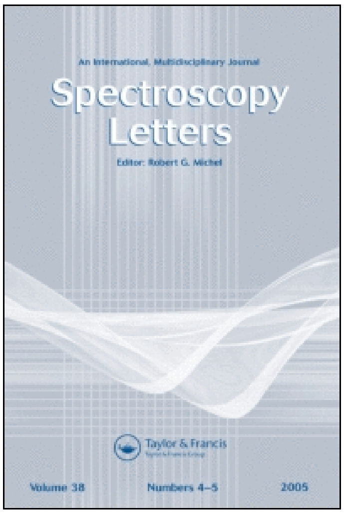

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SELECTIVE ESTERIFICATION OF GOSSYPOL BY COPPER ACETATE IN ACETONITRILE - SPECTROSCOPIC STUDIES

Key Words: FTIR, UV-visible absorption spectra, Gossypol, Copper Acetate

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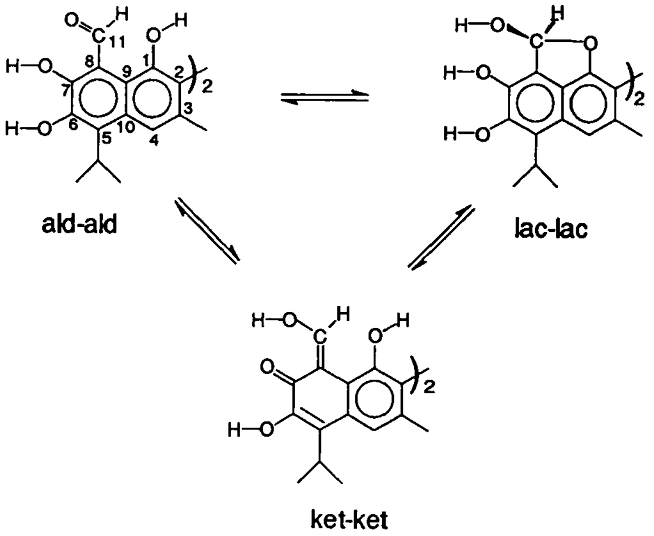
ABSTRACT

Gossypol and its 1:1 complexes with copper acetate in acetonitrile were studied by FTIR and UV-visible spectroscopy. With the complexation with Cu cation the tautomeric equilibrium of gossypol is completely shifted from the aldehyde-aldehyde to the lactol-lactol tautomer. The acidic character of $O_{11}H$ group in the gossypol-Cu complex led to the selective esterification of the lactol form of gossypol by the acetate group.

INTRODUCTION

Gossypol, 2, 2 '- bis (8-formyl -1, 6, 7-trihydroxy -5 -isopropyl-3-methylnaphthalene), is a yellowish compound present in various parts of cotton plants[1]. Its biological importance was the reason for many recent studies of spectroscopic properties of gossypol in solution[2-10]. NMR, IR and UV-visible spectroscopy studies proved that gossypol can be present in three tautomeric forms in solution:



In non-polar solvents gossypol is present in the aldehyde-aldehyde form, whereas in polar solvents the equilibrium between aldehyde-aldehyde and lactol-lactol tautomers is observed depending on the nucleophilicity of the solvent[2-6]. In alkaline solutions, the ketol-ketol form is found to be the main tautomer of gossypol[7].

As it has been shown recently by UV-visible and FTIR spectroscopy studies[9-11], the addition of $M(AuCl_4)_2$ or $M(ClO_4)_2$, where M = Be, Cu, Ni and Zn, to the solution of gossypol in acetonitrile leads to the formation of the 1:1 complexes of gossypol with M^{+2} cations. The tautomeric equilibrium of gossypol is completely shifted from the aldehyde-aldehyde to the lactol-lactol tautomer in the case of Be^{+2}, Cu^{+2} and Ni^{+2} complexes, whereas for Zn^{+2} complex to the ketol-ketol form.

In this paper the complexation of gossypol with copper acetate in acetonitrile is studied by FTIR and UV - visible spectroscopy. More acidic character of $O_{11}H$ group in the gossypol-Cu^{+2} complex (gossypol in the lactol- lactol form), suggested in ref. 11, may lead to an esterification reaction by the acetate group.

EXPERIMENTAL

Yellow microcristalline pure gossypol obtained from the Institute of Bioorganic Chemistry, Academy of Sciences of Uzbekistan, Tashkent, was recrystallized twice from the 2:1 (v/v) mixture of hexane-ethyl ether (m.p. 180 C; Elemental Analysis: calculated for $C_{30}H_{30}O_8$ (%): C, 69.5; H, 5.79; found: C, 69.3; H, 5.74). All solvent used were spectroscopic grade and were stored over 3A molecular sieves for several days. All manipulation with the solutions were performed in a carefully dried and CO_2 -free glove box.

The complex of gossypol and copper acetate was obtained by adding equimolar amounts of 0.1 mol dm^{-3} solution of copper acetate in carefully dried acetonitrile to the acetonitrile solution of gossypol.

The infrared spectra were taken with an IFS 113v FT-IR spectrophotometer (Bruker, Karlsruhe) equipped with a DTGS detector; resolution 2 cm^{-1} , NSS = 250. A cell with Si windows and wedge-shaped layers was used to avoid interferences (mean layer thickness 400 μs). The IR spectrum of gossypol was recorded in 0.05 mol dm^{-3} CH_2Cl_2 solution, whereas the spectra of copper acetate and 1:1 complex of gossypol with copper acetate were taken from 0.05 moldm^{-3} acetonitrile solutions.

The UV-visible absorption spectra were measured by means of a 8453A Diode Array (Hewlett Packard) spectrophotometer using the acetonitrile solutions of gossypol and copper acetate in the concentration range of $5x10^{-5}$ mol dm^{-3} .

RESULTS AND DISCUSSION

FTIR investigations

The FTIR spectra of gossypol in CH_2Cl_2 and its complexes with $Cu(CH_3CO_2)_2$ in CH_3CN are shown in Fig. 1. For comparison the

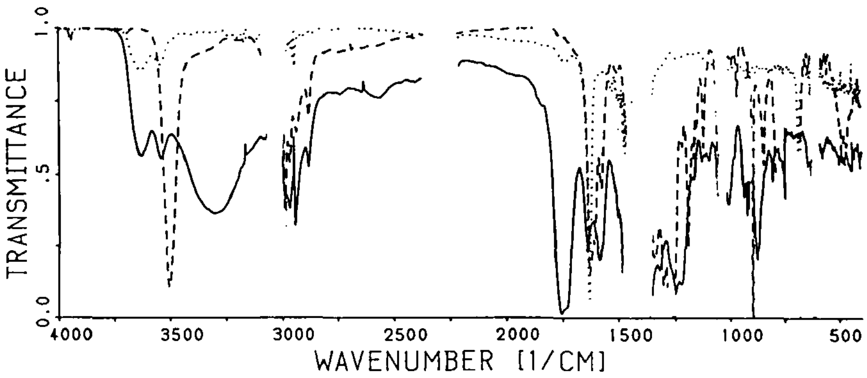
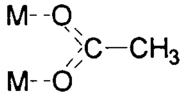


Fig. 1 FTIR spectra of: (- - -) gossypol in dichloromethane, (• • •) copper acetate and (----) 1:1 mixture of gossypol with copper acetate in acetonitrile.

spectrum of $Cu(CH_3CO_2)_2$ in CH_3CN is also given. The same spectra in the region 1800-1500 cm^{-1} are shown in Fig. 2.

The spectrum of the acetonitrile solution of $Cu(CH_3CO_2)_2$ (dotted line) shows the $\nu_{as}(CO_2^-)$ vibration at 1654 cm^{-1}, whereas the $\nu_s(CO_2^-)$ vibration overlaps with the solvent bands. The $\nu_{as}(CO_2^-)$ band is shifted to higher wave numbers in comparison with that in the spectrum of solid state, for which the following bridged structure was found by the x-ray analysis:[12,13]



For such structure the $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ vibrations were found at 1599 cm^{-1} and 1434 cm^{-1}, respectively.[14] According to the results obtained the structure of $Cu(CH_3CO_2)_2$ in acetonitrile solution involves other bridged structure, i.e., $Cu^{2+}\cdots{}^{-}OOC\text{-}CH_3$.

The spectrum of gossypol in various solvents have been studied extensively. In CH_2Cl_2 solution gossypol exists as the aldehyde-aldehyde tautomer, whereas in acetonitrile solution the aldehyde-aldehyde tautomer is predominant (67%) and the other tautomer is lactol (33%).[2]

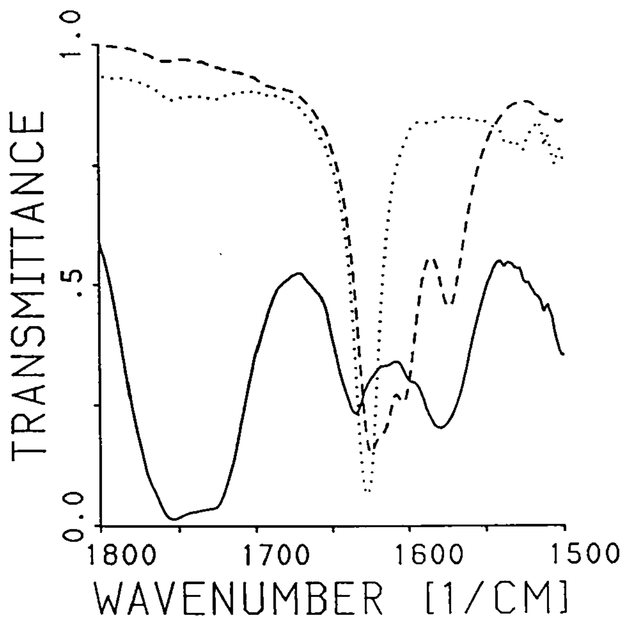
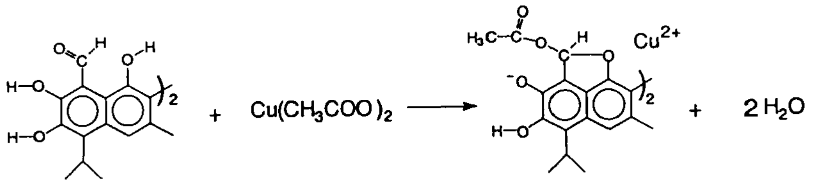


Fig.2 FTIR spectra of: (- - -) gossypol in dichloromethane, (• • •) copper acetate and (——) 1:1 mixture of gossypol with copper acetate in acetonitrile in the region 1800-1500 cm^{-1}.

The spectrum of 1:1 mixture of gossypol with $Cu(CH_3CO_2)_2$ is completely different than the spectrum of the sum of separated components. In the spectrum of the 1:1 mixture in the region 1800-1700 cm^{-1} two new, very intense bands arise. The positions of these bands at 1758 cm^{-1} and 1728 cm^{-1} indicate that they are non-bonded and bonded stretching vibrations of $COOCH_3$ groups, respectively. Furthermore, these bands demonstrate that with the mixing of gossypol and $Cu(CH_3CO_2)_2$ an esterification raction occurs.



In the region 1700-1500 cm^{-1} in the spectrum of aldehyde-aldehyde tautomer spectrum of gossypol the ν(C=O) vibration is observed at 1625 cm^{-1}. This vibration vanishes completely in the spectrum of 1:1 mixture (Fig. 2, solid line). The same is true with the ring vibration at 1570 cm^{-1}. Instead of this vibration new, intense ring vibration arises at 1580 cm^{-1}. Furthermore, the δ(OH) vibration of water molecules is observed at 1638 cm^{-1}.[15] These observations and the fact that in the spectral region no ν(C=O) vibration of ketol tautomer is found demonstrate the formation of the lactol-lactol tautomer in the 1:1 mixture. This result is in good agreement with changes in the region 1350-1100 cm^{-1} in which the vibrations of C-O-C groups arise. Because of the esterification reaction in the 1:1 mixture these vibrations are overlapped with those of ester groups.

The spectrum of the 1:1 mixture of gossypol with $Cu(CH_3CO_2)_2$ in the region 4000-3000 cm^{-1} shows two relatively sharp bands at 3600 cm^{-1} and 3551 cm^{-1} , which may be assigned to free ν(OH) and weekly hydrogen-bonded ν(OH) vibrations of two water molecules, respectively. The two water molecules are built up in the esterifacation reaction. It is interesting to note that these bands cannot be the alcoholic groups of the lactol-lactol tautomer, because they vanish completely when molecular sieves 3A is added to the 1:1 mixture. This result indicate that the esterifacation reaction take place at the alcoholic groups of lactol-lactol tautomer. Furthermore, at about 3300 cm^{-1} an very intense band of phenolic OH groups hydrogen-bonded to acetonitrile is observed.

In the region 3000-2200 cm^{-1} a very broad band is observed in the spectrum in the 1:1 mixture. Such band is very characteristic for hydrogen bonds between phenols and carbonyl groups of carboxylic acids or esters.[16,17]

The fact that the change of the aldehyde-aldehyde tautomer to lactol-lactol tautomer in the 1:1 mixture is caused by the Cu^{2+} cations, is in good agreement with well-known observations that this cations form strong complexes with ethers.[11,18]

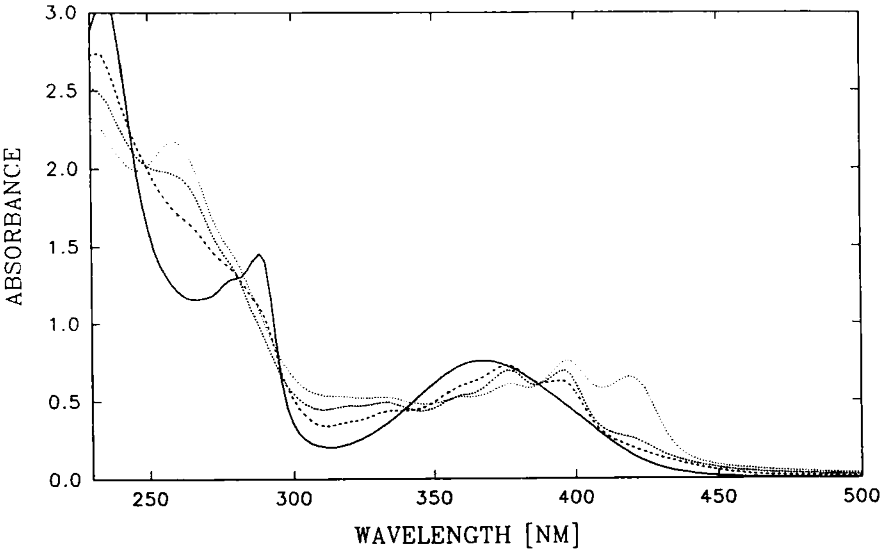
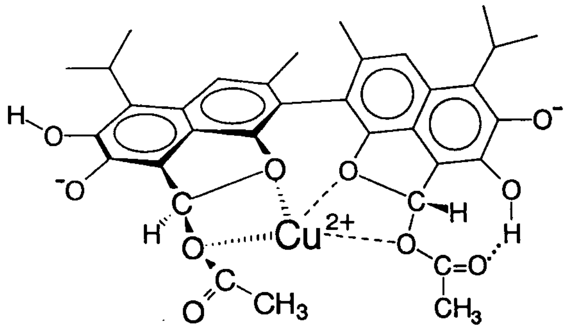


Fig.3 Changes in the UV-visible absorption spectra of gossypol-copper acetate system in etronitrile solutrion. Concentration of gossypol equal to $5x10^{-5}$ mol dm^{-3} in each sample. Concentrations of copper acetate 0; $5x10^{-5}$; $7.5x10^{-5}$; $1x10^{-4}$ mol dm^{-3}.

All spectroscopic results taken together demonstrate that in the 1:1 mixture the following structure is present in the acetonitrile solution



UV-visible absorption spectroscopy study

The changes in the absorption spectra of the solution of gossypol in acetonitrile with the addition of copper acetate are presented in Figure 3. The addition of $Cu(CH_3COO)_2$ leads to the decrease in the intensity of the three well separated bands of aldehyde- aldehyde tautomer of gossypol [5,6] at 370 nm, 290 nm and 235 nm and formation of new bands at about 310 nm and 260 nm, in addition to the formation of longwavelength bands at $\lambda>380$ nm. The appearance of new absorption bands at 310 nm at 260 nm is consistent with the formation of the lactol-lactol tautomer of gossypol [6,10], whereas the longwavelength absorption bands can be attributed to the formation of gossypol-Cu^{+2} or esterificated gossypol-Cu^{+2} complexes. The presence of two longwavelength absorption bands suggests more complex character of equilibria studied in the case of access of copper acetate. In addition, an absorption of $Cu(CH_3COO)_2$ observed for higher $Cu(CH_3COO)_2$ concentrations in the region 240-300 nm leads to more complicated equilibrium picture observed by the UV-visible absorption spectroscopy then in the case of gossypol-$Cu(ClO_4)_2$ system reported previously [10]

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