EXTRACTION OF CARTHAMIN FROM CARTHAMUS TINCTORIUS AND INVESTIGATING ITS DYEING OF WOOL USING POTASSIUM DICHROMATE MORDANT

N.Saadatjou

Departmant of Applied Chemistry, Faculty of Chemistry, Tabriz Univ, Tabriz, Iran.

(Received 4th Jan. 1988)
(Approved 8th Apr. 1991)

ABSTRACT

Carthamin, the natural dye of Carthamus tinctorius (Golrang) was separated by soxhlet extraction and further purified in good yields. Its mordant dyeing of wool, using potassium dichromate as mordant, showed a high washing fastness (above 4). Mordanting by "sweet chrome", "sour chrome", and "reduced chrome" proved that last one to be superior.

INTRODUCTION

Description of the plant:

Golrang is locally known as Kazireh, faked Saffran, Khosk daneh, Zardak flower and Tagalla. The colouring matter produced from the plant leaves are called Zardag and Maol-asfar (yellow water). Golrang is from chicovy family and its origin can traced to Saudi Arabia. The one year old plant contains pins and produces a lot of branches having a flower at top of each branch. The U shaped flowers are formed at the top of each branch in yellow, white and red colours. Golrang has a fruit called Fendogheh which contains 50-55% oil[1].

Planting geography:

Plantation of Golrang has been going on in south Asia and India for many centuries and currently being done in those areas as well as in South Europe, Northern Asia, Latin America, Northern Africa and Iran. Plantation of Golrang is very important in our country because of its interesting properties and climate conditions. It can be grown in Khora-

san,Azarbaijan and central parts of the country. Species of this plant in Iran include Carthamus Lanatus[2],Carthamus Oxyacantha [3],Carthamus Turkistanikus[4],which are planted in Northern and Western areas.

Applications of the plant:

Different parts of the plant can be used as;

Oil:

Times ago,the oil of Golrang was be used as an additive in preparation of paints,and polish,but because of its high content of Linoleic acid , it's importance as food was increased day by day. This oil, in its pure form or mixed with some other vegetable oils forms the main component of Margarin,salad and cooking oils . Its high content of Linoleic acid lowers the cholestrol levels in blood and thereby reduces the occurence of related diseases. But because of its rapid oxidation,it is corrosive and turns rancid. Nowadays,genetic improvements have made it possible to increase the amount of oleic acid vs lenoleic acid and thereby produce an oil resembling the olive oil [2 .

Pharmaceutical use of Golrang:

Seeds and flowers of Golrang have a laxative effect. The extracted oil also is laxative and it can be used as.a medicine in rhumatism by rubbing it on the affected areas[5].

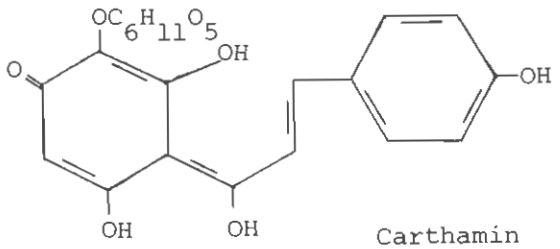
Disregrading other minor applications as fibre,powder, etc,we will arrive at its major usage i.e. as a dye.

The use of dried flowers of Golrang as a dye:

Carthamin is an important dye in Golrang flowers[6]which has a yellow water soluble colorant and can be used as a colorant in food stuffs like suhan (in the form of safran colour) [2]. An important part of the present investigation is related to extraction and application of carthamin in wool mordant dyeing.

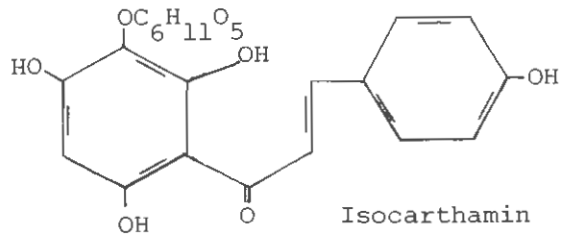
Historical usage of plant dyes for dyeing of natural fibres specially wool and silk traces back to the ancient times. Ancient people used plant dyes for dyeing of their clothing material but most of them were without fastness. Traditional dyers through experiment had found that by using some kind of inorganic salts like metal oxides and vitriols can alter and improve the chemical properties of the dyes. This type of dyeing was evolved in some eastern countries like India,China,Egypt,and Iran and caused a significant progress in carpets and clothing materials,thereby making it one of the most important arts of the world[7] some of which are exhibited in various world museums. The modern version of this process which is being used in today's dyeing industry is called Mordanting.

The major colorant of Golrang is the yellow dye which is extracted from its flower leaves and is listed as a natural yellow No.5 in the colour Index. This dye does not have a lot of usage in textile dyeing[8], but its more important dye from shalcon class,is called carthamin which is famous and has the following formula[9].



Carthamin

Carthamin produces a yellow coloured substance in the presence of HCl which is called isocarthamin, its structure is shown below. Red carthamin and yellow isocarthamin are isomers of each other[10]. In addition, another type of this plant with a reddish orange flowers also contain carthamin[11].



Isocarthamin

EXPERIMENTAL

Dye extraction:

Extraction of carthamin from Golrang requires elimination of the less usable yellow substance accompaning it. Elimination or separation was done by the following procedure. Dried flower leaves were ground into a fine powder and a weighed amount of the powder was placed in soxhlet apparatus. For this purpose 4.9, 4.0 and 2.9 g of powdered flower leaves were weighed and wrapped in separate filter papers and placed in the soxhlet apparatus,where water,ethanol and a mixture of both were used as solvent. In this respect water turned out better than the others economically and experimentally. After several extraction,complete separation of the yellow dye was carried out by distilling off the solvent.The residue was poured in a flask and its carthamin extracted with sodium carbonate(20% aq). The crude product was sticky and was extracted with ehtanol and subsequently precipitated which acetic acid. Presence of impurities was tested by thin layer chromatography separation done by coloumn chromatography(yield:32%,20%,11%). The suitable solvent was found to be a mixtrue of H_2O:EtOH (1:3). The resulting compound was further purified by crystallization.After trying several solvents,essentially acidic EtOH or MeOH(5 to 10% HOAc)was found to be suitable. The resulting crystals were needles with bright red colour (m.p 225 °C), Experimental results are as follows:

1-4.9 g Flower leaves

2.0 g yellow dye

0.4 g Carthamin(yield 8%)

2-4.0 g Flower leaves

1.41 g yellow dye

0.2 g carthamin (yield 5%)

3-2.9 g Flower leaves

1.7 g yellow dye

0.17 g carthamin (yield 6%)

The average yield of extracted red carthamin from dried flower leaves of Golrange was 6.3%(found:C,55.7%; H,5%; $C_{12}H_{22}O_{11}$,required:C,56%;H,4.9%).

Dyeing with the dye obtained (cartha - min):

As mentioned before,one of the best methods for improving fastness properties,especially washing fast - ness,is the application salts of metals like chromium as a mordant. The mor - dant is a compound or a compenent that fixes the dye on the fibre . In the present work,wool fibres were treated with the mordant before dye- ing by one of the following methods.

a:Mixture of potassium dichromate with acetic acid

b:Mixture of potassium dichromate with sulphuric acid

c:Mixture of potassium dichromate with formic or tartaric acid

Procedure:

Washed,scoured and dried samples of wool fibres(or fabrics)(5 g) were selected and three baths were prepa- red by liquor ratio of 50:1 (volume of liquor:substrate weight).The con - centration and amounts of dyes and other additives are calculated based on the weight of fibre(all dissolved in distilled water).

Bath No.1:1% dichromate+3% acetic acid(sweet chrome).

Bath No.2:1% dichromate+3% sulphuric acid(sour chrome).

Bath No.3:3% dichromate+3% formic acid or 6% tartaric acid (reduced chrome).

Fibre samples entered the baths while cold and the temperature was then raised to boiling in 20 min and mordanting was carried out for 45 min. After cooling the bath,fibres were taken out and then intered to the same bath with liquor ratio of 50 :1 having 5% of carthamin dye and 3% acetic acid. During 20 min, bath was boiled and dyeing carried out for 45- 60 min. Eventially wool samples were taken out of the bath and dried in the air[12].

Determination of washing fastness:

The term is used for showing fastness of dye in washing with soap solution at a specified temperature.

Procedure:

Dyed sample (10 cm x 4 cm) were placed between two pieces of undyed wool and nylon fabrics (4 cm x 4 cm) and were tested according to ISO2 test[13].

Test name:ISO2;solution:soap 5 g /l; Time:45 min;Temperature:50°C; Liquor ration:(50:1).

Linitest-Original Hanau was used

as the apparatus for above mentioned test. This apparatus is a universal laboratory washing machine which is used for rapid and accurate determination of washing fastness. After washing with cold water, the sample was washed in running water for 10 min. Dyed sample was separated from undyed samples, dried and then variations of colour in dyed and undyed samples was evaluated with Gray Scale and a fastness of 4 was found for the sample.

Determination of Cr^{VI} and Cr^{III}:

One of the modern methods in this regard is iodometric titration of Cr^{III} followed by determination of total chromium as Cr^{III} by atomic absorption spectrophotometry[14]. This method was used here.

For determination of Cr^{VI} in the three baths (Table 1), 100 ml of cold bath was poured in flask and 4 g KI, 2 g $NaHCO_3$ and 6 ml HCl were added. Titration of starch was carried out by 0.01 M sodium thiosulphate in the presence of starch. Rapid titration is required, because the concentration of Cr^{VI} in the bath tends to decreases, with time (the reason is probably the reaction between dichromate and organic compounds in solution). Then 1 ml of titrated solution was diluted to 2,5,8,10 ml and total amount of chromium determined via atomic absorption spectrophotometry. Standard solutions was prepared by dissolving specified amounts of potassium dichromate in distilled water and titrated as above. To study the effects of various acids in the dyeing bath, different baths were prepared with acids.

RESULTS

The results of the tests described are summarized in Table 1.

DISCUSSION

In mordant dyeing of wool (using chromium compounds) the mordant can be added by three different methods;

Table 1: Amounts of Cr^{VI}, Cr^{III} and total chromium in different bath and effects of various acids (ppm)

Bath / Acid	Mordant			Mordant + Wool			Dyeing		
	Cr^{VI}	Cr^{III}	Cr(T)*	Cr^{VI}	Cr^{III}	Cr(T)	Cr^{VI}	Cr^{III}	Cr(T)
No acid	260	2	262	45	5	50	22	21	43
3% Acetic acid	230	32	262	3	13	16	1	38	39
3% Sulphoric acid	195	65	260	60	40	100	9	123	132
3% Formic acid	195	66	261	35	20	55	1	148	149
6% Tartaric acid	30	230	260	0.5	24	24.5	0.5	102	102.5

Cr(T)*: Total Cr

chrome mordant,after chrome,and meta-chrome or chromate [15]. Anyhow when wool is treated with hot solution of dichromate the basic part of it reacts with dichromate in the first stage .

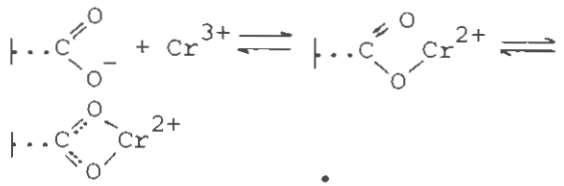
$$2\ \text{Wool}\text{-}{}^{+}NH_3\ {}^{-}OOC\text{-Wool} + Cr_2O_7^{2-} + 2H^+ \longrightarrow$$

$$(\text{Wool}\text{-}{}^{+}NH_3)_2Cr_2O_7^{2-} + 2\ \text{Wool}\text{-COOH}$$

As soon as the dichromate ions are absorbed,the hydrogen ions are taken simultaneously until the solution becomes neutral. As a result pH rises indicating that the solution is turned basic. In the next stage the dichromate anion is reduced gradually to Cr^{III} cation. This process accurs simultaneously with cleavage and oxidation of some of disulphide bonds of Keratin and Cysteine:

$$Cr^{VI}\ (\text{anion}) \longrightarrow Cr^{III}\ (\text{cation})$$

Cr^{III} then reacts with the carboxylic groups of wool. Although the reaction is reversible,because of the large activation energy for disappearance of Cr^{III} the process takes place extremely slowly[16].



Final dyeing results from the reaction of Cr^{III} with the rest of dye molecules to produce(1:1)and(1:2) complexes[17].

Absorption of dichromate ions from the neutral bath is slow but it will be enhanced by addition of acid and decreasing pH. Reduction of Cr^{VI} to Cr^{III} which is the main part of the process occurs with the change of the colour from yellow to greenish gray. In this stage,Cr^{III} reacts with the dye and forms the complex; i.e. wool is mordanted.

To neutralize the basicity of the mordant's bath,small amounts of acid (usually acetic acid)is added. Dichromate itself acts as a buffer and is changed to chromate by alkali.

$$Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O$$

Some of the chrome dyes are oxidized by chromic acid,therefore in these cases reducing acids are added to complete the reduction of Cr^{VI} to Cr^{III}. These acids acts as chelating agents. The produced mordant from these reductant acids is known as "reduced chrome" and mordant without reducing agent is called " sweet chrome". Third type of mordants is called "sour chrome" in which sulphuric acid is used in it. When wool is mordanted by sweet chrome and sour chrome methods,the mordant is oxidized and turns yellow , whereupon exposure to light,this yellow Cr^{VI} is reduced to greenish gray Cr^{III} and hence dyeing will not be pleas -

ant. For this reason usually the mordanted dye is not exposed to light for a long time.

The effects of different acids in three baths;mordant,wool without dye and dyeing are listed in Table 1 for comparison. With regard to reducing acids,it can be explained that produced Cr^{III} from reduction of Cr^{VI} is bonded to carboxylic groups [18]. Therefore bonding of Cr^{III} while it is in boiling state will direct the following reaction to the right.

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$$

Table 1 shows the optimum acids concentrations. For acetic,sulphuric and formic acids it is 3% and for tartaric acid 6% . Therefore, mordanting methods were based on these amounts. Of the two reducing acids , tartaric acid is more suitable than formic acid because the reaction of $Cr_2O_7^{2-} \rightleftharpoons Cr^{3+}$ is carried out more easily by this acid in each of the three baths. Specially it can reduce almost all of Cr^{VI} to Cr^{III} and complete the complex formation and wool mordant dyeing. Also sweet chrome mordant is prefered to sour chrome. Particularly in dyeing and wool without dye baths, acetic acid is more successful in reducing Cr^{VI} to Cr^{III} . However, in general relative to sweet and sour mordants the "reduced chrome" specially with tartaric acid is more effective and dyeing with this mordant is recomanded.

CONCLUSIONS

Separation of the less useable yellow dye and purification of important dye of Golrang (Carthamin) by sohxlet was successfully achieved with a suitable yield. Wool dyeing using potassium dichromate mordant was carried out by carthamin dye and showed a high washing fastness of above 4. Wool mordanting was carried out by three methods "sweet chrome ", "sour chrome" and "reduced chrome ". Of these three methods,the last showed better results,while sweet chrome mordanting is prefered to sour chrome mordanting.

REFERENCES

1. M.Moein,*"Farsi Dictionary"*, Amir Kabir Pub.,7th Ed,3,2785(1985).
2. H.Allyari,*" Lecture Notes"*,Facu - lity of Agriculture, Tabriz Univ., pp.38.
3. *Chem.Ber.*,109,3953(1976).
4. *Phytochemistry*,20,1429(1981).
5. A.Zargari,*" Medicined Plants"*, Tehran Uni.Pub., 1st.Ed.,3 , 563 (1973).
6. I.R.Seshadri,Sci.Proe.Roy, Dublin Soc.,27,82(1956).
7. N.Saadatjou,*"Chemistry and Technology of Colour"*,Nima Pub.1st.Ed., pp.138,221,222(1985).
8. *"The Colour Index"*,3rd Ed.,(1971),

supplement 1982,SDC(UK) & AATCC (USA).

9. P.F.Gordon and P.Gregory,*"Organic Chemistry in Colour"*, Speringer-verlag,Berlin,2,(1983).
10. *"The Throp's Dictionary of Applied Chemistry"*, Longmans Green,London, 5,655(1937-54).
11. T.R.Seshadri and R.S.Thakur,*Current Sci.*,(India),29,54(1960).
12. N.Saadatjou,*"Colour and Coloration"(Experimental)*,90(1987).
13. "Standard Methods for the Determination of Colour Fastness of Textiles",4th Ed.,SDC(UK),(1978).
14. F.R.Hartley and A.S.Inglis, *Analyst"*, 93,394(1968).
15. C.L.Bird,*"The Theory and Practice of Wool Dyeing"*,4th Ed.,SDC,112(1982).
16. C.L.Bird and W.S.Boston,*"The Theory of Coloration of Textiles"*,SDC, 416(1975).
17. Ref.16,64.
18. F.R.Hartley, *Aust.J.Chem.* ,21,2723 (1968).