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SYNTHESIS OF AMINOPICALINES WITH GOSSYPOL SCHIFF BASE AND PREPARATION OF METALLOCOMPLEXES WITH Cu^{2+}, Ni^{2+} SALTS

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Abstract: *Physicochemical properties of gossypol, their Schiff bases and metallocomplexes were synthesized. When synthesizing derivatives of Schiff's bases, gossypol and primary chiamin are taken in a 1:2 mol ratio, enough 96% ethyl alcohol is poured for its dissolution and stirred for three hours while heated in a magnetic stirrer. Structures of all obtained substances were analyzed using IR and UV spectra.*

Key words: *Gossypol, amino compound, Schiff's base, spectrum, biologically active substance, metallocomplex, polyphenol, triterpene, aldehyde, cotton plant, naphthalene.*

Introduction

Gossypol is a specific polyphenolic compound and is considered the main polyphenolic compound of the cotton plant. belongs to the group of triterpene aldehydes and is found in plants called Gossipium. Among such plants, the cotton plant is included, in various parts of it, including leaves, roots, and other parts of the body in different amounts (up to 0,56-3%, depending on the type of cotton). occurs.

Gossypol is an amorphous, crystalline, lemon-yellow natural substance that is soluble in various organic solvents. In addition to the presence of various polar groups in the gossypol molecule, it is practically insoluble in water due to the presence of two isopropyl groups in the naphthalene residue.

Gossypol is very soluble in methyl, ethyl, isopropyl and butyl alcohols, as well as diethylene glycol, dioxane, acetone, diethyl ether, ethyl acetate, chloroform, carbon tetrachloride, dichloroethane, phenol, pyridine and heated naphthalene, heated cottonseed oil. In addition, gossypol is soluble in limited amounts in glycerol, cyclohexane, benzene, gasoline, and petroleum ether.

As a result of a number of studies, it was determined that the aldehyde groups in the gossypol ($C_{30}H_{30}O_8$) molecule form internal hydrogen bonds with the two oxygen atoms of the hydroxyl groups in the second -ortho position.

Substances formed as a result of the reaction of substances containing an amino group with gossypol are called Schiff's bases or azomethine derivatives. When synthesizing derivatives of Schiff's bases, gossypol and primary chiamin are taken in a 1:2 mol ratio, enough 96% ethyl alcohol is poured in to dissolve it, and it is stirred in a heated state (70-80 ^{0}C) in a magnetic stirrer for three hours, the progress of the reaction is monitored using YuQX. After the reaction is complete, the resulting substance is left for one day to settle completely, then it is filtered and washed 2-3 times with ethyl alcohol. The obtained substance is dried in a place where sunlight does not fall.

Table-1

Physicochemical quantities of synthesized Schiff bases

	Synthesized Schiff base	Liquid ^{0}S	R_f	Color	Reaction product in (%).
	Di-(2-amino-4-pikolin)gossipol	213-214	0,49	yellow	89
	Di-(6-amino-3-pikolin)gossipol	209-210	0,44	yellow	92

Gossypol contains six –OH groups, two carbonyl, two methyl, two isopropyl and two naphthalene rings. In its IR-spectrum (n, cm-1) we can see the valence vibration frequencies belonging to the –OH group in the 3495, 3424 areas. The area between 1614 and 1441 indicates the presence of two naphthalene rings.

In the IR spectrum of the Schiff base formed by gossypol with 2-amino-4-picoline, we can see a clear change of the absorption maxima at 3240-3430 cm^{-1} belonging to the NH_2 group.

When analyzing the IR spectrum, it can be observed that the valence vibrations at 1712 cm^{-1} corresponding to the -CHO group have completely disappeared.

In the UV spectrum of the Schiff base of gossypol formed with 2-amino-4-picoline, a bathochromic shift occurs for this substance due to absorption in the 240,54 nm branch, and absorptions at 280, 427,98 nm are due to the hypsochromic shift of the Schiff base with N in the azomethine bond. is explained by the formation of a hydrogen bond with H of the aldehyde group in gossypol.

Rentgenografik tadqiqotlar izostrukturaviy klatratlarning ikkita guruhi mavjudligini aniqlab berdi, ular KK(A) va KK(V) kriptat guruhlariga tegishli deb aniqlandi. KK(A) kriptat guruhiga gossipolning benzol, brombenzol, izopropilbenzol, izopropilbrom va trixloretilen bilan hosil qilgan kriptatlar kiradi. Ushbu guruh kristallarida mezbon: mehmon nisbati 2:1, fazoviy guruhi R-1, z=4 ga teng.

Gossypol molecules are combined into dimers through hydrogen bonds, and later, these dimers are associated with columns using hydrogen bonds. When such columns are packed into the crystal structure, they form spaces where guest molecules are located.

Gossypol and its derivatives (mainly Schiff bases of gossypol) readily form complexes with many polar (only those with proton acceptor groups) and nonpolar substances. In addition, in clathration studies of gossypol derivatives, the phenomenon of polymorphism in the formation of host-guest complexes was revealed. It has been shown that gossypol derivatives can form different crystalline modifications with the same guest component. The reason for this is that the formation of clathrate depends on the thermodynamic conditions of deposition.

Gossypol Schiff bases were reacted with Cu^{2+}, Ni^{2+} salts in a 1:2 mol ratio. The duration of the reaction was monitored hourly by thin-layer chromatography, and the obtained metallocomplexes were analyzed by comparison with the Schiff base spectra, and the following results were obtained. The main characterizing bond of the Schiff base is the azomethine bond formed between the carbonyl in gossypol and the primary amino group. When analyzing the IR-spectrum of the metallocomplex formed by Gossypol Schiff base with Cu^{2+} salt, it was concluded as follows. In contrast to the IR spectrum of the Schiff base, in the spectrum of the metallocomplex, it can be seen that the valence vibrations of the azomethine bond are shifted to the region of 1619 cm^{-1}. This displacement occurs when the nitrogen atom participating in the formation of an azomethine bond forms a donor-acceptor bond with Cu^{2+} in the metallocomplex.

It can also be seen that the region of 3485 cm^{-1} belonging to the Schiff-based –OH group was shifted to the region of 3422 cm^{-1} in the spectrum of the metallocomplex, and a new absorption maximum appeared in the region of 3288 cm^{-1}. These changes are related to the formation of a covalent bond between the oxygen atom of 7-OH and Cu^{2+} on the Schiff basis. In the spectrum of the metallocomplex, we can consider the new absorption maxima at 544 cm^{-1} and 610 cm^{-1} as peaks belonging to metal-oxygen and metal-nitrogen bonds.

Table 2

Physicochemical quantities of Schiff base metallocomplexes

	Synthesized metallocomplexes	sol vent	Liqui d ^0S	f	C olor	Re action product in (%).
	Di-(2-amino-4-pikolin)gossipol +$CuCl_2 \cdot 2H_2O$	D MFA D MSO	291-292	,49	b rown	67 .8
	Di-(2-amino-4-pikolin)gossipol +$NiCl_2 \cdot 6H_2O$	D MFA D MSO	297-298	,44	q o‘ng‘ir y ashil	69 .3
	Di-(6-amino-3-pikolin)gossipol +$CuCl_2 \cdot 2H_2O$	D MFA D MSO	300<	,54	b rown	71 .3
	Di-(6-amino-3-pikolin)gossipol +$NiCl_2 \cdot 6H_2O$	D MFA D MSO	300<	,69	b rown	70 .8

System:- hexane:acetone (4:1)

Of the Schiff base formed by gossypol with 6-amino-3-picoline When studying the UV spectrum, 236,51 for this substance; It gave absorption maxima at 379,1 nm.When analyzing the UV-spectrum of the metallocomplex of the Schiff base of Gossypol with 6-amino-3-picoline obtained with

$CuCl_2 \cdot 2H_2O$, the metallocomplex is 247,64; It gave absorption maxima at 422,81 nm. The graph comparing these spectra to each other looked like this:

236.51 based on Schiff; The peak of the absorption maxima at 379.1 nm is lost in the metallocomplex, and the Schiff-based peak at 379.1 nm is shifted to 422.81 nm in the metallocomplex, this shift occurs due to coordination bonds in the metallocomplex.

Of the Schiff base formed by gossypol with 6-amino-3-picoline When analyzing the IR spectrum, obvious changes occur in the area of absorption maxima belonging to the NH_2 group at 3120,44 cm^{-1}. Based on the Schiff, we can see that the surface and distance between these peaks has expanded. These expansions occur due to Schiff-based hydrogen bonds. As a result, we can see absorption maxima at 1714,68 cm^{-1} due to valence vibrations of the new –N=CN– bond.

It is a Schiff base and a metallocomplex formed with $CuCl_2 \cdot 2H_2O$ When the IR spectrum was analyzed, it was found that the absorption maxima at 2966,25 cm-1 due to valence vibrations of the new –N=CN– bond did not change and 3479,34; Absorption maxima were observed at 3411,77 cm^{-1} due to coordination bonds in the metallocomplex. In the IR-spectra of the obtained metallocomplexes, the change of the valence vibration lines belonging to the OH group (area 2740-3300 cm^{-1}) and the weakening of the vibration frequencies of azomethine bonds (area 1600-1627 cm^{-1}) is observed; M-O (area 450-490 cm^{-1}) lines appear.

When studying the structure of metal complexes using UV spectroscopy, the presence of azomethine bonds (λC=N=272 nm) is proven by the appearance of an absorption line in the 260-300 nm region.

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