PHYSICOCHEMICAL PROPERTIES OF PLANT POLYPHENOLS

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Abstract: *plant secondary metabolites can be classified into four major classes: terpenoids, phenolic compounds, alkaloids and sulphur-containing compounds. These phytochemicals can be antimicrobial, act as attractants/repellents, or as deterrents against herbivores. Gossypol is secondary metabolite that play diverse role in plant adaptation to environment. Obtained from cottonseeds gossypol has valuable biological properties and forms an abundant number of clathrates with a large variety of compounds. One of the primary reasons why gossypol can form clathrates is its ability to organize extensive hydrogen bonding networks due to its hydroxyl and aldehyde functional groups. This natural polyphenol forms stable clathrates with acetic acid, acetone, ethyl acetate, 1,4-dioxane, chloroform and benzene. This work describes investigation of gossypol clathrates by single-crystal diffraction and thermal analysis.*
Keywords: *gossypol clathrates, polymorphism, X-ray analysis, TG-DSC analysis.*

ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА РАСТИТЕЛЬНЫХ ПОЛИФЕНОЛОВ

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Аннотация: *вторичные метаболиты растений можно разделить на четыре основных класса: терпеноиды, фенольные соединения, алкалоиды и серосодержащие соединения. Эти фитохимические вещества могут быть противомикробными, действовать как аттрактанты/репелленты или отпугивать травоядных животных. Госсипол – вторичный метаболит, играющий разнообразную роль в адаптации растений к окружающей среде. Полученный из семян хлопчатника госсипол обладает ценными биологическими свойствами и образует обильное количество клатратов с большим разнообразием соединений. Одной из основных причин, по которым госсипол может образовывать клатраты, является его способность организовывать обширную сеть водородных связей благодаря своим гидроксильным и альдегидным функциональным группам. Этот природный полифенол образует стабильные клатраты с уксусной кислотой, ацетоном, этилацетатом, 1,4-диоксаном, хлороформом и бензолом. В данной работе описано исследование клатратов госсипола методами монокристаллической дифракции и термического анализа.*
Ключевые слова: *клатраты госсипола, полиморфизм, рентгеноструктурный анализ, ТГ-ДСК-анализ.*

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Introduction

Polyphenols constitute one of the most and widely distributed groups of substances in the plant kingdom, with more than 8000 phenolic structures currently known. They can be divided into at least 10 different classes based upon their chemical structure, ranging from simple molecules, such as phenolic acids, to highly polymerized compounds, such as tannins. Secondary metabolites are substances manufactured by plants that make them competitive in their own environment. These small molecules exert a wide range of effects on the plant itself and on other living organisms.

The *Gossypium* tribe is enriched with a wealth of secondary metabolites. Among various metabolites, gossypol is a key secondary metabolite that shields the cotton plant against several pests. Cotton plants accumulate a large amount of gossypol as phytoalexins against pathogens and herbivores. They are stored in pigment glands of aerial organs and in epidermal layers of roots. Gossypol is a phenolic compound produced by pigment glands in cotton stems, leaves, seeds, and flower buds [1, 2].

Cotton plant

Cottonseeds

Pigment glands

Gossypol pigment

Gossypol, $C_{30}H_{30}O_8$, is a terpenoid aldehyde which is formed metabolically through acetate via the isoprenoid pathway (Fig. 1).

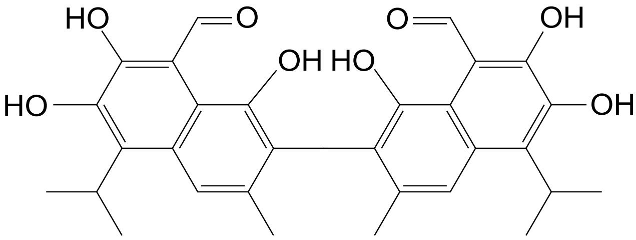

Fig. 1. Structural formula of gossypol.

Gossypol is a biologically active compound with a wide spectrum of action such as antiviral, immunosuppressive, antifertile. In the sense of inclusion complex formation, it is a unique compound. It gives clathrates with more hundreds tested low-molecular organic substances. Less hundred clathrates as single crystals have been obtained and their crystallographic parameters have been determined [3]. The structures of 30 inclusion complexes have been solved by diffraction methods [4,5]. The extreme divergence of gossypol clathrate structures is established: clathrates (H-clathrates) with cavities as isolated cells (cryptates), channels (tubulates), intersecting channels (intercalates), clathrates with mixed host-guest matrix and autoclathrates are observed (Fig. 2) [6].

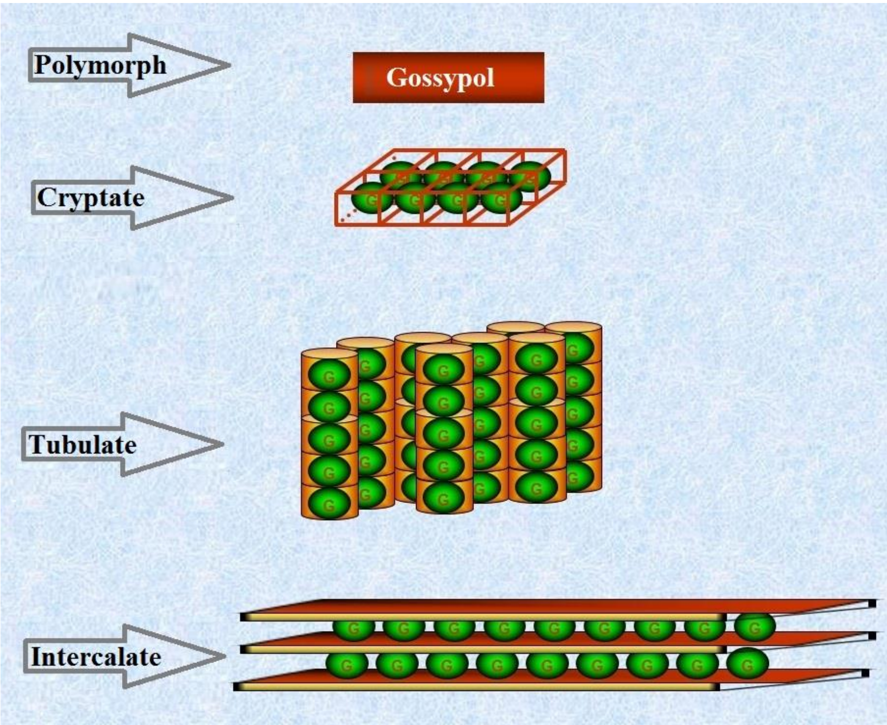

Fig. 2. Types of gossypol clathrates.

This work depicts the gossypol and its derivatives preparation and characteristics, especially of some gossypol clathrates through structural and thermal analysis.

Materials and Methods

Solutions were prepared by adding 0.5 g of gossypol and 6.0 ml of acetic acid, 4.0 ml of acetone, 5.0 ml of ethyl acetate, 2 ml of 1,4-dioxane, 9.0 ml of chloroform, 11.0 ml of benzene to six small glasses vials at room temperature. Samples were stored at dark places to promote the formation of primary nuclei. The grown single crystals were determined and refined on a Xcalibur R (Oxford Diffraction, England) multichannel CCD diffractometer using CuKα radiation (λ = 1.54178 Å, 2θ range of 2.11 to 56.74, graphite monochromator).

Typical thermic parameters of materials such as decomposition temperatures and temperature stability were determined by TG-DSC analysis.

Results and Discussions

The gossypol clathrates with solvents such as acetic acid – CH_3COOH, acetone – CH_3-CO-CH_3, ethyl acetate – $CH_3COOC_2H_5$, 1,4-dioxane – $C_4H_8O_2$, chloroform – $CHCl_3$ and benzene – C_6H_6 at the room temperature have been obtained. These gossypol clathrates have been analyzed by X-ray diffraction and results showed that gossypol accommodates different guest molecules by packing in a variety of forms. X-ray crystal structures and TG-DSC curves of thermal analysis of given clathrates are shown (Figures 3-8).

Acetic acid forms complex with gossypol/guest at a ratio of $C_{30}H_{30}O_8$:CH_3COOH = 1:1, and the compound crystallize in the triclinic system (Fig. 3A). Thermal analysis (TG-DSC curves) of clathrates gossypol/acetic acid shown what this clathrate stabile up to 180 ^{0}C. Solvent loss is 10,5 %, which begins at 165 ^{0}C. Water loss is 6,4 %, and continues from 175 ^{0}C to 210 ^{0}C (Fig. 3B). As may be concluded, clathrates gossypol/acetic acid lose the water when gossypol is converted to anhydrogossypol [7].

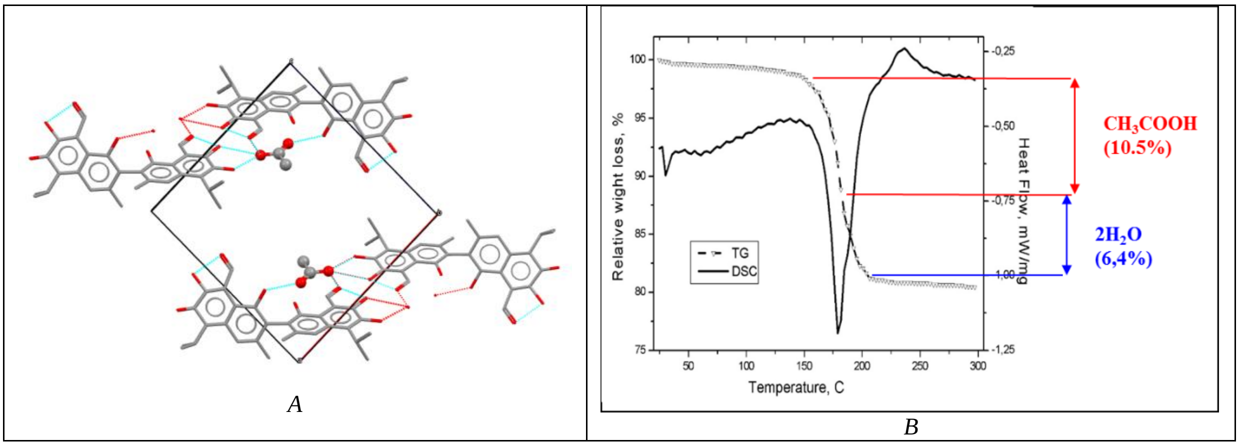

Fig. 3. Crystal structure of gossypol clathrates with acetic acid (A) and TG-DSC patterns of crystal forms of gossypol/acetic acid (B).

Acetone forms complexes with gossypol at a ratio of $C_{30}H_{30}O_8$:CH_3COCH_3=1:1. The crystals crystallizes in the triclinic system, space group *P1* (Fig. 4A). The 1:1 gossypol: acetone complex belongs to the acetone-type lattice inclusion complexes of gossypol.

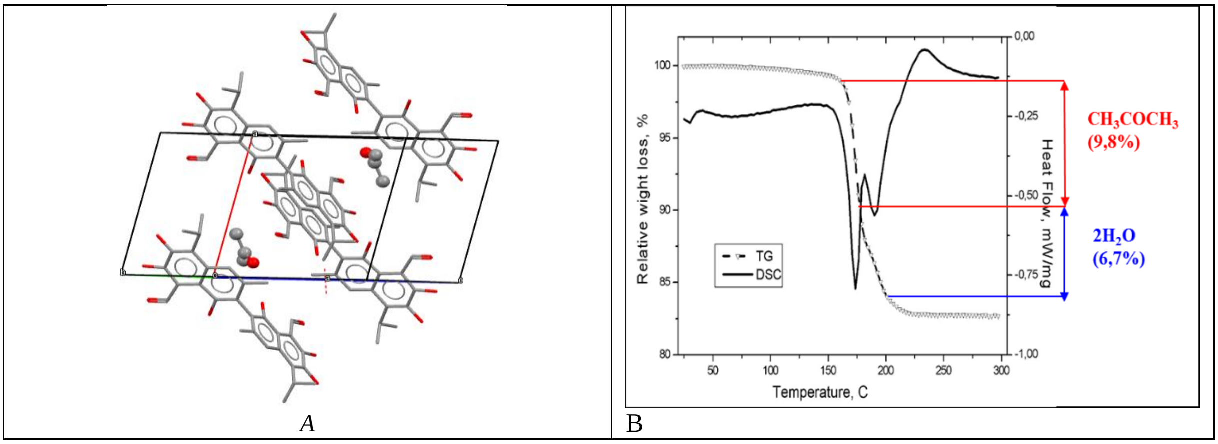

Fig. 4. Crystal structure of gossypol clathrates with acetone (A) and TG-DSC patterns of crystal forms of gossypol/acetone (B).

The thermal analysis of clathrates gossypol: acetone shown that this clathrate stabile to 180 ^{0}C. Solvent loss is 10.5 %, which begins at 165 ^{0}C. Water loss is 6.4 % and continues from 175 ^{0}C to 210 ^{0}C. (Fig. 4B) [7].

Ethyl acetate forms complexes with gossypol at a ratio of $C_{30}H_{30}O_8$:$CH_3COOC_2H_5$ = 2:1. The compound crystallizes in the monoclinic system, space group *C2/c*. (Fig. 5A). Thermal analysis of clathrates gossypol/ethyl acetate shown that this clathrate stabile up to 200 ^{0}C. Solvent loss is 7.8 %, which begins at 75 ^{0}C. Water loss is 6.4 %, which continues from 175 ^{0}C to 210 ^{0}C (Fig. 5B) [7].

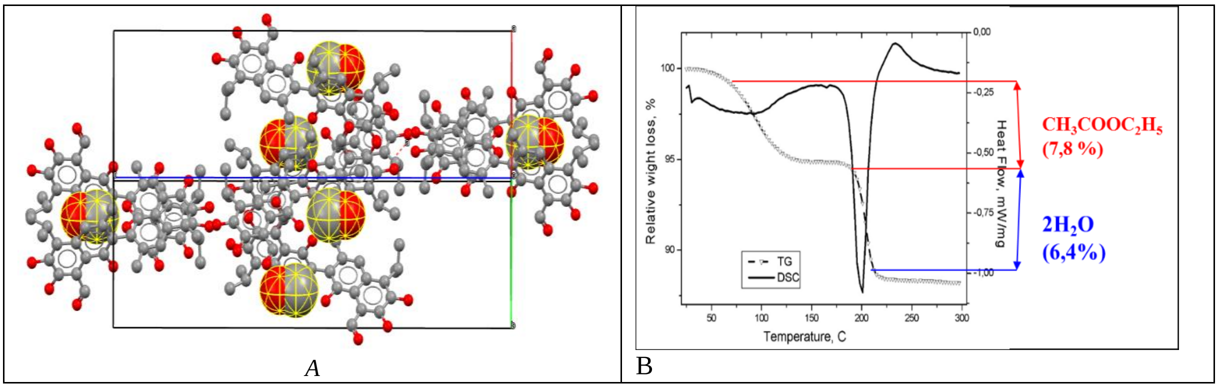

Fig. 5. Crystal structure of gossypol clathrates with ethyl acetate (A) and TG-DSC patterns of crystal forms of gossypol/ethyl acetate (B).

1,4 - dioxane forms complexes with gossypol/1,4-dioxane at a ratio of $C_{30}H_{30}O_8$:CH_3COOH = 1:3, with space group *Pbcn* (Fig. 6A). Thermal analysis of clathrates gossypol / 1,4-dioxane shown that this clathrate stabile up to 100 ^{0}C. Solvent loss is 27.0 %, which begins at 95 ^{0}C. Water loss is 5.5 %, which continues from 125 ^{0}C to 180 ^{0}C (Fig. 6B) [7].

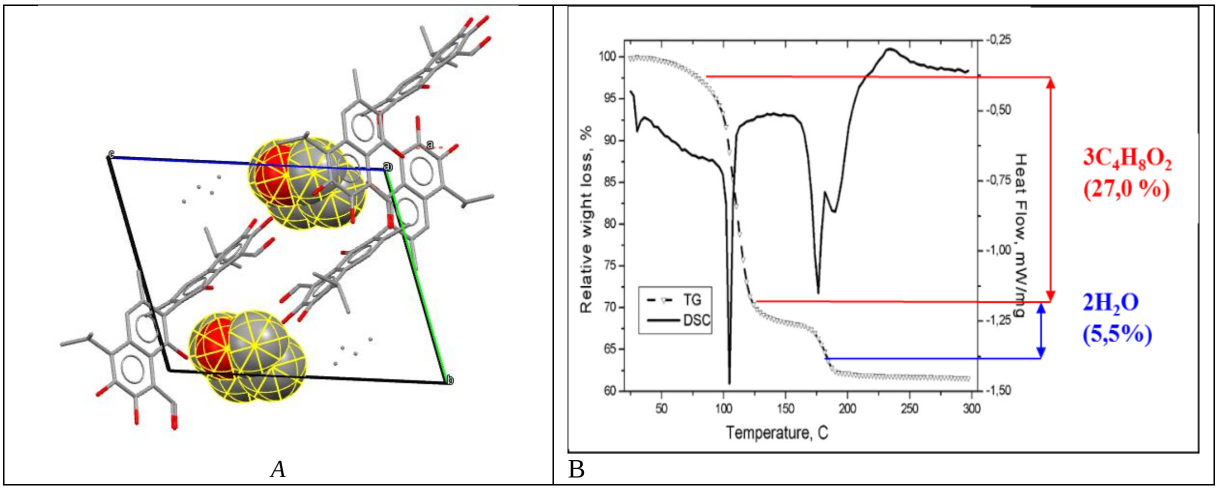

Fig. 6. Crystal structure of gossypol clathrates with 1,4 - dioxane (A) and TG-DSC patterns of crystal forms of gossypol/ 1,4 - dioxane (B).

The crystals of gossypol with chloroform, $C_{30}H_{30}O_8$:$CHCl_3$, crystallizes in monoclinic system, space group *C2/c* (Fig. 7A).

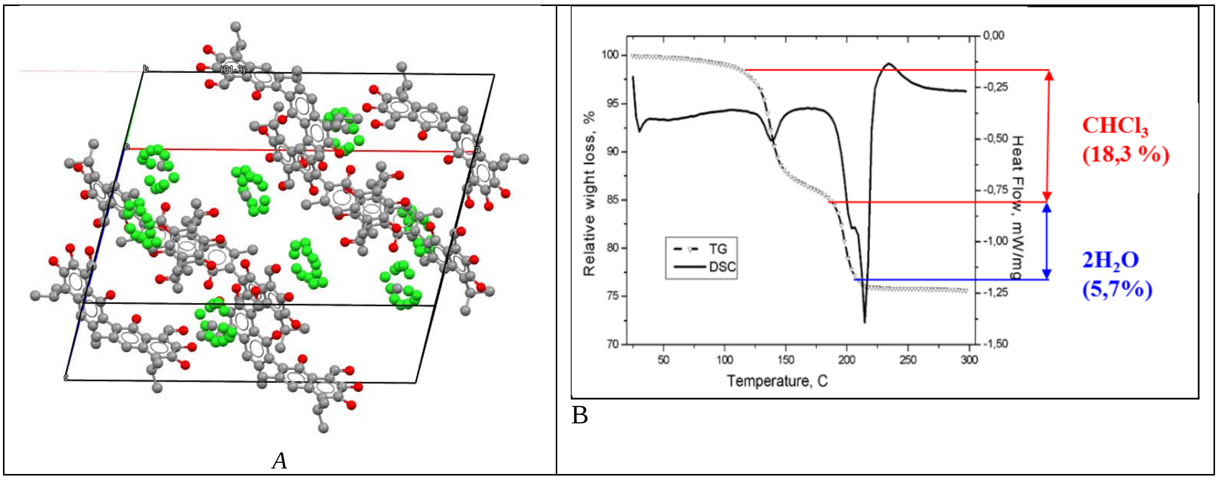

Fig. 7. Crystal structure of gossypol clathrates with chloroform (A) and TG-DSC patterns of crystal forms of gossypol/chloroform (B).

The clathrate of gossypol/ chloroform is stabile up to 150 ^{0}C. Solvent loss is 18.3 %, which begins at 125 ^{0}C. Water loss is 5.7 %, which continues from 175 ^{0}C to 210 ^{0}C (Fig. 7B) [7].

The crystal structures of the inclusion complexes of gossypol with benzene $(C_{30}H_{30}O_8)_2{:}C_6H_6$ = 2:1, crystallizes in the triclinic system, space group *P1* (Fig. 8A). The clathrate of gossypol/benzene is stabile up to 75 ^{0}C. Solvent loss is 7.0 %, which begins at 80 ^{0}C. Water loss is 6.8 %, which continues from 185 ^{0}C to 210 ^{0}C (Fig. 8B) [7].

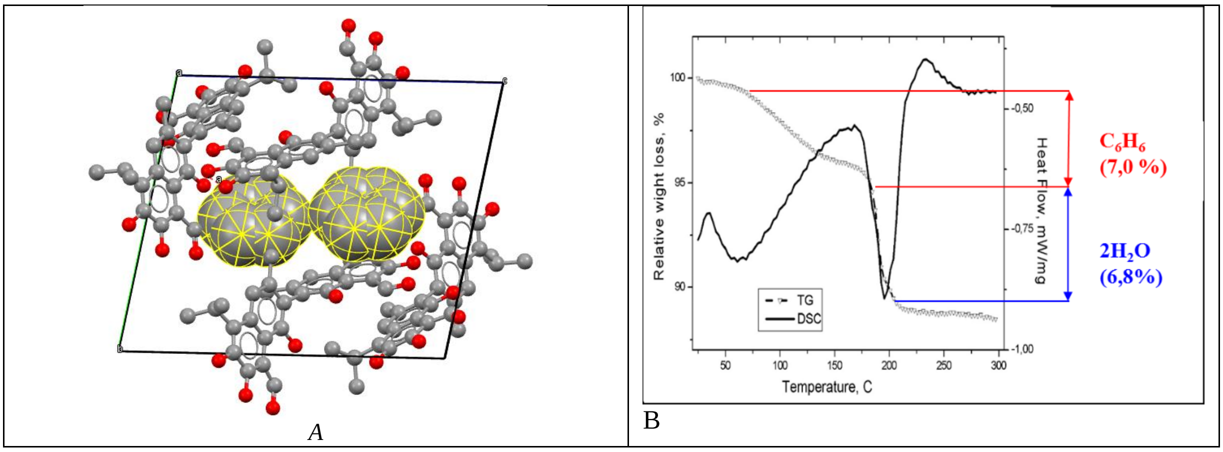

Fig. 8. Crystal structure of gossypol clathrates with benzene (A) and TG-DSC patterns of crystal forms of gossypol/benzene (B).

Conclusion

The results indicate that clathrates of gossypol/acetic acid and gossypol/1,4-dioxane form a tubulate-type structure, clathrates of gossypol/acetone, gossypol/ethyl acetate and gossypol/benzene form a cryptate-type structure, clathrate of gossypol/chloroform forms an intercalate-type structure.

Depending on the crystal structure of studied clathrates the decomposition processes proceed at different temperatures.

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