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STRUCTURE OF AJADIN

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We have continued the study of the new sesquiterpene lactone ajadin (I) [1].

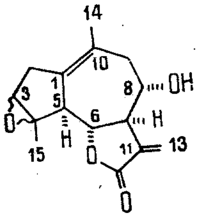
In the PMR spectrum of (I) (JNM-4H-100 MHz instrument, deuterochloroform, δ scale, internal standard HMDS) the following signals were observed: three-proton singlets at 1.58 ppm (methyl on a carbon atom attached to an oxygen atom) and 1.63 ppm (methyl on a double bond). A one-proton singlet at 3.32 ppm was due to a methine proton connected with an oxygen atom. The signal of a lactone proton appeared in the form of a triplet with its center at 3.58 ppm (J = 10 Hz). The signals of exomethylene protons were superposed on one another and appeared in the form of a doublet with its center at 6.1 ppm (J = 3 Hz). This behavior of the signals of the exomethylene protons is observed in cases where a hydroxy group is present in the β-position [2, 3].

With the composition $C_{15}H_{18}O_4$ and the presence of the functional groups described above, ajadin can have only a guaiane skeleton. The absence of the signal of an olefinic proton and the triplet nature of the lactone proton make it obvious that a double bond is present at C_1—C_{10}. The nature of the splitting of the signal of the lactone proton and the magnitude of the spin—spin coupling constant show that the lactone ring is attached at C_6—C_7 and has a trans linkage.

With acetic anhydride in pyridine, ajadin gave a monoacetyl derivative (II) with the composition $C_{17}H_{20}O_5$,mp 202-203°C (ether—hexane), $[\alpha]_D^{20}$ +112°(c 0.8; chloroform). Its IR spectrum showed absorption bands at (cm^{-1}) 1765 (γ-lactone ring), 1740 and 1245 (ester group), and 1668 and 1625 (C=C bond). The formation of a monoacetate showed the secondary nature of the hydroxy group.

Thus, the functions of all the oxygen atoms in the ajadin molecule have been determined. The absence from the IR spectrum of (II) of the absorption band of the hydroxy group and also the presence in the PMR spectrum of (I) of the signal of a methine proton shows that the fourth oxygen atom is present in an epoxide ring. The presence in the PMR spectrum of ajadin of the signal of the protons of a methyl group at 1.58 ppm determines the position of the epoxide group at C_3—C_4.

In the PMR spectrum of (II) three-proton singlets were observed at 1.63 ppm (CH_3—C—O) and 1.69 ppm (C=C—CH_3). The signal of the protons of the methyl group of an acetyl residue appeared at 2.07 ppm; and a broadened one-proton singlet at 3.34 ppm was due to a gem-epoxide proton. The lactone proton appeared in the form of a triplet at 3.66 ppm (J = 10 Hz). A one-proton sextet with its center at 4.71 ppm ($J_1 = J_2 = 10$, $J_3 = 3$ Hz) was due to a gem-acyl proton. The signals of the protons of an exomethylene group appeared in the form of two doublets



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with centers at 6.07 and 5.47 ppm (J = 3 Hz). The splitting of the signal of the exomethylene group into two doublets confirmed the presence of the acyl group at C_8.

The physicochemical and spectral characteristics of ajadin acetate correspond to those of arteglasin A [4]. Consequently ajadin has the structure of 8α-hydroxy-3,4-epoxy-5,7α(H)-guai-1(10),11(13)-dien-6,12-olide.

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TRITERPENE ACIDS OF RHODODENDRON PLANTS OF THE FLORA OF THE USSR

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Rhododendrons are rich in triterpenoids and the presence of ursolic acid in them is considered as a chemotaxonomic characteristic [1]. The application of the GLC method in the investigation of the triterpene composition of the acid fractions of extracts of rhododendrons permits the identification in these plants not only of ursolic acid but also of oleanolic acid [2].

In the present paper we give information obtained with the aid of GLC on the relative amounts of these acids in 16 species of Rhododendron growing in the USSR.

The plant raw material (leafy branches) was collected in the post-flowering phase.

For the quantitative determination of oleanolic and ursolic acids, they were converted into the methyl esters (I) and (II), respectively, by treating the acid fractions with a solution of diazomethane in diethyl ether.

The apparatus on which the GLC analysis was performed was the same as that employed previously [3]. As the stationary phases we used OV-17 and SE-30. The conditions of analysis (column temperature 280°C, rate of flow of carrier gas (argon) 40 ml/min) ensured a sufficient and approximately equal degree of separation of compounds (I) and (II) [3].

TABLE 1

Plant	Yield of acid fractions of chloroform extracts, % on the air-dry raw material	Ratio of the areas of the peaks of compounds (I) and (II)
Rh. ponticum L.	2,9	10:90
Rh. kotschyi Simk.	0,8	20:80
Rh. adamsii Rehd.	1,7	30:70
Rh. schlippenbachii Maxim.	1,4	30:70
Rh. camtschaticum Pall.	0,1	30:70
Rh. luteum Sweet.	1,2	30:70
Rh. ungernii Trautv.	0,8	30:70
Rh. tschonoskii Maxim.	1.5	30:70
Rh. caucasicum Pall.	1,0	30:70
Rh. parvifolium Adams.	0,5	30:70
Rh. fauriei Franch.	0,7	30:70
Rh. aureum Georgi.	0,9	30:70
Rh. ledebourii Pojark.	0,8	30:70
Rh. dahuricum L.	2,5	40:60
Ph. sichotense Pojark.	1,8	50:50
Rh. mucronulatum Turcz.	0,5	60:40

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