

IR spectra were taken on a Specord-75 instrument in CCl_4 and PMR spectra on a Tesla BS-467 instrument (with a working frequency of 60 MHz; internal standard TMS; CCl_4 ; δ scale). Mass spectra were obtained on a MKh-1302 instrument. The analyses of all the compounds corresponded to the calculated figures.

LITERATURE CITED

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2. L. M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd edn., Pergamon, Oxford (1969), pp. 84, 231, and 289.

AJAFIN - A NEW GUAIANOLIDE FROM *Ajania*

fastigiata

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

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Continuing an investigation of the lactones of the epigeal part of *Ajania fastigiata* (c. Winkl), Poljak [1, 2], we have chromatographed a benzene extract of chloroform-extracted material [3] on a column of silica gel (type KSK). From the fractions eluted by benzene-acetone (10:1) we have isolated a lactone with mp 212-213°C (benzene-acetone). The lactone proved not to have been described in the literature and has been called ajafin (I). Ajafin has the composition $\text{C}_{16}\text{H}_{20}\text{O}_6$, M^+ 308, $[\alpha]_D^{22} + 34.7^\circ$ (c 3.57 methanol). The IR spectrum of (I) (tablets with KBr) contains absorption bands at (cm^{-1}) 3410-3440 (OH), 1740-1750 (C=O of a γ -lactone and of a cyclopentanone), and 1659 (C=C) [4]. The PMR spectra of (I) (deuteropyridine, 0 - HMDS) shows signals at the following δ values (ppm): 1.53 (3 H, br. s, $\text{CH}_3\text{-C}=\text{C}$); 1.72 (3 H, s, $\text{CH}_3\text{-C-O}$); 3.15 (3 H, s, $\text{CH}_3\text{-O-}$); 3.85 (2 H, m, H-2 and H-6); and 6.26 and 6.51 (1 H each, Tr, $=\text{CH}_2$). The H-2 signal appears in the form of a singlet and is superposed on the central component of the triplet from H-6.

The values of the chemical shifts of the protons of the exomethylene group show the presence of a hydroxy group in the β position, i.e., at C-8 [5]. The hydrogenation of (I) with NaBH_4 gave dihydroajafin (II), $\text{C}_{16}\text{H}_{22}\text{O}_6$, M^+ 310, mp 223-225°C. The IR spectra of (II) showed absorption bands at (cm^{-1}) 1770 (C=O, carbonyl of a γ -lactone), 1750 (C=O of a cyclopentanone), and 1670 (C=C). The IR spectra of (I) and (II), and also the PMR spectrum of (I) permit ajafin to be assigned to the guaianolides. The PMR spectrum of (II), unlike that of (I), shows the signal of a methyl group at a secondary carbon atom in the form of a doublet at 1.55 ppm (3 H, J = 7 Hz; $\text{CH}_2\text{-CH}_3$).

The hydrogenation of (II) in the presence of PtO_2 in ethanol gave tetrahydroajafin (III). The acetylation of (III) with acetic anhydride in pyridine led to diacetyltetrahydroajafin (IV), $\text{C}_{20}\text{H}_{26}\text{O}_8$, mp 145-146°C (hexane-acetone); M^+ 396, the IR spectrum of which exhibited absorption bands at (cm^{-1}) 1787 (C=O of a γ -lactone), 1740 (C=O of a cyclopentanone), and 1730 and 1242 (OCOCH_3). The PMR spectrum of (IV) contained signals at the following δ values (ppm): 1.28 (3 H, d, J = 7 Hz, $\text{C}_{11}\text{-CH}_3$); 1.40 (3 H, s, $\text{C}_4\text{-CH}_3$; 3 H, br. s, $\text{C}_{10}\text{-CH}_3$); two singlets at 1.88 and 1.93 (3 H, OCOCH_3 , each) 3.07 (3 H, s, OCH_3); 4.20 (1 H, tr, $\Sigma^3J = 20$ Hz, H-6); 4.85 (1 H, d, tr. $^3J = 9.5, 9.5, \text{ and } 4.2$ Hz, H-8); 5.27 (1 H, d, J = 4.0 Hz, H-2).

The doublet splitting of the signal at 5.27 ppm and its spin-spin coupling constant (J = 4.0 Hz) show that one of the acetyl groups in (IV) is present in the cyclopentane ring at C-2, and the carbonyl group is at C-3. The absence of the signal of an olefinic proton and the triplet nature of the lactone proton indicate the position of the endocyclic double bond at $\text{C}_1\text{-C}_{10}$.

According to the information given, ajafin has the structure of 2,8-dihydroxy-4-methoxy-3-oxo-5,7 α (H)-6,8 β (H)-guaia-1(10),11(13)-dien-6,12-olide (I).

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