Thermal transformation of bioactive caffeic acid on fumed silica seen by UV-Vis spectroscopy, thermogravimetric analysis, temperature programmed desorption mass spectrometry and quantum chemical methods

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PURPOSE OF THE ABSTRACT
Plant foods are rich sources of phenolic acids, in particular hydroxycinnamic acid derivatives, such as caffeic (CAF), ferulic (FER), p-coumaric, chicoric, sinapic, rosmarinic acid, etc., which have recently become of great interest owing to their various biological effects [1,2]. The qualitative and quantitative composition of hydroxycinnamic acids in herbs is affected by many factors, such as genotype, environmental conditions, crop management and processing practices. It was found that Cynara Cardunculus L (globe artichoke) is a rich source of caffeic acid derivatives, and nowadays they are recovered in commercial quantities from agricultural and industrial waste of globe artichokes, for use in the pharmaceutical industry and medicine as a source of naturally occurring, instead of synthetic, antioxidants [3]. In addition, plant raw material contains significant amounts of hydroxycinnamates as structural blocks of lignocellulose, which nowadays is considered to be the most attractive renewable raw material for producing second generation biofuels and bio-chemicals [4, 5]. In view of the scarcity of thermochemical studies on hydroxycinnamate as well as the wide application of silica as a substrate for synthesis of new nano-sized catalysts, research into the thermal transformation of hydroxycinnamic acids such as lignocellulose units on a silica surface is of great practical importance, notably for the development of green technologies of heterogeneous biomass pyrolysis.

The investigations into caffeic acid loaded in different ways on finely dispersed silica (adsorption, mixing or co-milling) have revealed that it can form two types of surface complexes through phenolic or carboxyl groups. On heating under the conditions of the TPD MS experiment these complexes are chemically adsorbed by grafted phenolic or grafted ester group of caffeic acid respectively [6]. Thermal destruction of caffeic acid complexes chemisorbed through a grafted ester group proceeds via three parallel reactions producing ketene, vinyl, and acetylene derivatives of 1,2-dihydroxybenzene (Fig.1). For the acids investigated, Tmax of these reactions decreases in the order: cinnamic> ferulic> caffeic acid. On the contrary, thermal decomposition of surface complexes formed by a grafted phenolic group begins with the release of acetylenecarboxylic acid and is characterized by higher Tmax values than with pyrolysis of silica supported
ferulic acid (Fig.2).
In all cases surface complexes of caffeic acid formed via both carboxyl and phenolic groups decompose at a significantly higher temperature than the condensed acid. In general, immobilization of phenolic acids on the silica surface greatly improves their thermal stability that is a promising for further silica use as a carrier, filler and stabilizer of medicines, food and dietary supplements based on hydroxycinnamic acids.
On the other hand, the development of the technologies of thermochemical conversion of plant biomass containing hydroxycinnamic acids into the useful bio-based chemicals (in particular, the derivatives of benzene, naphthalene, etc.) requires further investigations. We are also considering the possibility to study the adsorption and kinetics of thermal transformations of cinnamic acid derivatives on the surface of metal-oxide catalysts. The application of such catalysts is expected to provide significant reduction of the biomass conversion temperature and the increase of the thermochemical processes selectivity.

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**FIGURES**

**FIGURE 1**
The decomposition of complex chemisorbed via a carboxyl group.

**FIGURE 2**
The decomposition of complex chemisorbed via phenolic group.

**KEYWORDS**
hydroxycinnamic acid derivatives | thermal transformation | caffeic acid | surface complexes

**BIBLIOGRAPHY**