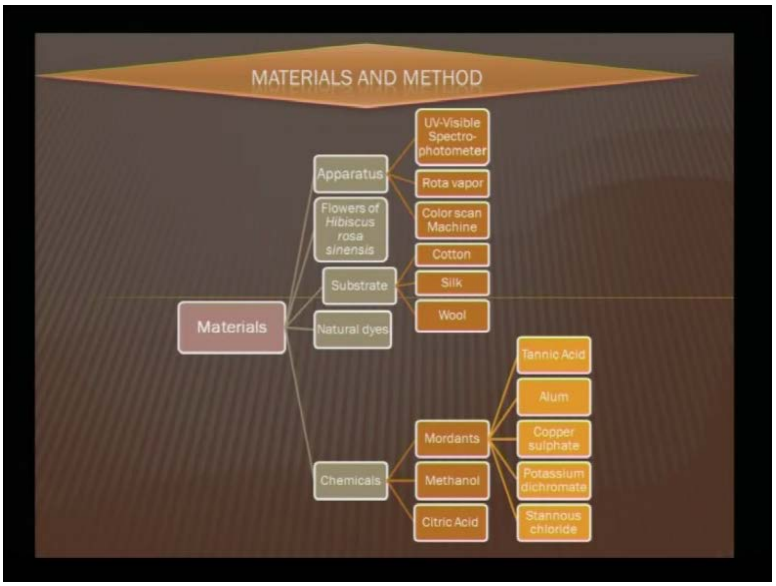

So, we carried out our own step of standardization, and the usual methods of you know, extraction operators and the usual methods of analysis by using UV visible spectrophotometer, colors scan machine for looking at the colored depth and on the hue color, we all use those particular methods and the for cotton tannic acid, and the modern such as alum, copper, potassium dichromate, stannous chloride, these were the four mordents that we try to use with hibiscus extract of course, hibiscus flowers were collected and they were extracted from there, if we also during the process of extraction, we try to standardize even the process of extraction of the dye.

Although this dye is water soluble, but a better extraction in an acidified methanalic solution, and hence is the color to come in to the aqueous medium, there are several methods available in the literature, and we have spent lot of time in learning about the extraction procedure, but for anthocyanin dyes, we have developed very special techniques. People used dilute hydro chloric acid and methanol, but you know whenever these harsh acids are used, it always can have a bad impact on the dying of delicate and natural fibers like cotton, silk and wool.

Therefore we thought that if citric acid is replaced replaces the hydrochloric acid, it will probably have a better impact and would do the needful, because basically it is only the acidified hydrolytic medium that is required for the you know, extraction of the

anthocyanidine from the anthocyanin. And therefore, we used methanolic citric acid solution for the extraction of the dye.

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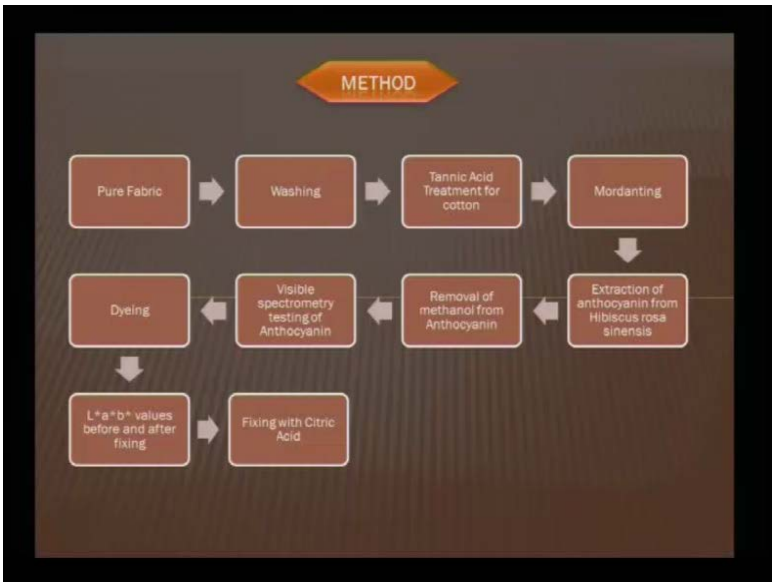

Now, usually the normal methodology is that a pure fabric is taken, it is washed and cotton particularly must go through the tannic acid pretreatment and then mordanting, we shows only four mordants as what I mentioned, we took sorry alum, copper sulphate, stannous chloride and these were the mordants that were used the extraction of anthocyanin dye was done with citric acid solution in methanol, and then the methanol was removed under vacuum. So, that you know the color is not destroyed, we did not heat too much, because over heating such dyes can create a dies coloration; we try to then analyze the…