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.

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AJAFIN - A NEW GUAIANOLIDE FROM Ajania fastigiata

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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 $C_{16}H_{20}O_6$, M^{\dagger} 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, $CH_3-C=C$); 1.72 (3 H, s, CH_3-C-O); 3.15 (3 H, s, CH_3-O-); 3.85 (2 H, m, H-2 and H-6); and 6.26 and 6.51 (1 H each, Tr, = 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 NaBH₄ gave dihydroajafin (II), C₁₆H₂₂O₆, 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; CH₂-CH₃).

The hydrogenation of (II) in the presence of PtO₂ in ethanol gave tetrahydroajafin (III). The acetylation of (III) with acetic anhydride in pyridine led to diacetyltetrahydroajafin (IV), $C_{20}H_{26}O_8$, mp 145-146°C (hexane-acetone); M^{\dagger} 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 (OCOCH₃). The PMR spectrum of (IV) contained signals at the following δ values (ppm): 1.28 (3 H, d, J=7 Hz, C_{11} -CH₃); 1.40 (3 H, s, C_{4} -CH₃; 3 H, br. s, C_{10} -CH₃); two singlets at 1.88 and 1.93 (3 H, OCOCH₃, each) 3.07 (3 H, s, OCH₃); 4.20 (1 H, tr, Σ ³J= 20 Hz, H-6); 4.85 (1 H, d. tr. ³J=9.5, 9.5, 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 C_1-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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ANHYDROAUSTRICIN FROM Artemisia leucodes

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By chromatographing on alumina the total lactones [1] obtained from the epigeal part of Artemisia leucodes Schrenk in the budding stage, we have isolated leucomisin, austricin, parishin C, parishin B, and a lactone with the composition $C_{15}H_{16}O_3$ (I), M^+ 244 mp 206-208°C (from ethanol), $[\alpha]_D^{20} + 180^\circ$ (c 0.43; methanol), R_f 0.43 (on Silufol, benzene-acetone (9:1)).

The IR spectrum of (I) shows absorption bands at (cm⁻¹) 1775 (carbonyl of a γ -lactone ring), 1680 (α , β -unsaturated cyclopentanone), and 1625 and 1600 (double bonds).

The UV spectrum shows the presence of three maxima at λ 245, 258, and 300 nm (log ϵ 4.29, 4.28, and 3.60), which are characteristic for a conjugated system.

In the PMR spectrum of (I) (taken in deuterochloroform on a JNM-4H-100/100 MHz instrument), a doublet at 1.27 ppm is the signal of the protons of a secondary methyl group attached to a lactone ring, singlets at 2.07 and 2.38 ppm are the signals of the protons of the two methyl groups at a double bond, and a doublet at 5.74 and a singlet at 5.99 ppm are those of two olefinic protons at C_6 and C_2 . A one-proton sextet with its center at 4.4 ppm ($I_1 = 5$, $I_2 = I_3 = 10$ Hz) belongs to a lactone proton. The nature of the splitting of the signal of the lactone proton shows the position of the lactone ring at C_7 - C_8 , and the spin-spin coupling constant shows its trans linkage.

The characteristic of (I) coincide with those of anhydroaustricin [2, 3]. The dehydration of austricin gave anhydroaustricin, which was shown to be identical with (I) by a mixed melting point test and a comparison of IR, UV, and PMR spectra.

This is the first time that the natural lactone anhydroaustricin has been detected in a plant.

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