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GLYCOSYLATION OF TRITERPENES OF THE DAMMARANE SERIES. III. REGIO- AND STEREOSELECTIVE SYNTHESIS OF 12-O-β-D-GLUCOPYRANOSIDES OF 20(S),24(R)-EPOXYDAMMARANE-3-12β,25-TRIOLS UNDER HELFERICH'S CONDITIONS

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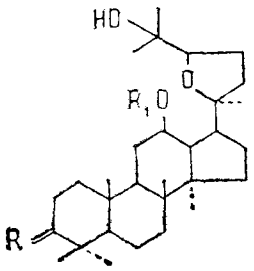
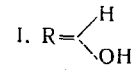
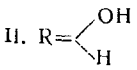
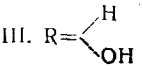
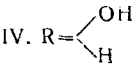
UDC 547.917+547.918+547.597

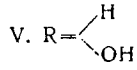


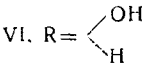
I. R =  R_1=H

II. R =  R_1=H

III. R =  R_1=Glc(Ac)$_4$

IV. R =  R_1=Glc(Ac)$_4$

V. R =  R_1=Glc

VI. R =  R_1=Glc

The high stereoselectivity of Helferich's method of glycosylation [1] has been demonstrated in the synthesis of glycosides both of comparative simple compounds of the type of cyclohexanol [2] and of more complex compounds — glycosides of polycyclic alcohols [3] and trisaccharides [4].

We have previously used these conditions successfully for the exhaustive glycosylation of 20(S),24(R)-epoxydammarane-3α,12β,25-triol and some of its derivatives [5].

The presence in the molecules of the initial triterpene alcohols (I and II) of a strong intramolecular hydrogen bond (intraHB) between the proton of the 12β-OH group and the oxygen atom of the tetrahydrofuran ring opens up the possibility of the regioselective synthesis of 12-O-glucosides without the preliminary protection of the OH groups not participating in the reaction.

The regioselectivity of the glycosylation of these triols with cholesteryl(β-D-glucose orthoacetate) is determined by the influence of the intraHB and depends on the nature of the glycosylating agent and the experimental conditions of performing the reaction [6].

We have studied the glycosylation of the triterpenes (I and II) at the C-12 OH group with α-acetobromoglucose under Helferich's conditions. In the performance of the reaction the order of mixing of the reactants, the temperature of the regime, and the amount of acylhalogenose added were varied. The best results were obtained with the use of equimolar amounts of the reactants under the conditions of the preliminary formation of an ion pair of

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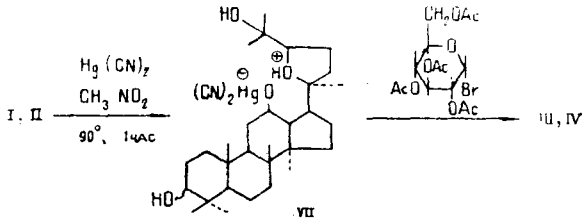
type (VII) when a homogeneous solution of the initial alcohol and mercury cyanide in nitromethane was kept at 90°C for 1 h and was then treated with α-acetobromoglucose.



The yields of the desired 12-O-glycosides (III and IV) in this case amounted to 73 and 72%, respectively (at conversions of 75 and 74%). The deacetylation of the glycosides obtained with a 0.1 N solution of sodium methanolate in methanol led to the free glucosides with yields of 95-98%.

The triol (I) was isolated from the unsaponifiable fraction of an ethereal extract of *Betula platyphylla* followed by purification on silica gel; mp 235-237°C (from acetone) [7]. The triol (II) was obtained from (I) as described in [5]; mp 218-220°C (acetone).

Column chromatography was performed on KSK silica gel (100-120 mesh) in the hexane–acetone (20:1)–(50:1) system.

12-O-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranosyl)-20(S),24(R)-epoxydammarane-3α, 12β,25-triol (III), mp 190-193°C (ethanol). 12-O-(2',3',4'6'-tetra-O-acetyl-β-D-glucopyranosyl) 20(S),24(R),epoxydammarane-3β,12β,25-triol (IV), mp 197-198°C (ethanol). Compounds (III) and (IV) were identical with those obtained previously [8].

12-O-β-D-Glucopyranosyl-20-(S),24(R)-epoxydammarane-3α,12β,25-triol (V); yield 95%; amorphous $[\alpha]_D^{20}$ −16.4 (c 1.0; pyridine).

12-O-β-D-Glucopyranosyl-20(S),24(R)-epoxydammarane-3β,12β,25-triol (VI); yield 98%; amorphous, $[\alpha]_D^{20}$ − 15.2° (c 1.0; pyridine).

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