

MASS-SPECTROMETRIC STUDY OF THERMAL DECOMPOSITION OF SOME POLYKETIDES IN CONDENSED AND ADSORBED STATES

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Abstract

A study has been conducted on adsorption of semisynthetic flavonoid venoruton on the surface of highly dispersed silica (HDS) modified with polyvinylpyrrolidone (PVP). It has been found that an adsorption value of venoruton for the modified silica was 20% higher than that of hydroxylated silica surface. By the temperature-programmed desorption technique with the mass-spectrometric registration of volatile constituents (TPD MS) a research has also been made into decomposition of venoruton adsorbed by system PVP-HDS. It has been shown that the number of stages of thermolysis of carbohydrate parts of venoruton molecules adsorbed on the modified surface decreases down to one while in the case of the condensed state there are two stages of carbohydrate portion thermolysis and in the situation with the adsorption on the hydroxylated HDS surface there are three stages. As far as the system venoruton-PVP-HDS is concerned, the maximum rate of volatile constituent elimination (destruction of carbohydrate parts of molecules) is shifted towards high temperature region by 130°C in comparison with the condensed state and by 200°C in comparison with the state set up during adsorption on the hydroxylated HDS surface. The increase in the thermal stability of venoruton adsorbed by the PVP-HDS system is related to the effect of PVP polymer chains, which block the access of venoruton molecules to active sites of the silica surface.

Introduction

Recently the interest in phytopreparations of folk medicine increased throughout the world [1-2]. Active components of most of them are polyketides. Formerly we studied the following series of polyketides: bioflavonoid quercetin, semisynthetic flavonoid venoruton, alizarin red S anthraquinone, and structural isomer of quercetin, namely morin [3-5]. The results achieved revealed a correlation between the chemical structure of morin and venoruton and mechanisms of their thermolysis which occurred through rupture of chemical bonds by three main routes A, B and C. The thermolysis of morin took place in three stages whereas that of venoruton proceeded in four stages. The presence of a carbohydrate residue in a venoruton molecule brought about additional thermolysis stages corresponding to destruction of this carbohydrate fragment.

Research into adsorption of polyketide (flavonoids in particular) on the surface of highly dispersed mineral matrices may to some extent clear up the processes, which occur on the cell membrane surface in the presence of biomolecules. The role played in these processes by the hydroxyl group in the para position of a carbonaceous ring was not completely elucidated yet, although this group is known to be responsible for biological activity of flavonoids. Venoruton is analogous to flavonoids acting in living systems. The rate of its adsorption from water on the dispersed silica surface is more than two orders of magnitude

larger than that of morin, quercetin, and alizarin red S from water-ethanol mixtures. The comparison drawn between the available physicochemical parameters of venoruton adsorption and those obtained in our previous works has shown that the venoruton adsorption on the HDS surface takes place by binding carbohydrate residues. This inference is corroborated by the experimental data collected when investigating thermal decomposition of venoruton in the condensed state and that of venoruton adsorbed on dispersed silica by the method of temperature-programmed desorption with mass-spectrometric registration of volatile constituents.

Results and Discussion

Venoruton in the condensed state (Fig. 1) and in the state set up after its adsorption on the surface of highly dispersed silica (HDS) was already studied by the TPD MS technique [4]. In general, it was found that the routes of its decomposition did not change during its adsorption on the surface of HDS. However, in the case of the adsorbed state in the low-temperature region there appeared additional peaks for 109, 110, 111 m/z . (at about 220°C; destruction by mechanism C) and for 72, 97, 126 m/z (at 180°C; destruction of carbohydrate residues) (Fig. 2). The formation of these peaks was related to the character of adsorption on the surface, namely to the fact that it was carbohydrate residues that directly participated in binding with the surface. At higher temperatures the number of thermal decomposition stages, their temperature intervals, and their sequence were approximately identical to those observed for the condensed state (Table).

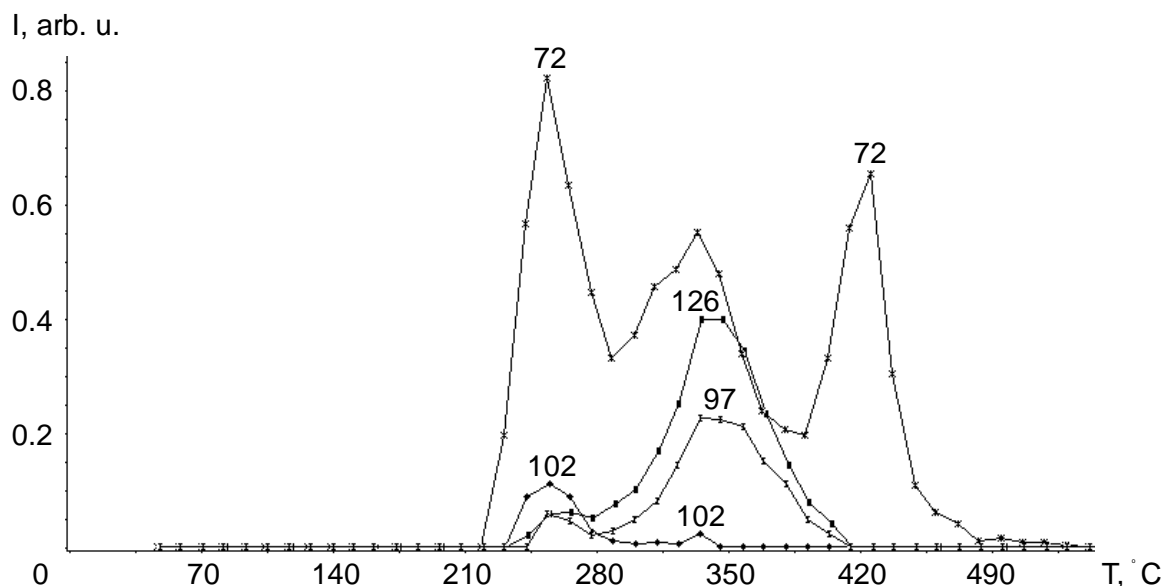


Fig. 1. Thermograms of m/z : 126, 102, 97, 102; decomposition of carbohydrate substituent - glucose-ramminose for venoruton in the condensed state.

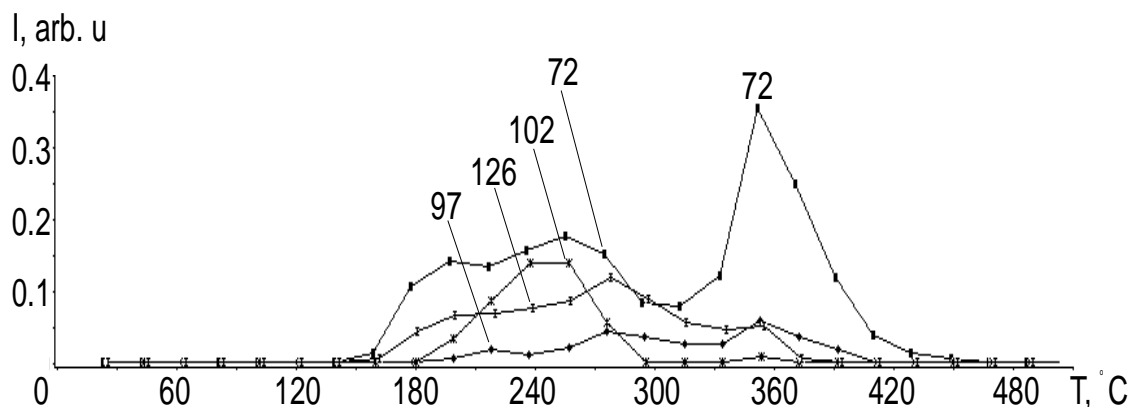


Fig. 2. Thermograms of m/z : 126, 102, 97, 102; decomposition of carbohydrate substituent - glucose-rhamnose for venoruton adsorbed on highly dispersed silica surface.

Thus, as is seen from Table, the thermolysis of morin proceeds in three main stages. The presence of a carbohydrate substituent in the structure of chromone (venoruton) leads to appearance of an additional stage of the thermal decomposition, with the carbohydrate residue decomposition and chromone decomposition (routes B and C) proceeding in synchronism. The observation result is explained by the fact that rhamnoglucosyl is in position 3 of chromone, i.e. it is a component of the structure whose fragments are detected in the mass spectra recorded in the case of the thermolysis by route B. The adsorption occurred on the silica surface manifests itself by peaks in a low-temperature region. During the first stage of the carbohydrate residue thermolysis under these conditions the chromone thermolysis by route B is somewhat delayed from that of sugar (approximately by 40°C), while during the other two stages (II and III) the chromone thermolysis by route B and carbohydrate residue thermolysis proceed at the same rate.

A research was also conducted into kinetics of venoruton adsorption on the surface of silica modified with polyvinylpyrrolidone (PVP) (Fig. 3). It was found that the adsorption value was 16–20% larger in comparison with the hydroxylated surface. The mass-spectrometric investigations were made using samples of highly dispersed silica modified with polyvinylpyrrolidone and samples of venoruton adsorbed by system HDS-PVP. The adsorption of PVP from an aqueous solution on the surface of highly dispersed silica was affected under steady-state conditions at room temperature. A weighed sample (1.1 g) of HDS was added to 110 mL of 10% solution of polyvinylpyrrolidone in distilled water. The suspension was let stand 5 h with periodic stirring, following which it was centrifuged, washed two times with water (2×50 mL), and dried at room temperature. To 0.1 g of the silica modified with polyvinylpyrrolidone 5 mL of solution of venoruton in distilled water were added, and the mixture was let stand 1 h with periodic stirring. Then, the suspension was centrifuged, washed with water, and dried.

The samples prepared have been studied by the TPD MS technique. It has been shown that the onset of thermal destruction of venoruton adsorbed by the HDS-PVP system takes place at a temperature above 210°C as it was in the case for the free state. During the first stage the main contribution to the thermolysis is made by destruction of venoruton molecules according to route C (release of pyrocatechin in its molecular form). The destruction of a venoruton molecule by route C proceeds at temperatures up to 450°C and leads to formation of two peaks at 280°C and at about 370°C.

Table. Data on decomposition of venoruton

T, °C	Venoruton condensed			Venoruton adsorbed on highly dispersed silica			Venoruton adsorbed on PVP-highly dispersed silica		
	Stage	Destruction type	(<i>m/z</i>)	Stage	Destruction type	(<i>m/z</i>)	Stage	Destruction type	(<i>m/z</i>)
180	-	-	-	I	Carbohydrate:	126, 97, 72.	-	-	-
220	-	-	-	I	Chromone type: C	109, 110, 111.	-	-	-
250	I	Carbohydrate: Chromone type: B C	126, 97, 72; 112, 95; 109, 110, 111.	-	-	-	-	-	-
280	-	-	-	II	Carbohydrate: Chromone type: B C	126, 97, 72; 112, 95; 110.	I	Chromone type: C	109, 110, 111.
360	II	Carbohydrate: Chromone type: B C	126, 97, 72; 112, 95; 111.	III	Carbohydrate: Chromone type: B C	126, 97, 72; 112, 95; 110.	-	-	-
380	-	-	-	IV	Chromone type: A	136, 108, 91	II	Carbohydrate: Chromone type: A B C	126, 97, 72; 136, 108, 91; 141, 123, 95; 110.
420	III	Chromone type: A	136, 108, 91.	-	-	-	-	-	-
450	-	-	-	V	Chromone type: A	108, 91	-	-	-
480	IV	Chromone type: A	136, 108, 91.	-	-	-	-	-	-

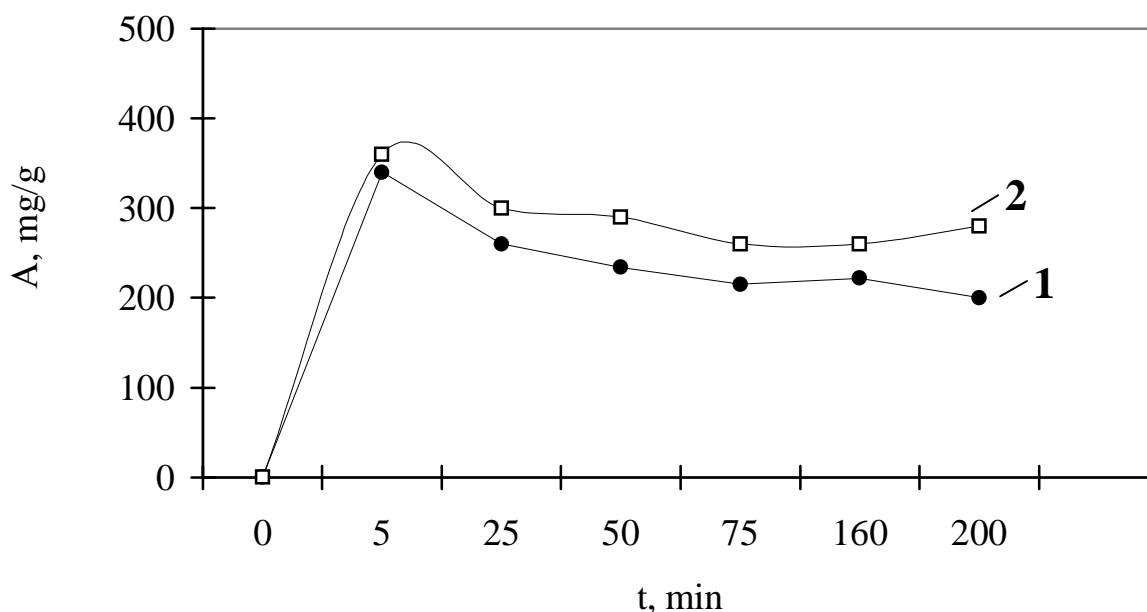


Fig. 3. Kinetics of venoruton adsorption by highly dispersed silica (1) and PVP-HDS (2).

Of note here is the fact that in the mass spectra recorded at temperatures below 320°C there are no lines which might be attributed to the thermal decomposition of carbohydrate substituents and to destruction by route B, whereas during the first stage of the free venoruton thermolysis (the thermal destruction maximum is observed at 280°C) some contribution to the process is made by the carbohydrate residue decomposition and by the destruction of molecules by route B.

The kinetics curves characterizing the destruction of a venoruton molecule by routes A and B have peaks at about 380°C. The thermal analysis curves plotted for fragments of 141, 108, 95, 91 m/z (destruction by route B) have a gently sloping trailing edge, with the release of the fragments being observed at temperatures above 500°C.

The greatest changes brought about by the adsorption are characteristic of the thermolysis stages that involve destruction of the carbohydrate part of a molecule. The venoruton adsorption on the surface of the system HDS-PVP leads to a decrease in the number of the peaks observed on the thermal analysis curves plotted for volatile constituents released during destruction of carbohydrate fragments (in the case of the free state and the state set up upon adsorption on HDS there are two and three peaks respectively). It is well illustrated by Fig. 4 and Table. The maximum on the thermal analysis curves for 126, 97, 72 m/z (destruction of the carbohydrate part of a molecule; 380°C) in the case of the system venoruton-HDS-PVP is shifted towards high temperatures by 130°C in comparison with the free state and by 200 C in comparison with the state set up after the adsorption on hydroxylated silica.

The observed enhancement of the thermal stability of venoruton in the state set up during its adsorption by the system HDS-PVP in comparison with the state after its adsorption on the HDS surface may be explained by the influence of polyvinylpyrrolidone polymer chains that block approach of venoruton molecules to active sites on the silica surface which function as agents of dehydroxylation. The active sites on the surface facilitate the thermal decomposition of carbohydrate residues, with the decomposition involving abstraction of water if the venoruton molecule is in the state set up during its adsorption on the hydroxylated silica

surface. It should be emphasized that it is the carbohydrate fragment that makes a main contribution to binding with the highly dispersed silica surface.

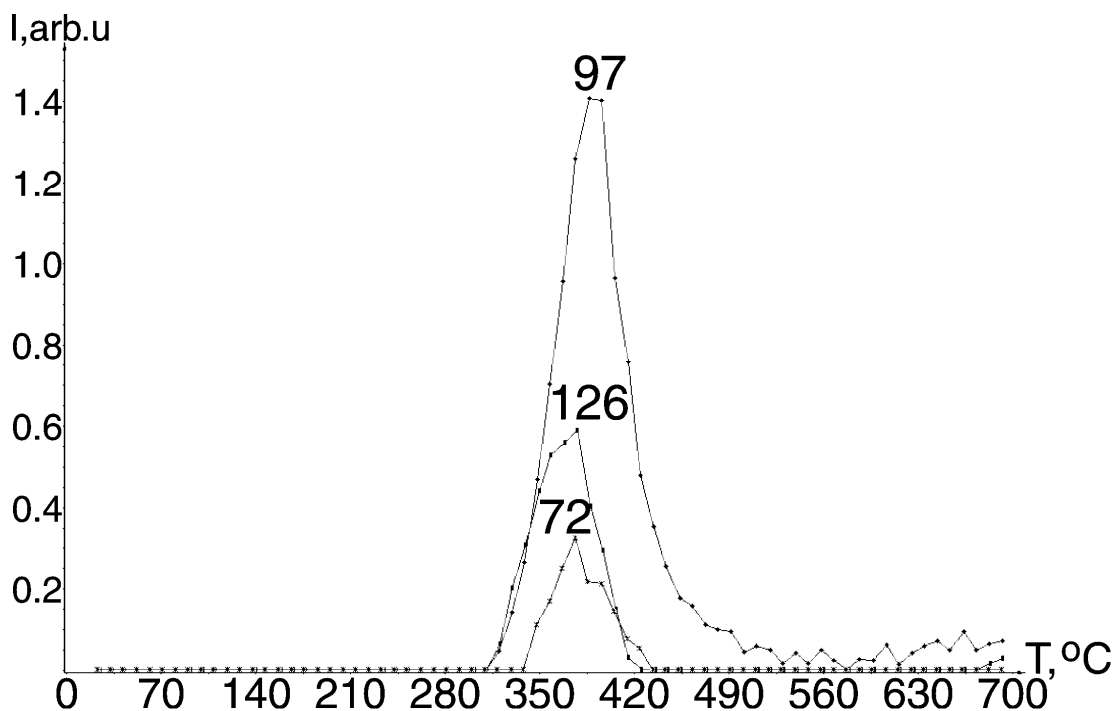


Fig. 4. Thermograms of m/z: 126, 102, 97, 102; decomposition of carbohydrate substituent - glucose-rhamnose for venoruton adsorbed by PVP-HDS surface.

The destruction of the carbohydrate part and chromone by routes A and B takes place in the narrow interval of temperatures 320–450°C with the maximum of the elimination rate for volatile constituents at 380°C, i.e. in the temperature region where destruction of polyvinylpyrrolidone proceeds. Thus, one can infer that decomposition of the prevailing majority of venoruton molecules occurs in synchronism with destruction of polymer chains of polyvinylpyrrolidone.

Conclusions

The changes in the silica surface structure caused by modification of silica with polyvinylpyrrolidone (PVP) lead to corresponding changes in thermal desorption curves characteristic of the thermal decomposition of venoruton in the system PVP-highly dispersed silica. The most significant changes are observed during the thermolysis stages, which involve the destruction of carbohydrate fragments of molecules. The number of the decomposition stages for the system venoruton-PVP-HDS reduces to one, whereas in the case of the condensed and adsorbed states there are two stages and three stages respectively. The maximum of the carbohydrate fragment decomposition for the system venoruton-PVP-HDS is shifted towards high temperatures by 130 C in comparison with the condensed state and by 200 C in comparison with the state set up as a result of adsorption on the hydroxylated silica surface.

The enhancement of the thermal stability characteristic of venoruton adsorbed by the silica-PVP system in comparison with that characteristic of the substance adsorbed by highly

dispersed silica may be explained by influence of polyvinylpyrrolidone whose polymer chains impede access of venoruton molecules to active sites of silica surface which possesses dehydroxylation properties. The active sites present on silica surface promote thermal decomposition of carbohydrate residues, with the decomposition being accompanied by elimination of water. It should be emphasized that the main contribution to binding with the silica surface is made by carbohydrate residues.

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