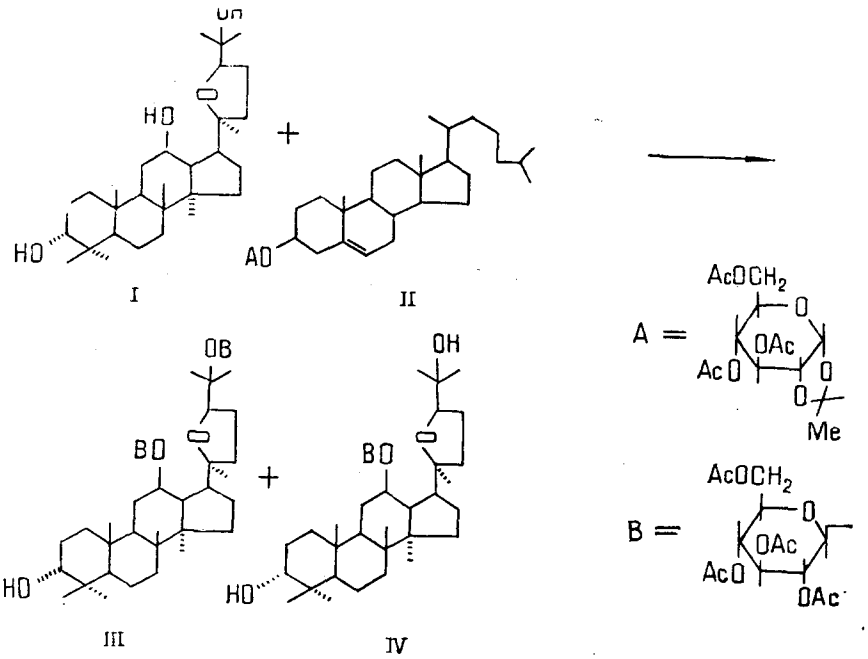
REGIO- AND STEREOSELECTIVE GLYCOSYLATION OF 20(S),24(R)-EPOXYDAMMARANE-3,12β,25-TRIOLS WITH CHOLESTERYL(α-D-GLUCOSE ORTHOACETATE). IV. PREPARATION OF 12,25-DIGLUCOPYRANOSIDES OF EPOXYDAMMARANETRIOL

N. F. Samoshina and N. I. Uvarova

UDC 547.455+547.597+547.918 +547.922

We have previously reported that the glycosylation of 20(S),24(R)-epoxydammarane-3,12β, 25-triols with cholesteryl (α-D-glucose orthoacetate) under the conditions of the previous formation of an ion pair with a Lewis acid leads to the selective formation of the corresponding 12-monoglucosides with the trans configuration of the glucosidic bond [1]. It was shown that the nature of direct glycosylation depends both on the type of glycosylating agent and, to an even greater extent, on the experimental conditions of glycosylation, which was connected with the presence of a strong intramolecular hydrogen bond (intraHB) between the proton of the 12β-OH group and the oxygen atom of the THF ring in the initial triols.



However, according to the IR spectrum of the 12-monoglucoside of betulafolienetriol oxide (BFTO) an intraHB also exists between the proton of the hydroxy group at C^{25} and the alkoxyl oxygen atom of the glucosidic grouping at C^{12} [2], which makes it possible to glycosylate the tertiary hydroxyl in this compound preferentially, with the formation of the 12,25-diglucoside of BFTO. The results of the glycosylation of BFTO (I) in nitromethane in the presence of mercury bromide are affected by the amounts of catalyst and of glycosylating agent — cholesteryl (α-D-glucose orthoacetate) (II). Depending on the ratio of these components ($HgBr_2$ and compound (II)), it is possible to obtain as the main product either the 12-monoglucoside of BFTO (IV) or its 12,25-diglucoside (II), or a mixture of these glycosides in comparable amounts. Compound (III) has been obtained previously with a yield of 42% by the catalytic rearrangement of a di(α-D-glucose orthoacetate) based on BFTO [2].

An equimolar ratio of cholesteryl (α-D-glucose orthoacetate) (II) and BFTO (I) led to the formation of a single glycosylation product — the 12-monoglucoside of BFTO (IV) — with a yield

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of 55% [1]. The addition of an excess of (II) (1.0 mmole per 0.5 mmole of (I)) to the reaction mixture gave a 67.9% yield of the monoglucoside (IV) and a 14.7% yield of the 12,25-diglucoside (III). The maximum yield of (III) (50%) was obtained with a threefold excess of (II) and 0.72 mmole of mercury bromide per mmole of the alcohol [3]. The formation of (IV) (21%) took place simultaneously. When the amount of catalyst was halved and the threefold excess of (II) was retained, a mixture of the 12-mono- and 12,25-diglucosides of BFTO (37 and 43%, respectively) was formed. The cholesterol present in (II) was recovered from the reaction mixture with an unchanged structure in a yield of the order of 80%.

In no case was the formation of the 3-monoglucoside of BFTO observed, which confirms the influence of the intraHB on the regiochemistry of glycosylation.

The structures of the compounds obtained were determined on the basis of the identification characteristics of ^{13}C NMR spectroscopy and the absence of a depression of the melting point of mixtures with authentic samples.

LITERATURE CITED

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MESACONITINE AND HYPACONITINE FROM *Aconitum czekanovskyi*

Ts. Zhapova, L. D. Modonova, and A. A. Semenov

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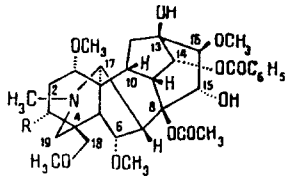
The epigeal part of *Aconitum czekanovskyi* Steinb., collected in the flowering phase in the Irkutsk province containing 0.23% of combined alkaloids. Two cases were isolated by column chromatography on alumina in hexane—acetone and with the aid of repeated recrystallization.



I. R = OH

II. R = H

The first was identified as mesaconitine (I): its mp of 195.5-196°C (methanol), $[\alpha]_{546}^{20}$ + 32.75 (c 3.74; $CHCl_3$), elementary composition $C_{33}H_{45}NO_{11}$, and molecular weight M^+ 631, coincided with those given in the literature [1] for (I). The majority of the signals in the ^{13}C spectrum of the alkaloid were identical with those reported in [2]. However, for some carbon atoms of ring A deviations in the chemical shifts of up to 1 ppm were observed. We ascribe these deviations to the conformational mobility of this ring. In order to refute another possible reason — epimerization at positions 1 and 3 — we analyzed the PMR spectrum of the alkaloid. PMR spectrum, $CDCl_3$, 25°C, δ, ppm (J, Hz): 4.86, d (5.0), H-14; 4.45, dd (5.5, 2.5), H-15; 4.35, d (2.5), OH-15; 4.03, d (6.5), H-6; 3.94 s, OH-13; 3.72, dd (10.0, 5.0), H-3; 3.73, s, OCH_3-16; 3.59, dd (9.0), 2 H-18; 3.32, d (5.3), H-16; 3.29, s, OCH_3-18; 3.27, s, OCH_3-6; 3.15, s, OCH_3-1; 2.87, br.s, H-17; 2.33, s, N-CH_3; 1.36, s, $COCH_3$. In deuteropyridine at 80°C ring A is stabilized in the chair form [3], the H-3 resonance being

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR.

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