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SOME WAYS OF INCREASING EFFICIENCY IN UTILIZATION OF DYES PRODUCED FROM RENEWABLE PLANT RAW MATERIALS FOR COLOURING OF TEXTILE MATERIALS

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Approximately until the middle of the 19th century only natural dyes have been used for colouring of textile materials, which were extracted from plant-based raw materials, minerals and insects. In spite of the fact that they were poetically called "dyes presented by nature", natural dyes can hardly be considered as "presents" since their price had always been high.

Experience with the use of dyes, extracted from plant raw materials, has also revealed a number of drawbacks, inherent to them; these are, first of all, the following: as usual, low percentage of coloured compounds in raw materials, undetermined composition of admixtures extracted from natural raw materials during extraction of coloured compounds, alternate composition of extracts, and as consequence bad repeatability of colour characteristics of dying materials, difficulties to obtain mixed dyes. In addition to the above said, in order to fix dyes on fibres, there is a need to use, in most cases, salts of heavy metals (mordants) which have negative effect on ecological characteristics both of dying process, as well as dying materials, etc.

Therefore, it is not surprising that with advance of industrial fabrication of synthetic dyes, natural dyes became insignificant and they were practically of no interest in 19th century.

At the same time, a number of advantages of natural dyes over synthetic ones, for instance, extraction (sometimes several times within the year) from the renewable plant raw materials, safe use, quite a wide range of colours, as well as environmental situation that worsened over the past decades, aroused interest of chemists for research aimed to overcome the drawbacks mentioned above. Let us dwell on some of these studies.

To increase the percentage of coloured compounds in plant-based raw materials, it has been suggested to employ, in particular, methods of genetic engineering [1].

Another approach to increase percentage of coloured compounds in extracts has been suggested in paper [2]. With this aim in mind, crops of Saint-John's wort (Hypericum perforatum L) were treated 10…15 days prior to harvesting with plant growth stimulant– gibberellin.

The obtained benzine and ethanolic extracts from the treated and untreated raw materials were tested for content of coloured compounds. It has been established that about 14% of coloured compounds are extracted from the untreated raw materials (from total mass of dry raw materials). When treated with plant growth stimulant, quantity of extracted coloured compounds increased up to 8…19%, with unchanged extraction conditions.

Electronic adsorption spectra (EAS) of extracts obtained from the treated and untreated raw materials are identical and have 2 pronounced maxima by 400 and 670 nm. Significantly higher optical density of absorption spectra indicates bigger quantity of coloured compounds in the extract of the treated raw materials.

Evaluation of the relative quantitative amount of coloured compounds in the obtained extracts has been made also by colour characteristic of samples of cloth coloured with these extracts, calculated by means of uniform contrast system SIE Lab. The obtained results confirmed high content of coloured compounds in the treated raw materials.

Moreover, colour shade of obtained coloured samples practically does not change. This fact may serve as prove that as a result of treatment with plant grouth stimulant, probably, accumulation of coloured compounds takes place and no any other substances are formed.

Though influence of pH medium on the extraction process of coloured compounds had long been known, no systematic research had been conducted. In the study [3] effect of acidity of the extraction medium on the quantity of extracted coloured compounds was examined.

Extraction from Saint-John's wort plant raw material has been carried out by means of water-bath during 60 min with pH ranging from 5 to 10. We were able to reach maximum extraction of coloured compounds in acid medium. Yield of dry residual averaged 23%, whereas dry residual in the neutral and acid media made up 13 and 18% correspondingly.

It has been shown in the study of Mongolian scientists [4] that utilization of ultrasound during extraction of coloured compounds from plant raw materials enables to considerably increase the yield. Investigations were conducted in the temperature range from 50 to 70°C and with ultrasound exposure (22 kHz power) during 3, 5, 10, 15, 20 and 25 min. Optimal conditions for the process appeared to be the following: time – 20 min and temperature – 70°C. Under these conditions, depending on the type of raw materials, amount of extracted coloured compounds accounts for 30…70%. Process procedures for preparation of dye solutions has been suggested and process scheme has been developed on the basis of the worked out laboratory methods.

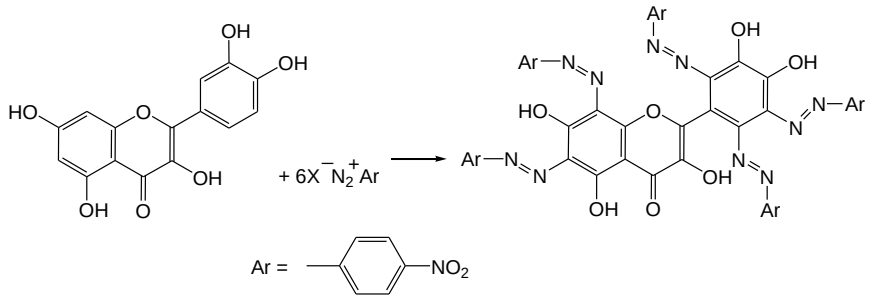
A conceptually new approach to solve problems with the use of coloured compounds of plant origin for colouring textile materials has been suggested by authors of this paper. The approach under development is based on the concept that derivatives of phenolic nature, such as flavonoids, antraquinone compounds, etc. are part of coloured compounds;

in principle, this enables them to be involved into reaction of electrophilic substitution.

To confirm the possibility for implementation of the above mentioned approach, azo coupling reaction of quercetin (1), being part of extracts of Saint-John's wort with p-nitrophenyl diazonium chloride, has been investigated as a model reaction, which was not described so far.

Azo coupling was carried out during 30 minutes in aqueous-alcohol medium (30:70), pH = 9÷10 and at temperature 10°C, with quercetin ratio: diazonium salt equaling to 1:1, 1:4, 1:6.

Reaction has been carried out until diazo compound was completely consumed (it was determined by means of testing with acid solution of R-salt). Sediment formed in the reaction was filtered in a drying kiln and in an exsiccator over P_2O_5



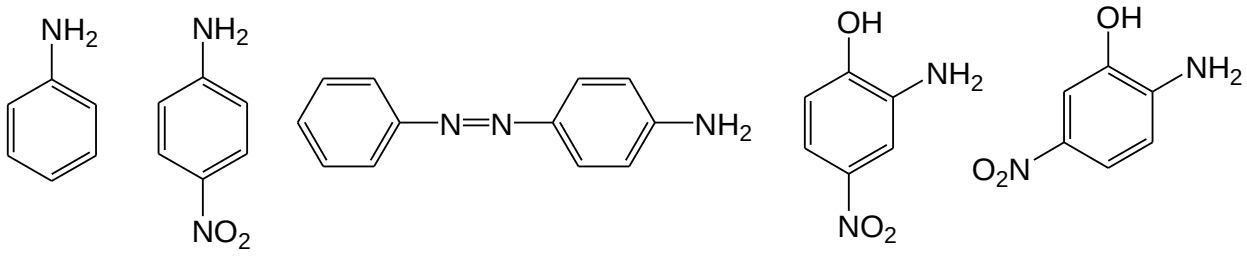
1 2

Analysis of products isolated by means of ^1H NMR spectroscopy revealed that with quercetin:diazonium salt ratio, equaling to 1:1 and 1:4, reaction proceeds non-selective – resultant represents a mixture of compounds of different degree of substitution. In the spectrum of the product (2) isolated from the reaction mixtures with reagent ratio 1:6 signals of protons of the original quercetin in the range of 6,0…7,6 m.d. are missing; there are only signals of aromatic protons of p-nitro-phenyl radicals available, with chemical shifts in the range 7.65-8.36; this enables to make a conclusion on the fact of complete substitution of all aromatic protons in the molecule of quercetin.

Comparison of electronic adsoption spectrum (EAS) of original quercetin and coupling product (2) testifies the appearance of new chromophoric systems. In the EAS of quercetin there are three intensive absorption bands (AB): λ_{max} = 204 nm, λ_{max} = 256 nm and λ_{max} = 374 nm, curve with λ_{max} = 222 nm. In the EAS of the product (2) band with λ_{max} = 256 nm is bathochromically displaced for 5 nm and new ABs appear with λ_{max} = 390 nm and λ_{max} = 480 nm.

Taking into account the obtained results, possibility for chemical modification of extracts of Saint-John's wort has been investigated.

Reaction has been carried out according to the following method: a certain amount of dry extract obtained during extraction of a whole plant was dissolved in the alkaline solution (pH 9-10) and cooled down to 0-5°C. While constantly mixing, diazonium salt solution was added to the liquid for 3…4 hours. Diazonium salts have been used as diazo compounds obtained from the following amines: aniline (3), p-nitro aniline (4), p-amino azobenzide (5), 4-nitro-2-amino phenol (6), 5-nitro-2-amino phenols (7)



3 4 5 6 7

Reaction was considered to be completed, when after adding next portion of diazonium salt outflow test with R-salt was positive, and test with diazonium salt solution was negative. Sediment was filtered, washed with water and dried in an exsiccator under vacuum over P_2O_5. Since extract of Saint-John's wort has multicomponent composition, we were able to obtain mixtures of azo compounds of similar structure as a result of azo-coupling reaction.

Analysis of EAS of obtained products revealed that all of them have changes, compared to EAS of original extract of Saint-John's wort, similar to those for above mentioned EAS of quercetin and the product of its modification. These changes (appearance of new AB which are notably displaced into the long-wave region) testify to the appearance of new chromophoric systems.

We turned then our attention to the study of the possibility to employ coloured extracts of Saint-Jon's wort and products of their chemical modification for colouring of textile materials.

Since separation of individual compounds both from extracts, as well as from a mixture of azo derivatives from the point of view of practical use is not advisable, we have employed them without separation.

The conducted investigation revealed the following. When extract of Saint-John's wort is employed for colouring, wool fabric changes colour to beige. Colour fastness to washing at 40°C equals to 3/3/4 degree. Utilization of mordants ($CuSO_4$, $K_2Cr_2O_7$, $SnCl_2$) with 2% concentration from fiber results in significant saddening, as well as in increase of colour fastness to wet treatment – 4-5/4-5/5 degree. However, we failed to dye polyester fabric with extract of Saint-John's wort.

Dying with products obtained as a result of modifying Saint-John's wort according to disperse dyeing technology revealed that polyamide fabric is dyed with synthesized compounds into yellow, yellow-brown, brown and red-brown colours, and polyester fabric - into pink-beige, yellow and light-brown colours. It has been established that colour fastness for these types of fabric is: to washing at 40°C: 4…5 degree; to dry and wet rubbing: 4…5 degree. The obtained "azo dyes" are also able to dye wool according dyeing technology with acid dyes with good colour fastness index (to washing at 40°C: 4/4/5 degree; to dry and wet rubbing: 5 and 4 degree correspondingly).

This way, utilization of modified coloured compounds of plant origin enables to discontinue to use mordants – heavy metal salts, and at the same time to ensure high indices of colour fastness to physical-chemical actions.

In conclusion, it should be noted that in countries with developed textile and chemical industries there is a process of assessment of economic, technological and environmental advisability of utilizing natural dyes for colouring textile materials currently under way.

World production of natural dyes accounts for 10,000 tons, i.e. ~1% from production output of synthetic dyes. World market in monetary terms reaches 100 million US dollars. Consequently, price of dye averages 10-20 US dollars per kilogram, which is comparable to the value of synthetic dyes and therefore is not a limiting factor for their utilization.

According to estimates of some experts, utilization volume of natural dyes in the first half of 21st century should make up about 10% of the total volume of consumed dyes.

Modern history of development of natural dyes can be characterized in short as follows.

Industry of natural dyes is apparently related to social issues. For many remote regions of our planet cultivation of plants, serving as raw materials for dyes, and their processing are sources of income and means of subsistence for whole settlements. Besides, primitive manual multi-stage methods of textile colouring are a part of natural crafts and belong to cultural heritage of nations.

In the developed countries natural dyes are utilized as auxiliary materials for different hobbies, especially in the USA, where numerous hobby groups, workshops are organized; there are even courses for art of batic painting, discharge printing, moire dyeing, etc.

Ecological standards, which become more and more strict, force us to pay attention to the nature as a source of harmless, harmonious and user-friendly products. A category of consumers appeared in the West who are ready to pay any possible amount of money for natural goods, including garments, produced from plants which are not treated with pesticides and artificial fertilizers, and which are dyed with dyes produced from natural raw materials.

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