THERMOGRAPHIC STUDY OF GALLIC ACID

V. A. Oridoroga, I. I. Korobeinikova,
and B. G. Yasnitskii

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Gallic (3,4,5-trihydroxybenzoic) acid (GA), obtained from *Gallas turcicea, Rhus coriaria* L., and other plants, has long been known and has been fairly well studied. However, up to the present time its thermal stability has not been investigated and its melting point has not been accurately established. In various literature sources [1, 2] melting points in the range from 220 to 240°C are given, which is due to the imperfection of the instruments and methods of investigation used previously. A knowledge of temperature intervals of the phase transitions and chemical transformations of GA is necessary to select rational conditions for its production and use for obtaining other products such as pyrogallol. In view of this, we have undertaken a thermographic study of GA by the methods of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using a derivatograph with a rate of heating of 6 deg/min and an alumina standard at 26-600°C. As the material investigated we used GA obtained from Turkish galls.

Figure 1 gives a thermogram of GA. With a rise in the temperature to 400°C (curve (TA) a number of processes took place in the sample investigated which were reflected on the DTA curve by several maxima. The endomaximum at 122°C is due to the elimination of water of crystallization. As can be seen from the TGA curve its amount is 9.6% (1 mole), which agrees with literature information [2]. At 258-260°C a second endomaximum is observed. Judging from the shape of the TA curve it corresponds to an endothermic phase transformation, i.e., it reflects the process of the melting of GA accompanied by its decomposition (compare the TGA curve). In the interval from 220 to 240°C in which the melting point of GA was previously stated to occur, no changes in the shape of the TA and DTA curves showing the existence of a phase transition were detected. Thus, the melting point of GA must be corrected.

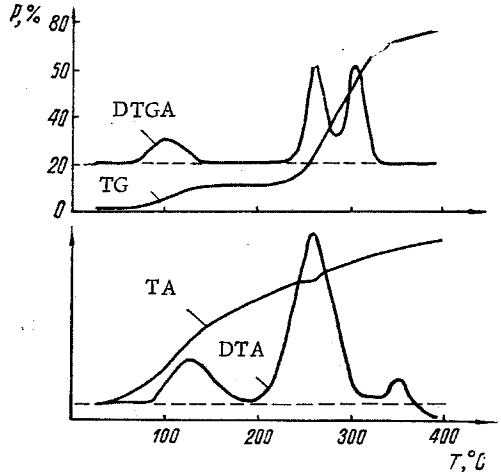

Fig. 1. Curves of the thermogravimetric (TGA), differential thermogravimetric (DTGA), thermal (TA) and differential thermal (DTA) analyses of gallic acid obtained from Turkish galls.

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It can be seen from a comparison of the TGA and DTGA curves that the beginning of the melting of the GA coincides with a rapid loss in weight of the sample due to two processes taking place with the evolution of gaseous products. The maximum of the first of these corresponds to the melting point of the GA and from a quantitative estimate (26%) is a consequence of its decarboxylation (23.4% of CO_2) with the formation of pyrogallol (below, PG). The somewhat greater fall in the weight of the sample is due to the partial sublimation of the PG.

The following process takes place with a weight loss of about 30%. Its maximum (310°C) corresponds to the boiling point of PG, which takes place, as is well known, with decomposition, which also leads to a loss in weight. Apparently, under these conditions polycyclic systems are formed through the high-temperature condensation of the polyphenol ring with the evolution of water (approximately 3 moles or 28.7%). On heating above 330°C, the loss in weight slows down, which is probably connected with a process of further polycyclization going as far as graphitization.

Thus, it has been established that when GA monohydrate is heated, there is an elimination of water of crystallization in the interval from 80 to 122°C. At 258-260°C, the GA melts, which is accompanied by a process of decarboxylation with the formation of PG. The latter boils at 310°C with decomposition. In this process, apparently, polycyclic compounds are formed with the liberation of three molecules of water of reaction.

LITERATURE CITED

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CAROTENOIDS OF THE FRUIT OF *Sorbus aucuparia*

S. A. Deren'ko

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In the territory of the USSR 36 species of the genus *Sorbus* grow [1] and their fruit is a good source of carotenoids having great value in medicine and the food industry. The most widely distributed species is *Sorbus aucuparia* L. (European mountain ash). The total amount of carotenoids in the fruit reaches 18 mg % [2]. It has been established previously that they include α- and β-carotenes [3, 4], and it has recently been shown that the carotenoid composition is: β-carotene, cryptoxanthin, and β-carotene monoepoxide [5]. Thus, the information on the qualitative composition of the carotenoids is contradictory. This has induced us to make a detailed study of the qualitative composition of the carotenoids of the fruit of the European mountain ash.

Specimens of the fruit were collected in the environs of Ryazan over two years (1976-1977). The carotenoid composition was determined in the air-dry fruit since it is just in this state that they are sent for processing with the aim of obtaining vitamin preparations. A sample (~3 g) was ground in a porcelain mortar with Al_2O_3 until a homogeneous powder had been obtained, the mixture was poured onto a 2-cm layer of alumina in a glass tube (0.7 × 25 cm), and the carotenoids were exhaustively extracted with petroleum ether.

The mixture of carotenoids was separated by thin-layer chromatography on a layer of silica gel (LS 5/40 mesh) fixed with gypsum in the hexane—diethyl ether (17:3) system. They were chromatographed in the presence of "markers" — carrot carotenoids, consisting of a combination of α- and β-carotenes. The chromatograms showed the presence of five orange zones with R_f 0.82, 0.63, 0.45, 0.10, and 0.00. The last zone migrated in the hexane—diethyl ether (1:1) system and we have convinced ouselves that it forms a single carotenoid with R_f 0.05. The carotenoid zones were scraped off and eluted with chloroform. The carotenoids were identified from the absorption maxima in an SF-4A spectrophotometer in hexane.

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