STRUCTURE OF AJANIN

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On the basis of the results of a study of the sesquiterpene lactone ajanin from Ajania fastigiate (Winkl.) Poljak. by the methods of IR and PMR spectroscopy and chemical transformations, its structure has been established as 3,4,8α-trihydroxy-5α,6β,7α(H)-guaia-1(10),11(13)-dien-6,12-olide.

We have previously reported the isolation of a new sesquiterpene lactone from Ajania fastigiata (Winkl.) Poljak., ajanin (I), with the composition $C_{15}H_{20}O_5$, mp 186-188°C, $[\alpha]_D^{22}$ +26.5° (c 2.24; ethanol) [1]. In the present paper we give the results of a study of its structure.

The PMR spectrum of (I) is characterized by the following signals (ppm): 4.37 (1 H, triplet with ^3J 10 Hz each, lactone proton); 3.80 (1H, multiplet, >CH–OH); 4.11 (1 H, triplet, >CH–OH); 5.86 (1 H, singlet, tertiary OH); 6.19 and 6.51 ppm (1 H each, doublets, secondary OH groups). The signals of the protons of an exocyclic methylene group in the lactone ring at 6.19 and 6.48 ppm overlap with the doublets from the secondary OH groups. Three-proton singlets at 1.57 and 1.92 ppm (the first appreciably broadened) correspond to methyl groups attached to a carbon atom with a double bond and to a carbon atom with a tertiary OH group, respectively. The components of the signals of the gem-hydroxylic protons are appreciably broadened through coupling with the protons of the secondary hydroxy groups.

With the composition $C_{15}H_{20}O_5$ and the presence of the functional groups mentioned and two double bonds, ajanin can have only a guaiane structure, as is confirmed by the production of chamazulene by the dehydrogenation of (I) with selenium. The absence of the PMR spectrum of (I) of the signal of an olefinic proton and the triplet nature of the signal of the lactone proton show that the endocyclic double bond is located at C_1–C_{10}. Consequently, the second methyl group (1.92 ppm) and the tertiary hydroxyl are present at C_4. The triplet structure of the signal of the lactone proton shows that the lactone ring is at C_6–C_7, and the size of the spin–spin coupling constants (SSCC) with ^3J of 10 Hz each show its trans-linkage with the main skeleton.

The acetylation of (I) with acetic anhydride in pyridine gave a diacetyl derivative (II), which confirmed the presence of two secondary hydroxy groups in the molecule of (I). The IR spectrum of (II) showed the absorption bands of a hydroxy group (3480 cm^{-1}), of a lactone carbonyl (1778 cm^{-1}), of an ester group (1742 and 1245 cm^{-1}), and of double bonds (1665 and 1640 cm^{-1}). The retention of the absorption band of a hydroxy group in the IR spectrum of (II) also shows the presence of a tertiary hydroxy group in the molecule of (I).

In the PMR spectrum of (II), the signals of the exomethylene protons appeared in the form of two doublets at 5.64 and 6.65 ppm with J values of 3 Hz each; the signals of the gem-acylic protons appeared in the form of a doublet with broadened components at 5.27 ppm (^3J = 4 Hz, value of the second vicinal SSCC less than 1 Hz) and a multiplet at 4.48 ppm. The chemical shift of the signal of the lactone protons scarcely changed on acetylation. The signals of the protons of the methyl radicals of the acetyl groups appeared at 1.91 and 1.97 ppm. The signal of the methyl group present at C_4 was shifted in the upfield direction by 0.2 ppm, which indicates the presence of a hydroxy group on the neighboring C_3. This change in the chemical shifts of the exomethylene protons on the acetylation of (I) shows the position of one α-oriented OH group in the β-position to the exomethylene group, i.e., at C_8.

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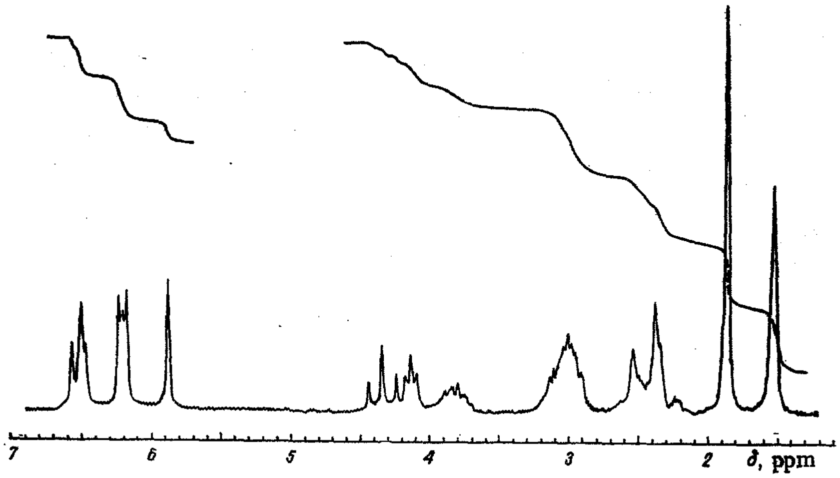
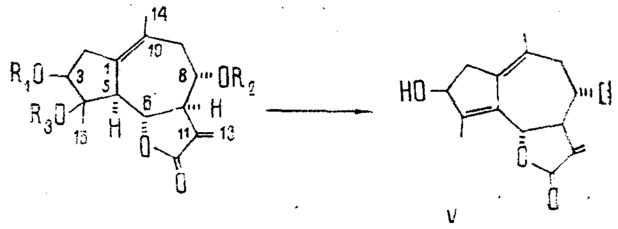


Fig. 1. PMR spectra of ajanin.

The acetylation of (I) with acetyl chloride gave the triacetyl derivative (IV), which also shows the presence in the ajanin molecule of three hydroxy groups. The absorption bands of an OH group were not detected in the IR spectrum of (IV). Ajanin was oxidized by periodic acid with difficulty, forming two products, with mp 179-181°C and 206-207°C. Their IR spectra showed additional absorption bands of a carbonyl group at 1712 and 1715 cm^{-1}, respectively. The oxidation of (I) with periodic acid showed the presence of an α-diol group in the molecule [3]. The difficulty of oxidation shows the trans orientation of the hydroxy groups, since in the case of cis orientation the reaction takes place in 30 min [4]. The treatment of (I) with a 10% solution of H_2SO_4 in ethanol gave the anhydro product (V).

In the PMR spectrum of (V), the signal of the protons of the methyl group with a tertiary hydroxyl in the geminal position had disappeared and the signal of the protons of a methyl group at a double bond had appeared (1.60 ppm). The signal of the lactone proton appeared in the form of a doublet with J = 10 Hz at 6.05 ppm, which shows the existence of a double bond at C_4-C_5. The same nature of the downfield shift of the lactone proton has been observed for artabsin [5].

According to the results obtained, ajanin has the structure of 3,4,8α-trihydroxy-5α, 6β,7α(H)-guaia-1(10),11(13)-dien-6,12-olide.



I. $R_1 = R_2 = R_3 = H$
II. $R_1 = R_2 = Ac$, $R_3 = H$
IV. $R_1 = R_2 = R_3 = Ac$.

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument (KBr tablets) and the PMR spectra on a JMN-4H-100 spectrometer in deuteropyridine solution with O-HMDS.

Ajanin Diacetate (II). A solution of 100 mg of ajanin in 1 ml of pyridine was treated with 1 ml of acetic anhydride. After 2 h, the reaction mixture was evaporated in vacuum. Separation on a column of silica gel followed by recrystallization from a mixture of benzene and acetone gave compound (II) with the composition $C_{19}H_{24}O_7$, mp 127-129°C.

Dehydrogenation of Ajanin (III). A mixture of 100 mg of ajanin and 100 mg of selenium was heated at 230-250°C for 5 min. The product obtained was identified as chamazulene.

Ajanin Triacetate (IV). A solution of 130 mg of ajanin in 7 ml of acetyl chloride was kept for 3 h, after which it was evaporated in vacuum. The residue was separated on a column of silica gel. Elution with benzene and with benzene–acetone (20:1) yielded compound (IV) with the composition $C_{21}H_{26}O_8$, mp 182-183°C (ether).

Oxidation of Ajanin. Solutions of 300 mg of ajanin in 3 ml of ethanol and 400 mg of periodic acid in 2 ml of water were mixed. After four days, the mixture was treated with ethyl acetate. Separation on a column yielded substances with mp 179-181°C and 206-207°C.

Anhydroajanin (V). A solution of 200 mg of ajanin in 10 ml of ethanol containing 0.5 ml of concentrated H_2SO_4 was kept at 70°C for 7 h. The excess of acid was neutralized with sodium bicarbonate to a weakly acid reaction, and the mixture was shaken with chloroform. Separation of the chloroform extract on a column of silica gel with a mixture of benzene and acetone (40:1) yielded a product with the composition $C_{15}H_{18}O_4$, mp 220-221°C (benzene).

SUMMARY

The new sesquiterpene lactone ajanin has been isolated from the epigeal part of the plant *Ajania fastigiata* (Winkl.) Poljak. It has been shown that it has the structure of 3,4,8α-trihydroxy-5α,6β,7α(H)-guaia-1(10),11(13)-dien-6,12-olide.

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STRUCTURE AND CONFIGURATION OF A NEW DITERPENOID LACTONE FROM *Lagochilus hirsutissimus*

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The epigeal part of the plant *Lagochilus hirsutissimus* has yielded a new diterpenoid lactone — lagohirsidin, $C_{22}H_{34}O_5$, mp 144-145°C, $[\alpha]_D^{22}$ − 17.5° (c 1; ethanol). Reduction with $LiAlH_4$ has yielded a diol $C_{22}H_{38}O_5$, mp 165-166°C $[\alpha]_D^{20}$ −1.2 (c 0.6; ethanol). Acid hydrolysis of the diol has led to the formation of lagochilin, $C_{20}H_{36}O_5$, mp 167-168°C, $[\alpha]_D^{20}$ −3.9° (c 1; ethanol). The synthesis of lagohirsidin from lagochilin has been effected.

The plant *Lagochilus hirsutissimus*, family Labiatae, contains lagochilin and tanning substances [1]. From the epigeal part of this plant we have isolated a new crystalline substance, $C_{22}H_{34}O_5$, with mp 144-145°C, $[\alpha]_D^{22}$ −17.53°, which we have called lagohirsidin (I).

Lagohirsidin possesses a neutral character and it is readily soluble in methanol, chloroform, acetone, and benzene, sparingly soluble in ether, carbon tetrachloride, and petroleum ether, and insoluble in water.

On being heated with aqueous alkali, (I) passed into solution and on subsequent acidification it was liberated in the unchanged state, which indicates that it belongs to the class of lactones. The presence of a lactone group was also shown by absorption at 1800 cm^{-1}

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