EFFECTIVE METHOD OF OBTAINING N-GLYCOSIDES OF UREA

V. A. Afanas'ev and Zh. A. Dzhamanbaev

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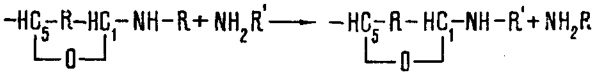
The production of N-glycosides with weakly basic aglycones by direct condensation of amines with unsubstituted monosaccharides [1] is difficult because of the length of the process and a number of side reactions which reduce the yield and the purity of the end-product. It appeared of interest to determine the possibility and the advantages of the reaction of N-trans-glycosylation



$$-\underbrace{HC_5-R-HC_1}_{O}-NH-R+NH_2R' \longrightarrow -\underbrace{HC_5-R-HC_1}_{O}-NH-R'+NH_2R$$

over the direct synthesis of N-glycosides. The kinetic investigations performed previously showed that the introduction of a N-aglycone into the molecule of a monosaccharide increases the reactivity of the glycosidic center (C_1) in reactions of nucleophilic substitution under conditions of acid catalysis [2-4]. The results of these investigations permitted the formulation of a number of rules for addition and substitution reactions at C_1, from which it follows that the efficiency of trans-glycosylation depends on the ratio between the basicity indices of the attacking amine and the initial N-aglycone. We have used these rules to develop a method for obtaining glycosides with feebly basic N-aglycones. In the present paper we describe a method for obtaining urea N-glucoside. As a result of a study of trans-glycosylation in the arylamine N-glucoside–urea system, it was established that the highest yield of N-glucoside urea is obtained by using m-nitroaniline N-glucoside as the starting material.

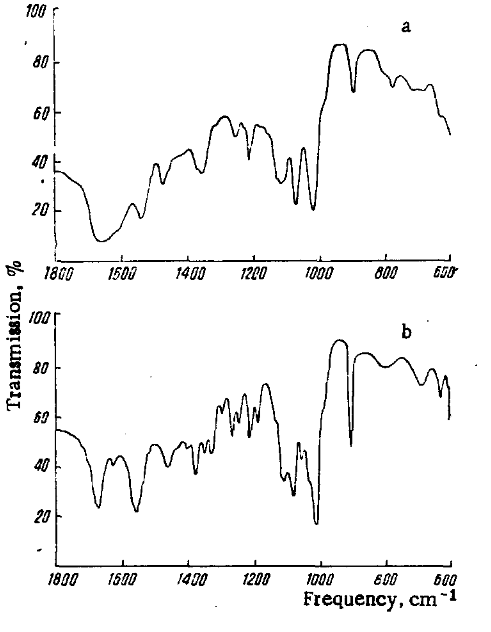


Fig. 1. IR spectra of the crude product (a) and of pure N-glucosylurea (b) obtained by trans-glycosylation in the m-nitroaniline N-glucoside–urea system.

EXPERIMENTAL

Urea N-Glucoside. A solution of 1.8 g of urea in 12 ml of methanol containing 0.25 ml of concentrated hydrochloric acid was added to 15 ml of methanol containing 2 g of m-nitroaniline N-glucoside. After cooling to room temperature and rubbing with a seed of N-glucosylurea, a yellow crystalline precipitate (crude product) precipitated during half an hour. After two recrystallizations from aqueous methanol (water was added dropwise to hot methanol until the crude product dissolved), N-glucosylurea was obtained in the form of a white crystalline powder with a yield of 40% (after evaporation of the filtrate in vacuum it is possible to obtain additional portions of product). The total yield was 65%, mp 205-206°C, $[\alpha]_D^{20}$ −20.5° (c 0.68; water). Found %: C 34.94; H 6.60; N 11.50. Calculated, %; on the assumption that the substance is N-glucosylurea monohydrate: C 35.00; H 6.71; N 11.66. When chromatographed on type "S" ["fast"] paper of the Leningrad No. 2 paper mill in the butan-1-ol–acetic acid–water (4 : 1 : 5) system for 18 h with subsequent revelation by aniline hydrogen phthalate, the product was identified in the form of a single spot with R_f 0.11.

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To establish the structure of the urea N-glucoside, the IR spectra of the crude product a and of the desired product b were taken in the solid state on a Perkin–Elmer (model 457) spectrophotometer with samples molded into tablets with cesium iodide (2 mg of 800 mg of CsI). The spectra given in Fig. 1 are completely identical with the spectra of the N-glucosylurea described by Jones and Ross [5]. The absorption close to 1140 cm^{-1} (C–O–C stretching vibrations) and the band at 1460 cm^{-1} (C_1–N stretching vibrations) showed the cyclic structure of the product investigated. The presence in the spectra of strong absorption bands at 905 cm^{-1} shows according to Barker et al. [6] that the N-glucosylurea is in the form of the β-glucopyranoside. This conclusion is confirmed by the absence of a band at 844 cm^{-1}, which is characteristic for the α form of the carbohydrate fragment (type 2a in Barker's classification).

The advantage of the proposed method is the speed of performance of the reaction (from 10 to 30 min) with a simultaneous increase in the yield of pure N-glycosylurea.

CONCLUSIONS

On the basis of information on the kinetics of trans-glycosylation in arylamine N-glycosides, a rapid method has been developed for obtaining urea N-glycosides using m-nitroaniline N-glycosides as donors of glycosyl residues.

LITERATURE CITED

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