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Obtaining of inulin acetate

Abstract: In the article first obtained inulin ester — inulin acetate, by etherification of inulin with acetic anhydride has been exposed. Obtained product has been studied using elementary analysis and IR — spectroscopy.

Keywords: inulin, acetic acid, acetic anhydride, moisture, sulfuric acid, acetamide, acetylation, inulin acetate.

In previous work [1, 401–402] we have shown the possibility of obtaining inulin ether — nitroinulin. In order to expand the derivatives of inulin in this paper shown results of investigations to obtain inulin acetate. Now, the basic reagent used for acetylating is the acetic anhydride applied at acetylation of cellulose.

Acetylation of inulin spent acetic anhydride in a solution 60%-s' acetic acids. Reaction proceeds under the following scheme:

$$[R\text{-}(OH)_3]_n + 3n\,(CH_3CO)_2O \rightarrow$$
$$[R\text{-}(OCOCH_3)_3]_n + + 3n\,CH_3COOH$$

Allocated at acetylation of acetic acid, is the solvent, formed acetate inulin. As the reaction catalyst acetylation the widest application was received by mineral acids, in particular, sulfuric acid. The role of sulfuric acid in the process of acetylation essentially differs from its role at nitration of inulin. As we marked before [2, 37–41; 3, 104; 4, 131–132], at nitration of inulin in the structure of nitrate mixes the significant

amount of sulfuric acid (to 60% from all nitrate mixes) is input and its basic purpose in a mix — to increase swelling of inulin and to reduce the nitric acid expense (at the same module of a bath). Presence of sulfuric acid in nitrate mixes does not influence considerably on conditions of nitration of inulin. Nitration of inulin as it was specified in work [5, 24–27], can be carried out with the same speed and one nitric acid. Hence, sulfuric acid at the nitration process is not the catalyst. At the acetylation of inulin in the structure of mix the small amount of sulfuric acid of 3–12% (from weight of inulin), not causing appreciable increase in swelling of acetylated object is input. As opposed to nitration, at the acytilation of inulin the presence of sulfuric acid in the structure of etherification mix is necessary. At the acetylation of inulin sulfuric acid is the active catalyst, besides it is quite accessible. Hereby it is also spoken its wide application at acetylation of polysaccharides, in particular, cellulose.

Except the catalyst, on the speed of acetylation process, also the big influence renders humidity of inulin. The above humidity of inulin, more its swelling and that occurs acetylation faster. Figure 1 shows the dependence of acetylation speed from the moisture content in the inulin.

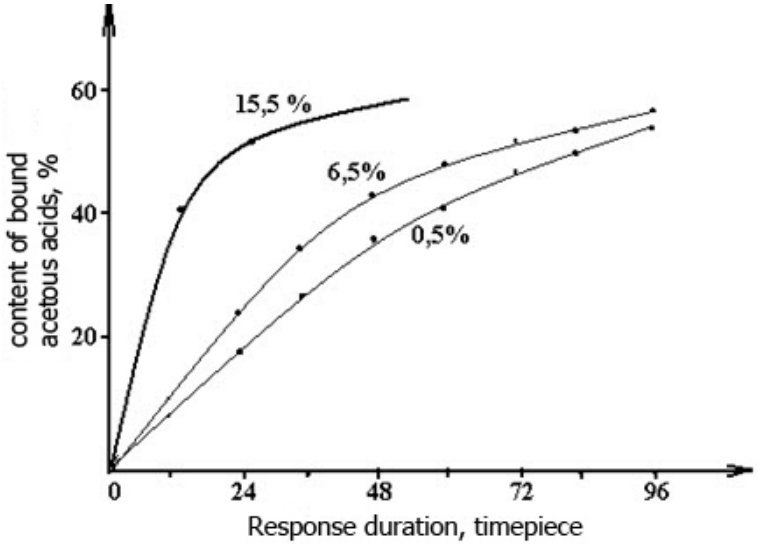

Fig.1. Influence of inulins moisture on its acetylation speed.

Apparently from drawing, the humidity increase of inulin leads to acceleration the reaction of acetylation.

However, application for acetylation of inulin with the raised humidity is inexpedient, as thus the expense of acetic anhydride in the reaction with the water which is in inulin considerably increases.

It is more expedient to carry out preliminary swelling of inulin in ice acetic acid. As a result of this processing speed of acetylation process, spent to the same conditions, raises several times. The quantity of the acetic acid applied to preliminary swelling of inulin, is considered at the subsequent addition of acetylated mixes. Hence, the specific expense of reagents at acetylation does not raise. This method of activation has received the widest application by the manufacture of acetyl cellulose.

The first stage at obtaining acetates of inulin is hydration of acetic anhydride, i. e. interaction of the water which are in a mix with a part of acetic anhydride.

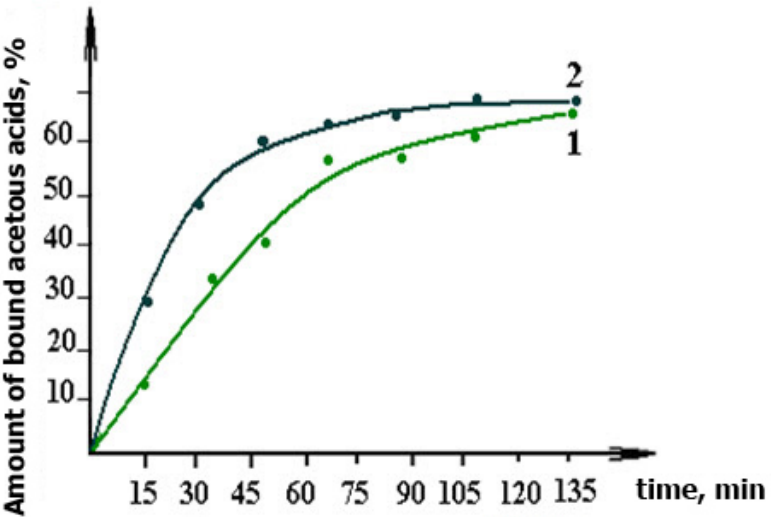

Fig. 2. Dependence of the amount bounded acetic acid for catalyst type.
1 — Catalyst H_2SO_4; 2 — catalyst H_2SO_4: acetamide (1:2)

Acetylation reaction of inulin begins with a powder surface. In the process of acetateinulin formation its macromolecules are dissolved in acetylated mixes and liberate hydroxyl groups of inside layers of inulin powder. Thus, in the acetylation process completely proacetylated molecules of inulin pass in a solution.

After acetylation reaction end the product precipitate in the distilled water, a deposit filter and wash out water for the purpose of removal of acetic acid, mineral acids, acetamide, and partially, low-molecular fractions of inulin acetates.

Acetic anhydride in the absence of catalysts co-operates with inulin very slowly, therefore at the reception of acetates, it is necessary to use catalysts — mainly sulfuric, chloric acids or their mixes.

Application of chloric acid at obtaining inulin acetates an acetic method in some cases leads to gelatinization of the obtained syrup. In practice, as a rule, the mixtures of chloric and sulfuric acids are used.

Recently more often steels to apply acetamide (CH_3CONH_2) which is used in the form of a solution in a mix of acetic acid and acetic anhydride where its basic property amplifies also it can enter reaction with protons of acids. Figure 2 shows the acetylation of inulin using acetamide as the catalyst.

This is due, seems, the fact that the role of acetamide is binding greater portion of the catalyst in the initial stage of acetylation and a deceleration rate in the final period of the acetylation reaction. In the process of increase in temperature and the expense of acetic anhydride at the expense of complex disintegration the additional quantity of the catalyst that allows finishing completely acetylation process is allocated.

As a result of acetylation it turns out acetateinulin with degree of polymerisation 27–32, with the maintenance of the connected acetic acid to 61–62%. The obtained powder washes out cold water before neutral reaction.

In figure 3. the IR-spectrum of acetateinulin where there is a peak of absorption in the region of 3421 sm^{-1} which characterises the presence of free hydroxyl groups is resulted. Such spectra are characteristic to the samples, obtained with insufficient quantity of acetic anhydride. There are strips of absorption of 2925 sm^{-1} — for intracomplex groups; 2032 sm^{-1} — for primary-$OCOCH_3$ groups; 1738 sm^{-1} — for CH_2 — $OCOCH_3$ groups; 1133 sm^{-1}, characteristic for (C — O — C) bonds; and also 935 sm^{-1} — for α — polysacharides;

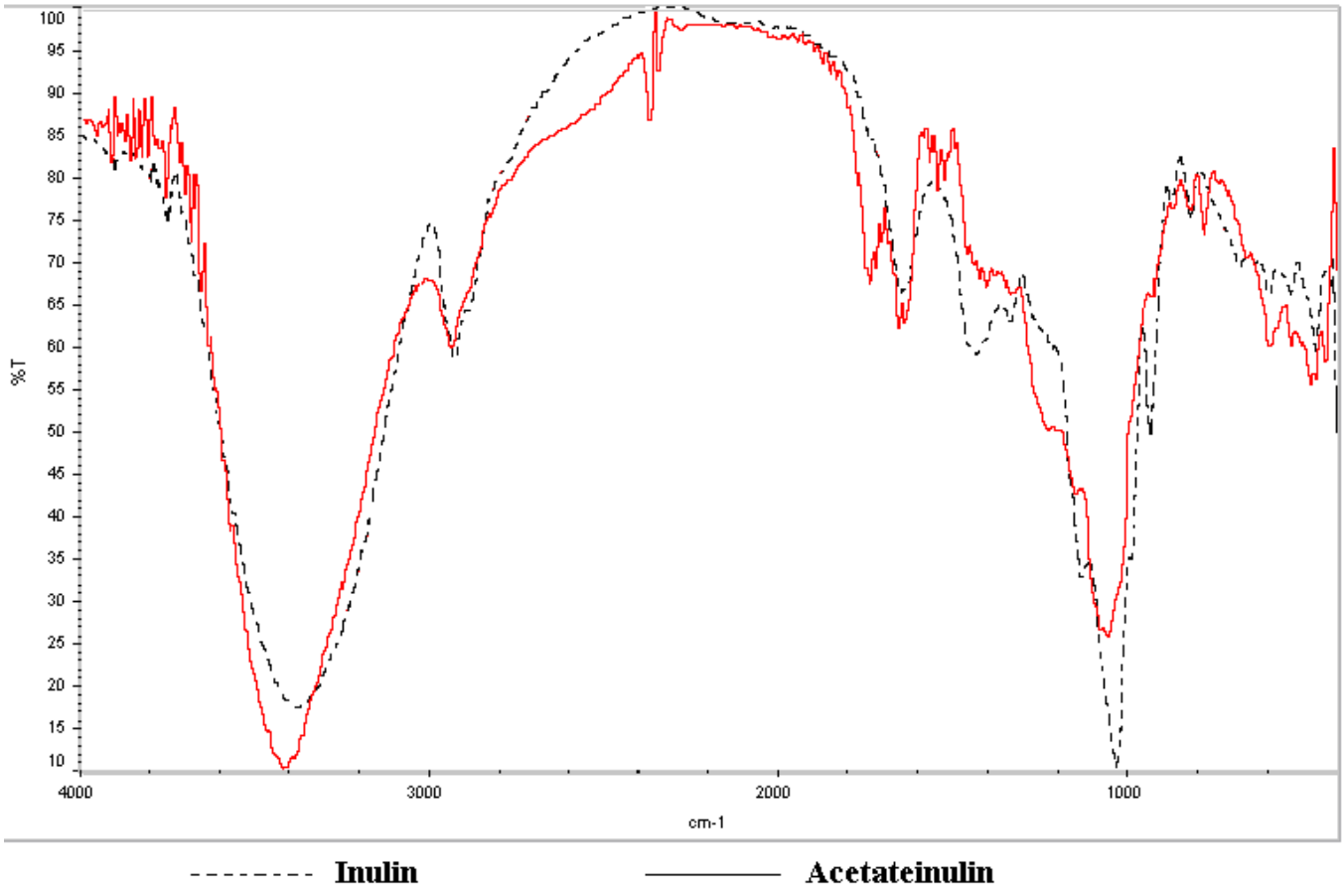

Fig. 3. IR — spectrum of acetateinulin

Acetateinulin (Inulinacetate) — a difficult ether of organic acid and polysaccharide — inulin, containing a little — $OCOCH_3$ radicals with molecular weight 9000–11000, a representing loose powder of dark brown colour. It has humidity of 3,78% which defined by hydrometer — «Sartorius Ab COTTINGEN», Germany, at temperature 105^0 C, fusion temperature defined by the device of firm "BUCHI" Switzerland, BUCHI Melting point B-540, (0^{0}C — 540^{0}C), $\mathbf{T_{пл.}}$ = 238,7–240,6^0 C. Acetateinulin under the resorcin action and hydrochloric acid it is not painted in red colour (Selivanov's reaction).

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