STRUCTURE OF AJAFININ

M. I. Yusupov, Sh. Z. Kasymov,
N. D. Abdullaev, and G. P. Sidyakin

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We give information on the determination of the structure of the sesquiterpene lactone ajafinin (I) isolated previously [1].

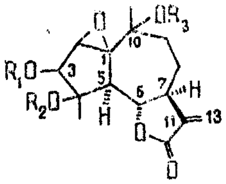
The PMR spectrum of (I) (C_5D_5N, 0 — HMDS, H_0 = 100 MHz) is characterized by the following signals: singlets at 1.22 and 1.76 ppm (3 H each, 2 CH_3—C—O); doublet at 2.55 ppm (1 H, ^3J = 11 Hz, H-5); broadened multiplet at 2.62 ppm (1 H, H-7); two doublets at 5.31 and 6.06 ppm (1 H each, J = 3 Hz, C═CH_2 at a lactone ring). The chemical shifts (CSs) of the latter show the absence of an OH group in the β position relative to an exomethylene group [2]. The CSs of the three one-proton signals at 6.19 ppm (s), 6.26 ppm (s), and 5.75 ppm (d, ^3J = 8 Hz, C$\underline{H}$—OH) depend on the temperature of the solution of the sample, which shows the presence of tertiary and secondary hydroxy groups. In view of the fact that there are two other oxygen atoms in the lactone ring, the sixth oxygen atom probably forms an epoxide ring. The signal of the lactone ring is located at 5.31 ppm in the form of a quartet and is overlapped by the doublet of an exomethylene group. There is a doublet at 3.99 ppm (1 H, ^3J = 3 Hz, proton at an epoxide ring), and a quartet at 4.13 ppm (1 H, ^3J = 3 and 8 Hz, gem-hydroxylic proton).

The assignment of the signals is in harmony with the results of the analysis of the PMR spectra of the mono-, di-, and triacetyl derivatives of ajafinin (II, III, and IV, respectively). These were obtained when (I) was treated with acetic anhydride in pyridine at room temperature for 3 and 120 h, and 70°C for 35 h, respectively. For example, in the PMR spectrum of (II) (C_5D_5N) there is a singlet at 2.00 ppm which is due to the protons of an acetyl group. The signal of the lactone proton appears in the form of a quartet at 5.38 ppm (^3J = 11 and 10 Hz), which shows the position of the lactone ring at C_6—C_7, while the SSCC shows a trans linkage with the main skeleton. Doublets at 4.12 and 4.91 ppm with ^3J = 3 Hz belong to the protons at an epoxide ring and a gem-acetyl group. Consequently, on passing from (I) to (II), under the influence of the acetyl group the CSs of the signals of the protons mentioned change by $\Delta\delta$ = 0.13 and $\Delta\delta$ = 0.78 ppm, respectively. Furthermore, a double-resonance experiment showed that the doublets at 4.12 and 4.91 ppm are coupled only with one another. This means that these two protons are present on neighboring carbon atoms, and the SSCC (^3J = 3 Hz) shows their position in a five-membered ring of the guaiane skeleton of (I).

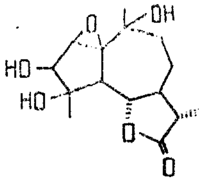
In the PMR spectra of the acetyl derivatives in $CDCl_3$, the signals of methyl groups appear at 1.06 and 1.37 ppm (II), 1.09 and 1.54 ppm (III), and 1.34 and 1.66 ppm (VI). As we see, on passing from (II) to (III) and (IV) a paramagnetic shift is experienced alternately by the signals of the two methyl groups, which indicates the location of the epoxide ring at C_1—C_2 and of the secondary OH group at C_3. This was also confirmed by a comparative study of the mass spectra of chrysartemin B, rupin A, bibsanin, and ajafinin [3]

When (I) was hydrogenated with sodium tetrahydroborate, a dihydro product (V) was formed with mp 213-214°C.

Thus, ajafinin has the structure of 3,4,10-trihydroxy-1,2-epoxy-5,7α(H)-6β(H)-guai-11(13)-en-6,12-olide.



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



V

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INTERACTION OF CEMBRENE WITH N-BROMOSUCCINIMIDE. CRYSTAL STRUCTURE OF THE CYCLIZATION PRODUCT

Yu. V. Gatilov, I. Yu. Bagryanskaya,
N. I. Yaroshenko, and V. A. Raldugin

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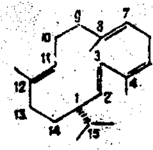
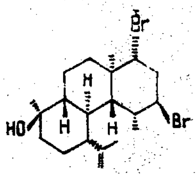
The addition of the elements of hypobromous acid (reaction with N-bromosuccinimide in aqueous acetone) to cembrene (I) takes place predominantly with the formation of three stereoisomeric 4,5-bromohydrins, as has been shown previously [1]. Among the minor products of the reaction we directed our attention to a product giving on TLC (spraying with sulfuric acid) a spot which after 15-20 min acquired a blue-violet coloration not characteristic for cembrene derivatives. When isolated by chromatography on silica gel, it had the form of colorless crystals with mp 123-124°C (from acetonitrile), $[\alpha]_D^{20}$ −52.2° (c 2.68; chloroform) and the empirical formula $C_{20}H_{32}OBr_2$ (elementary analysis and mass spectrometry), and its yield was about 1.5%. These crystals were used for x-ray structural analysis, which was carried out on a "Syntex $P2_1$" diffractometer (λ Mo K_α, ω scanning, $2\theta < 50°$, 4088 reflections with $I > 2\sigma$, absorption being taken into account on the basis of the experimental transmission curve, direct method). Crystallographic results: a = 9.900(2), b = 13.329(4), c = 31.320(8) Å, β = 96.56(2)°, z = 8 space group $P2_1$. The choice of observed configuration was made on the basis of the following results of refinement by the method of least squares (block-diagonal anisotropic approximation without H atoms and taking the anomalous scattering of the Br atoms into account) of two enantiomeric structures: R = 0.080, R_W = 0.061, and R = 0.082, R_W = 0.065, respectively.

The structure and absolute configuration of the product obtained are expressed by formula (II). All three carbon rings have the chair form with the equatorial positions of the isopropenyl and hydroxy groups, and also of the bromine atom at C_7. Both methyl groups and the bromine atom at C_5 have the axial configuration. The mean length of the $C-Br_{ax}$ bond for the four independent molecules is 2.02 Å, and for $C-Br_{eq}$ 1.98 Å.



I



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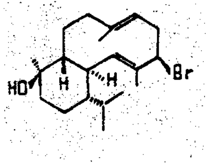

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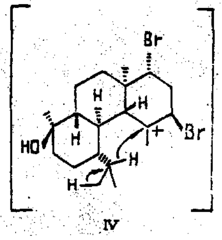

IV

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