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KINETICS OF THE ACIDIC HYDROLYSIS OF TANNIN

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In this communication we present the results of an investigation of the kinetics of the acid-catalyzed hydrolysis of tannin (I), which was realized in order to obtain gallic acid (II).

The alkaline hydrolysis of I used to produce II requires the consumption of large amounts of alkali and, subsequently, acid for its subsequent neutralization and the isolation of II. In the case of acidic hydrolysis there is no need to consume alkali, and the consumption of acid is reduced sharply.

As the subject of the investigations we selected I from gallnuts, which is a mixture of polyesters of an equilibrium mixture of α- and β-D-glucose, primarily penta- and hexagalloylglucoses. One molecule of I contains an average of five galloyl groups [1]. In addition to II, a small part of the ester groupings are formed by m-digallic and trigallic acids. The ester bonds in I are possible at both the primary and secondary OH groups of glucose. The II and digallic acid fragments that enter into the composition of I may cause steric hindrance during hydrolysis. One must also take into account the fact that each of the forms of D-glucose exists in different conformational states. Taking the stated information into account, as well as the fact that the noted peculiarities of the structure may change during the successive cleavage of individual ester bonds and, in particular, as a result of mutarotation of glucose, one might expect an extremely complex pattern of the kinetics of the acidic hydrolysis of I. Moreover, the acidic hydrolysis of the esters is reversible in this case.

Overall, the hydrolysis of I can be represented by Eq. (1):

$$\begin{gathered} C_6H_7O[OCC_6H_2(OH)_3]_5 + 5H_2O \xrightleftharpoons{HCl} \\ C_6H_{12}O_6 + 5HOOCC_6H_2(OH)_3 \end{gathered} \tag{1}$$

and may be realized via several mechanisms [3]: a monomolecular mechanism with cleavage at the Ac–O bond (an $A_{Ac}1$ mechanism) or at the Alc–O bond (an $A_{Alc}1$ mechanism) or a bimolecular mechanism (an $A_{Ac}2$ mechanism). The course of the reaction via a specific mechanism or in some combination is determined by both the structures of R' and R and by the acidity of the medium. The formation of an oxonium ion or the conjugate acid ion $R'COOHR^+$ is the first step. The subsequent transformations of the oxonium ion determine the mechanism of the process and the overall rate of the reaction. The rate-determining step via the $A_{Ac}2$ mechanism may proceed as reversible addition with subsequent cleavage and as nucleophilic substitution through the transition state, but the coexistence of both reaction pathways occurs most often.

EXPERIMENTAL

For the study of the hydrolysis we used I that satisfies the requirements of GFKh (item 658) and II that satisfies the requirements of FS-42-1456–80. Aqueous solutions of I and hydrochloric acid with definite concentrations previously heated to 102 ± 2°C were mixed rapidly in a vessel, after which the mixture was maintained at this temperature for a certain time with the removal of samples at fixed time intervals. Slowing down the reaction

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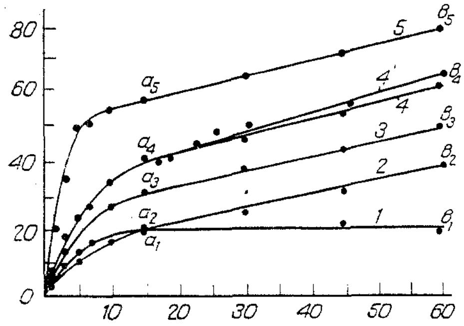

Fig. 1

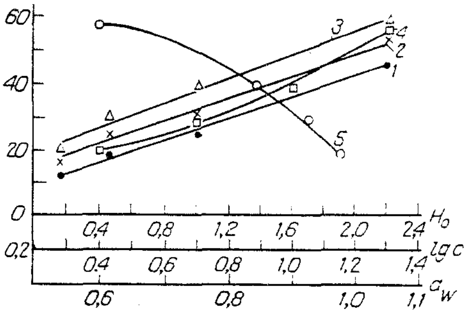

Fig. 2

Fig. 1. Kinetic curves of the hydrolysis of I in the presence of hydrochloric acid solutions with various concentrations (in percent by mass): 1) 0.54; 2) 2.5; 3) 5; 4) 10; 5) 20; 4') 10 (for a model mixture of I, glucose, and hydrochloric acid; see the explanation in the text). The time (in minutes) is plotted along the axis of abscissas, and the yield of II (in percent of the theoretical value) is plotted along the axis of ordinates.

Fig. 2. Dependence of the yield of II on the Hammett acidity function (H_0) for various times [1) 5; 2) 10; 3) 15 min], the hydrochloric acid concentration (in percent by mass) (4), and the activity of water (a_w) (5). The H_0, log c, and a_w scales are plotted along the axis of abscissas, and the yield of II (in percent of the theoretical value) is plotted along the axis of ordinates.

in the sample selected was accomplished by rapid cooling. A 2-ml sample of the cooled hydrolyzate was transferred to a 50-ml volumetric flask, and the volume of the solution was brought up to the mark with alcohol. The alcohol solutions of the hydrolyzates obtained were analyzed for their II content by means of a chromatographic-spectrophotometric method [2] ($n = 5$, $\alpha = 0.95$, $A = \pm 1.22\%$). It was established beforehand that the hydrolysis of I without a catalyst proceeds extremely slowly: Only traces of II were detected in the reaction mass after 6 h at 100°C. The experimental data were subjected to statistical treatment by the method of least squares (MLS).

In the study of the acidic hydrolysis of I under various conditions we did not observe any distortions of the kinetic curves that would constitute evidence for a stepwise (consecutive) process with splitting out of individual II fragments (Fig. 1). The rates of hydrolysis of the individual fragments are evidently commensurable, and the kinetic curves of the accumulation of II in the hydrolysis products are the overall curves for all of the simultaneously and successively occurring processes. The latter was reflected in the fact that they do not obey first- and second-order equations but have a more complex dependence on the concentration of the reaction ingredients. In Fig. 1 it is apparent that all of the kinetic curves can be divided into two periods: curvilinear $0a_i$ is the reaction time up to 15 min, and rectilinear $a_i - b_i$ is the reaction time beyond 15 min.

In all of the tested hydrochloric acid concentrations except 0.54% by mass (0.15 mole/liter), in the second period of the reaction the rectilinear sections of the kinetic curves are almost parallel. In this period the rate of the process is constant and does not depend on the ratio of the I and hydrochloric acid concentrations, and the point of transition of the curves from the curvilinear section to the rectilinear section (a_1—a_5) lies higher, the higher the hydrochloric acid concentration.

At a hydrochloric acid concentration of 0.54% by mass (0.15 mole/liter) the reaction virtually ceases, having reached a degree of conversion at point a_1 of ~20%. This makes it possible to conclude that II, inasmuch as it is a base with respect to hydrochloric acid, suppresses the activity of the acid as a catalyst, thereby promoting the reaction from the right to the left:

$$(OH)_3C_6H_2COOH + H^+ \rightleftarrows (OH)_3C_6H_2COOH_2^+. \qquad (3)^*$$

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*No equation listed as Eq. (2) is given in the Russian original — Publisher.

Evidently it is precisely this process that is the reason for the creation in the system of a steady-state concentration of the acylium ion at points a_1—a_5, at which the rate of the process no longer depends on the concentrations of both I and hydrochloric acid (lines a_i—b_i). To verify this assumption we composed a model mixture from I, glucose, hydrochloric acid, and II in concentrations corresponding to the theoretically calculated values for point a_4 (see Fig. 1, curve 4). It is apparent from Fig. 1 (curve 4') that the line of accumulation of II in this system with time proved to be extremely close to line 4 – the accumulation of II in an experiment in which the starting materials were I and hydrochloric acid with the same concentration.

In order to evaluate the most likely mechanism of the acidic hydrolysis of I in the first period of the reaction we constructed a graph (see Fig. 2) that illustrates the dependence of the yield of II on the Hammett acidity function (H_0), the logarithm of the hydrochloric acid concentration (c), and the activity of water (a_w) in hydrochloric acid solutions of the tested concentrations. It is apparent that a rectilinear dependence is observed only for the Hammett acidity function. This provides a basis for the assumption that the acidic hydrolysis of I in the first period of the reaction proceeds primarily monomolecularly via decomposition of the acylium ion via the $A_{Ac}1$ or $A_{alc}1$ mechanism. This is also confirmed by the inverse dependence of the accumulation of II on the activity of water (a_w) in hydrochloric acid solutions. The linear dependence of the yield on the Hammett acidity function makes it possible to assume that the hydrolysis proceeds primarily via the $A_{Ac}1$ mechanism [3]. For this mechanism the reaction rate should not be sensitive to steric hindrance. In fact, an increase in the rate of the process as bulky II fragments are split out from the D-glucopyranose ring is not observed. However, the absence of a linear dependence of the logarithm of the concentration of the reacting substance on the reaction time provides evidence that this mechanism is not the only one and coexists to a certain extent with other mechanisms, for example, the $A_{Ac}2$ mechanism.

To ensure the possibility of determining the principal parameters of the process by computation when it is carried out, we found its mathematical expressions.

We rectified the curvilinear sections of the kinetic curves (0–a_i) by the method of semilogarithmic anamorphoses in the Y–log t system; this made it possible to find the analytical expression of the kinetics of these processes at 102 ± 2°C for the period from 0 to 15 min

$$Y_{0a} = K_a \lg t + B, \tag{4}$$

where Y is the yield of II in percent of the theoretical value, and K_a and B vary as a function of the hydrochloric acid concentration.

It was found that the dependence of K_a on the logarithm of the hydrochloric acid concentration in moles per liter is rectilinear and for $0.7 \leq c$ (moles/liter) ≤ 5.7 [$2.5 \leq c$ (percent by mass) ≤ 20] is expressed by the equation

$$K_a = 22.07 \lg c + 18.42. \tag{5}$$

The dependence of index B on the hydrochloric acid concentration is a hyperbola that is rectified in the c – (1/B) system of coordinates, where B can be expressed by the equation

$$B = \frac{1}{0.3056 - 0.045c}. \tag{6}$$

Taking into account the derived K_a and B values [Eqs. (5) and (6)] general Eq. (4) takes on the form

$$Y_{0a} = (22.07 \lg c + 18.42) \lg t + \frac{1}{0.3056 - 0.045c}. \tag{7}$$

It is valid for the determination of the yield of II in the hydrolysis of I with hydrochloric acid with concentrations from 2.5% to 20% for the period from 0 to 15 min. Resinification of the product is observed at a higher hydrochloric acid concentration.

The yield of II for times greater than 15 min is expressed by the kinetic equation

$$Y_{ab} = A + 0.44\,(t - 15), \tag{8}$$

where A can be calculated from the equation

$$A = 16.75 + 8c. \tag{9}$$

Taking Eqs. (8) and (9) into account the yield of II can be determined from the equation

$$Y_{ab} = 8c + 0.44t + 10.15, \tag{10}$$

when $t > 15$ min, $0.7 \leq c$ (moles/liter) ≤ 5.7, and $Y_{ab} \leq 100\%$, where c is the hydrochloric acid concentration, and t is the total time of the process in minutes.

According to Eq. (10), the complete hydrolysis of tannin in the presence of 10% hydrochloric acid (2.8 mole/liter) can be achieved in 2.5 h. Experimental verification showed that a yield of 96% is achieved for this period of time, which coincides quite well with the calculated value.

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MICROBIOLOGICAL HYDROXYLATION OF ANDROST-4-ENE-3,17-DIONE AND ANDROSTA-1,4-DIENE-3,17-DIONE

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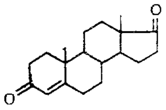
We have previously studied the 11α-hydroxylation of androst-4-ene-3,17-dione (I) by means of Rhizopus nigricans [2], as well as the transformation of I and androsta-1,4-diene-3,17-dione (II) by means of a Beauveria sp. culture [1]. As a continuation of the research we investigated the possibility of the hydroxylation of I and II with Tieghemella hyalospora and Tieghemella orchidis cultures, which, respectively, bring about 11α- and 11β-hydroxylation in the pregnane series [3].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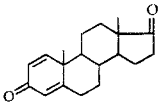
II

The transformation of I and II by means of these cultures proceeds with the formation of a mixture of three hydroxylation products: 11α-hydroxyandrost-4-ene-3,17-dione (III), 11β-hydroxyandrost-4-ene-3,17-dione (IV), and 7α-hydroxyandrost-4-ene-3,17-dione (V) and 11α-hydroxyandrosta-1,4-diene-3,17-dione (VI), 11β-hydroxyandrosta-1,4-diene-3,17-dione (VII), and 7α-hydroxyandrosta-1,4-diene-3,17-dione (VIII) (Table 1).

In growing the T. hyalospora fungus we used three media in which glucose was the source of carbon, and the sources of nitrogen differed: corn extract (medium 60), a mixture of peptone and the extract (medium A), and all three components (medium P). The best results were obtained in media A and P.

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