Photolysis of 3-Phenyl-4-benzylidene-1H-naphtho[2,3-h]quinazoline-2,7,12-trione (VI). A 0.13-g (0.7 mmole) sample of a 1:1 mixture of Z- and E-isomers VIa, b was applied to 15 Silufol plates (150 × 150 mm), and the plates were maintained in light until the color changed from red brown to yellow. The photolysis products were extracted with chloroform, chromatographed with a column packed with silica gel (elution with chloroform), and recrystallized from dioxane to give 0.07 g (65%) of anthrapyrimidine V with mp 325-328°C. The IR spectrum was identical to the spectrum of a sample obtained from amine IV.

The authors thank A. V. Piskunov for providing us with a sample of 1-amino-2-phenylethynylantraquinone.

LITERATURE CITED

SYNTHESIS OF 5-HYDROXY-6-METHYLURACIL 3-β-D-RIBOFURANOSIDE

G. A. Tolstikov, L. A. Baltina, L. M. Khalilov, L. V. Spirikhin, V. R. Sultanmuratova, and Yu. I. Murinov

3-(β-D-Ribofuranosyl)-5-hydroxy-6-methyluracil was synthesized by the silyl method in the presence of SnCl₄ using 1-O-acetyl-2,3,5-tri-O-benzoyl-β-D-ribofuranose as the carbohydrate component. The structures of the glycosides were confirmed by spectral methods.

5-Hydroxy-6-methyluracil (I, hydroxymethacil) is of interest as an immunomodulator and cardiostimulator [1-3]. To obtain the transport form of this compound we began research on the synthesis of nucleosides that are analogs of 6-methylpyrimidine nucleosides [4, 5]. The present communication is devoted to the synthesis of 3-(β-D-ribofuranosyl)-5-hydroxy-6-methyluracil by the silyl method [6].

5-Hydroxy-6-methyluracil (I) was obtained by the method in [7] and was silylated with excess hexamethyldisilazane in the presence of trimethylchlorosilane in dry dioxane as in [8]. The yield of 2,4,5-tris(trimethylsilyloxy)-6-methyluracil (II) was 59%. 1-O-Acetyl-β-D-ribofuranosyl tribenzoate (III) was obtained by our modification of the method in [9].

using KU-2-8 cation-exchange resin (H+ form) in the step involving the synthesis of the methyl-substituted D-ribofuranoside. The reaction of silylated base II with protected ribofuranose III in dry dichloroethane at 20°C proceeds stereospecifically to give N3-13-D-glycoside IV (40-43% yield).

Nucleoside IV was isolated by column chromatography on silica gel. Its deblocking with a 0.1 N solution of NaOMe in MeOH leads to 3-β-D-ribofuranosyl)-5-hydroxy-6-methyluracil (V). The purity of the compounds obtained was monitored by TLC and HPLC.

The structures of glycosides IV and V were established on the basis of data from the IR, UV, and 1H and 13C NMR spectra. An 11.4 ppm diamagnetic shift of the signal of the C1(1') atom as compared with 1-O-acetate III is observed in the 13C NMR spectrum of nucleoside IV, and the chemical shifts (CS) of the C2(1')—C4(1') atoms in the spectrum of nucleoside IV are virtually the same as those in the spectrum of starting sugar III, which indicates a β configuration of the anomeric center in nucleoside IV.

Signals of protons of a uracil fragment — a singlet of a methyl group (2.14 ppm) and broad signals of NH (10.8 ppm) and OH (3.67 ppm) groups — are observed in the PMR spectrum of nucleoside IV.

In the spectrum of starting acetate III the 1-H proton is observed in the form of a singlet at 6.43 ppm, i.e., a vicinal constant of spin-spin coupling (SSC) of the 1-H and 2-H protons is virtually absent, which indicates a gauche-equatorial-equatorial orientation of the 1-H and 2-H protons or a trans orientation of the substituents attached to the C(1) and C(2) atoms (a β configuration of the anomeric center). In the spectrum of nucleoside IV the signal of the 1-H proton (6.64 ppm) also has the form of a singlet, which indicates retention of the β configuration of the anomeric center. In addition, it is known [10] that the presence of singlet of a 1-H proton in the spectra of substituted 6-methylpyrimidine nucleosides is a confirmation of the β configuration of the anomeric center.

The formation of 1,2-trans isomers is generally preferable for the glycosylation of sugar derivatives with 2-O-α1 groups; this is explained by the formation of a 1,2-acyloxonium ion in the rate-determining step of the reaction [11, 12].

The N-glycoside structure of IV was confirmed by its IR spectrum, in which strong carbonyl absorption (νc=O) of a uracil ring is observed at 1660-1675 and 1700-1730 cm⁻¹, which excludes an O-glycoside structure.

The assignment to an N(3)-glycoside structure was made on the basis of the UV spectra of nucleoside V, for which a bathochromic shift of the absorption bands in an alkaline medium of ~30 nm, which is typical for N(3)-substituted uracil derivatives [10, 13], is characteristic.

**EXPERIMENTAL**

The 1H NMR spectra of solutions of the compounds in CDCl₃ were recorded with a Tesla BS-567 spectrometer (100 MHz) with tetramethylsilane (TMS) as the internal standard. The 13C NMR spectra of solutions in CDCl₃ were obtained with a JEOL FX-90-Q spectrometer (22.5 MHz) with broad-band and extra-resonance suppression of the protons and TMS as the internal standard. The IR spectra were recorded with a UR-20 spectrometer. The electronic absorption spectra were recorded with a Specord M-40 spectrophotometer. The melting points were measured with a Boetius apparatus (East Germany). The specific rotation was determined with a Perkin—Elmer 241-MC polarimeter in a 1-dm long tube. Thin-layer chromatography was carried out on Silufol UV-254-366 plates (Czechoslovakia) using the following solvent systems: A) chloroform—methanol (19:1); B) chloroform—methanol (4:1). The spots of the substances were detected with UV light and iodine vapors. Silica gel L (40/100μ, Chemapol, Czechoslovakia) was used for column chromatography. Analysis by HPLC was carried out with a Du Pont chromatograph with columns packed with Zorbax CN (for IV) or Zorbax ODS (for V): the mobile phase was a mixture of chloroform with hexane (9:1) or distilled water, respectively, and a UV detector was used. Gas-liquid chromatography was carried out with a Chrom-5 chromatograph (Czechoslovakia) with a glass column packed with SE-30 sorbent; the length was 1.2 m, the inner diameter was 3 mm, the temperature was 150°C, the detector temperature was 200°C, the vaporizer temperature was 200°C, the carrier gas was helium, and the flow rate was 40 ml/min.

The dichloroethane was fractionated twice over P₂O₅. The dioxane was maintained for 24 h over KOH and was then fractionated over sodium metal.

The results of elementary analysis for C, H, and N were in agreement with the calculated values.

2,4,5-Tris(trimethylsilyloxy)-6-methylpyrimidine (II, C₁₄H₂₇N₂O₃Si₃). A mixture of 14.2 g (100 ml) of I [7], 40 ml of hexamethyldisilazane, and 2 ml of trimethylchlorosilane in 50 ml of dry dioxane was refluxed without access to moisture until the solid material had dissolved (3 h), after which the solvent and excess silylating agent were removed by vacuum distillation. The residue, which, according to GLC data, contained ~5% admixed silylated 6-methyluracil, was subjected to fractional distillation in vacuo to give 22.9 g (59%) of silylated base II in the form of a colorless oil, which crystallized on standing (to give white crystals) and was homogeneous according to GLC data. IR spectrum (liquid film): 760, 850, 1250 [Si(CH₃)₃]; 1040 (C—O—Si); 1460, 1580 cm⁻¹ (pyrimidine ring). PMR spectrum (CDCl₃,