THE STRUCTURE OF LAPIDOLIDIN

L. A. Golovina, A. I. Saidkhodzhaev, and
V. M. Malikov

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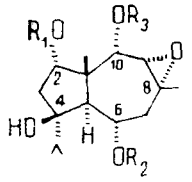
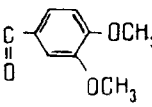
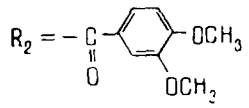
Continuing a study of the neutral components of the roots of *Ferula lapidosa* Eug. Korov [1-3], we have isolated a new compound with the composition $C_{26}H_{36}O_9$, mp 163-164°C (from ether) $[\alpha]_D$ + 26.7° (c 1.0; ethanol) which we have called lapidolidin (I).



I R_1 = Ac; R_2 =  R_3 = H

II $R_1 = R_2 = R_3 = H$

III $R_1 = R_3$ = Ac; R_2 = 

The IR spectrum of (I) showed absorption bands of hydroxy groups (3545, 3430 cm^{-1}), of ester carbonyl groups of aromatic (1700 cm^{-1}) and aliphatic (1740 cm^{-1}) acids, of an aromatic nucleus (1600, 1520 cm^{-1}), and of ester bonds (1230-1250, 1275 cm^{-1}). According to the UV spectrum (λ_{max} 220, 263, 295 nm (log ε 4.36, 4.03, 3.78), the esterifying aromatic acid was 3,4-dihydroxy-substituted.

From the products of the alkaline hydrolysis of lapidolidin we isolated veratric acid and a carotane alcohol, $C_{15}H_{26}O_5$, mp 260-261°C (decomp.), $[\alpha]_D$ +58.0° (c 1,1; ethanol) identical with the lapidolinol (II) isolated previously as a component of the esters lapidolin and lapidolinin from the same plant [1-4].

The PMR spectrum of lapidolidin showed the signals of the protons of an isopropyl group (d, 0.84 and 1.04 ppm, J = 7 Hz), of methyl groups at an angular carbon atom (s, 1.21 ppm) and at an epoxide ring (s, 1.48 ppm), and of two gem-acyl protons (m, 5.30 ppm, $W_{1/2}$ = 23 Hz) d, 5.04 ppm, J = 6 Hz). Doublets at 4.19 ppm (J = 5 Hz) and 2.91 ppm (J = 5 Hz) were due to vicinally interacting gem-hydroxylic and epoxide protons. Two three-proton singlets (3.85 and 3.83 ppm) and a group of signals in the region of aromatic protons [d, 6.82 ppm (J = 9 Hz); d 7.4 ppm (J = 2.5 Hz); q, 7.55 ppm (J = 9 and 2 Hz)] were assigned to the veratric acid residue. A narrow singlet at 2.04 ppm corresponded to the protons of an acetyl group.

It is clear from the facts given that lapidolidin is a diester of lapidolinol with acetic and veratric acids. The positions of the acid residues were determined in the following way.

The acetylation of (I) gave lapidolidin (III), which led to the unambiguous conclusion that the veratric acid residue in the lapidolidin was located at C-6.

In the PMR spectrum, the proton geminal to the acetyl group resonated in the form of a doublet (5.04 ppm, J = 6 Hz) with broadened components, which is characteristic for a proton at C_2 of a five-membered ring in lapidolinol derivatives. This means that in (I) the acetic acid esterified the hydroxy group at C_2.

What has been said above shows that lapidolidin has the structure and configuration of 2α-acetoxy-4β,10α-2α-acetoxy-4β,10α-dihydroxy-6α-veratroyloxy-8α,9α-epoxytranscarotane (I).

LITERATURE CITED

1. L. A. Golovina, A. I. Saidkhodzhaev, V. M. Malikov, and S. Melibaev, Khim. Prir. Soedin., 787 (1982).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent.
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2. L. A. Golovina, A. I. Saidkhodzhaev, N. D. Abdullaev, V. M. Malikov, and M. R. Yagudaev, Khim. Prir. Soedin., 296 (1983).
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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

L. N. Atopkina, V. L. Novikov,
V. A. Denisenko, and N. I. Uvarova

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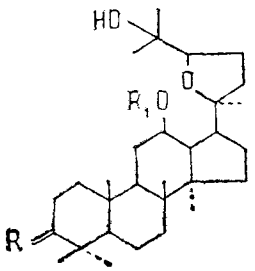
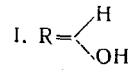
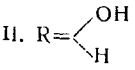
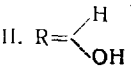
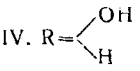
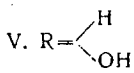


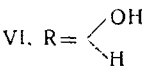
I. R =  R_1=H

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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