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PREPARATIVE SYNTHESIS OF β-SITOSTEROL TETRAACETYL-β-D-GLUCOPYRANOSIDE

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UDC 547.918+547.926

β-Sitosterol β-D-glucoside (I) is widely distributed in the vegetable kindgom [1, 2]. It exhibits a hypocholesteremic action [3] and inhibits prostaglandin synthetase [4]. It must be mentioned that (I) is a component of the glycoside preparation synthesized from the total sterols of tall oil, which possesses an antipyretic and antiinflammatory action [5]. The broad action spectrum and relative accessibility of the initial sterol [6] is stimulating the development of convenient methods of synthesis [1]. Several syntheses of β-sitosterol tetraacetyl-β-D-glucoside (II) carried out on decigram amounts of β-sitosterol have been described. Salway obtained (II) with a yield of 20% when the glycosylation reaction was performed under the Koenigs-Knorr conditions [7]. Pegel and Walker synthesized (II) by adding a twofold excess of α-acetobromoglucose (α-ABG) in toluene to a boiling mixture of β-sitosterol and silver carbonate in toluene with the simultaneous removal of the water formed by azeotropic distillation with the toluene [4]. The yield of (II) after crystallization from ethanol was 30%.

We have synthesized (II) under the conditions proposed for obtaining steroidal aryl glucuronides [8], with a change in the order of adding the components to the reaction mixture.

A solution of 7.0 g (17 mmole) of β-sitosterol and 8.7 g (21.2 mmole) of α-ABG in 80 ml of toluene was added dropwise over half an hour to a boiling suspension of 3.6 g (21.3 mmole) of cadmium carbonate (ch. ["pure"] grade) in 250 ml of toluene (kh.ch. ["chemically pure"] grade) with the simultaneous distillation of an azeotropic mixture of water and solvent. Boiling was continued for 2 h with the volume being kept constant. After the end of the reaction (TLC: absence of α-ABG), the catalyst was filtered off and was washed with a small amount of chloroform, and the solution was evaporated to a syrupy consistency. The residue was treated with 50 ml of methanol. The precipitate that deposited was separated from the mother liquor and crystallized from 400 ml of hexane. This gave chromatographically homogeneous crystalline (II) with a yield of 5.8 g (46%), mp 165-167°C, showing no depression of the melting point in a mixture with an authentic sample. The mother liquor contained mainly by-products of the glycosylation reaction: an acetate and di-β-sitosteryl ether, with trace amounts of (II) and its α anomer. The addition of the reagents in the order given by Conrow and Bernstein [8] led to a fall in the yield of (II) to 36%.

A solution of 3.3 g of (II) in 30 ml of absolute ethanol was treated with 5 ml of 0.1 N sodium methanolate in methanol. The mixture was stirred at room temperature for a day. The precipitate that had deposited was filtered off and washed with a small amount of methanol to give 2.3 g (yield 90%) of chromatographically homogeneous (I), identical with an authentic sample.

The high stereospecificity of glycosylation, the good yield, the ready availability of the reagents, and the ease of isolation of the product make the proposed modification convenient for use in the preparative synthesis of (II).

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STEROLS OF THE NYSTATIN-RESISTANT YEAST *Saccharomyces cerevisiae*

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Sterols obtained microbiologically may prove to be useful precursors of steroid vitamins and hormones.

In this investigation we used nystatin-resistant and nystatin-sensitive strains of the yeast *Saccharomyces cerevisae* of Petergof genetic lines derived from race XII. The nystatin-resistant mutants were obtained under the action of UV radiation and of 6-N-hydroxyamino purine. All the mutants considered in the present paper belong to a single genotypic class, denoted NYS I.

The sterols in the unsaponifiable fraction of the lipids were isolated from the yeast cells by the method of Breivik and Owades in Woods' modification [1].

The GLC analysis of the mixture of sterols was performed on a Pye-Unican chromatograph. As the stationary phase we used 3% of SE-30 on the support Chromosorb Q. The rate of flow of He was 35 ml/min, and the temperature of the column 250°C. Mass spectra were obtained on an LKB-2091 instrument at 70 eV.

In contrast to strains of the wild type in which the main sterol is ergosterol [2], in the mutants we found cholesterol derivatives. Analysis of mass spectra, comparison of retention times with the results obtained for known compounds, and also comparison with literature information [3, 4] enabled the following compounds to be identified in mutants with respect to the NYS I gene of the yeast *Saccharomyces cerevisiae*: cholesta-5,7,22,24-tetraen-3β-ol (I), cholesta-5,7,24-triene-3β-ol (II), and cholesta-8,24-diene-3β-ol (III) in relative amounts of 5-8, 9-20, and 60-80%, respectively.

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