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ATISIDERITOL, A NEW ent-ATIS-13-ENE FROM A SIDERITIS PUSILLA (Lag) Pau ssp (*)

by

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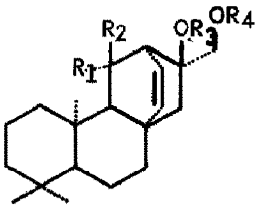
ABSTRACT: From Sideritis pusilla subspecia has been isolated an ent-11β,16α,17-trihydroxy-atis-13-ene diterpenoid, and the trivial name atisideritol is proposed for it.

At the begining of this study on Sideritis pusilla only five non-nitrogen containing diterpenoids with the ent-atis-13-ene skeleton were known (1)(2)(3). All of these, two of whic also occur naturally as acetates (4), have been isolated from species belonging to the genus Sideritis (Labiataes), which because of numerous species and subspecies can present some problems of classification (5). In a previous study (6) we have found in this plant five previously identified diterpenoids with the ent-beyer-15-ene and ent-atis-13-ene skeletons as well as three new natural acetates (two ent-beyer-15-enes and one ent-atis-13-ene). We now report a minor product of this plar for which we propose the trivial name atisideritol (I).

The product I is a white solid, m.p. 155-7º C and $^{20}_{D}$ -15.4º(c 1, Cl_3CH). Its estimated molecular formulae being $C_{20}H_{32}O_3$ (M^+ 320). The IR spectrum shows an -OH band (3400 cm^{-1}) as well as a C=C band (700 cm^{-1}), and the characteristic atis-13-ene band at 750 cm^{-1}. In the ^1H-NMR spectrum of I, a quasi collapsed AB system could be demonstrated at 3.27 ppm (2H, J= 10 Hz) whi was asigned to the $-CH_2-O-$ group. At about 6.20 ppm the AB part of an ABX system, typical of a atis 13-ene skeleton, could also be seen. The X part of this system is localized at 2.79 ppm, as a complex signal which was confirmed by double resonance experiments. Irradiation of part X yieldedan AB system at 6.20 ppm (2H, dd, J= 9 Hz). Irradiation at 6.20 ppm yielded a broad singlet at 2.79 ppm. A signal at 2.22 ppm could also be observed (1H, bd, J= 11 Hz) as well as a methyl singlet at 1.00 ppm (3H) and 0.98 ppm (6H). Product I yields an acetonide (II) by reaction with $(CH_3)_2CO$/anhydrous $CuSO_4$. A reaction typical of the 16,17-dihydroxy group of Sideritis ent-atis-13-enes.

Considering the other hydroxyl group present en I. The geminal proton produces a broad doublet at 4.77 (1H, bd, J= 8 Hz). This signal is coupled with the $H-C_{12}$ band, and is confirmed because irradiation at 2.79 ppm changed the broad doublet at 4.77 ppm into a double doublet (J_1= 8 Hz, J_2= 2 Hz). The irradiation at 4.77 ppm alters the signal of $H-C_{12}$, transforming it into a sharp doublet (J= 6 Hz). These experiments allow us to assign the other hydroxyl group at posi-



	R_1	R_2	R_3	R_4
I	OH	H	H	H
II	OH	H	CMe_2	
III	O		CMe_2	
IV	H	H	CMe_2	

tion 11, configuration ent-11β. This configuration, and not ent-11α, is in accordance with the J lues and dihedral angles. In product II the geminal proton at C-11 is a well resolved double doub at 4.58 ppm (1H, dd, J_1= 8 Hz, J_2= 4 Hz), and the AB system at C-17 is now a double doublet at 3. ppm (1H,d, J= 9 Hz) and 3.30 ppm (1H, d, J= 9 Hz). The Jones oxidation of II yields the ketone (I In this product, the allylic H-12 group is now observed as a doublet at 3.10 ppm (1H, d, J= 8 Hz), which was confirmed by double resonance experiments. The methyl signals of III are observed at 0. ppm, 0.76 ppm and 0.68 ppm (3H, each). The ^{13}C-NMR spectra of I and II confirm the proposed struc re. The assignment are based on the spectra of several 16,17-diisoprpilidendioxy derivatives of e atis-13-enes (7), this being the first time that a ^{13}C-NMR spectrum of 11-hydroxy-atis-13-ene has been reported. Since the product IV as been isolated only in very small quantities, its spectrum was calculated from the ent-atis-13-enes with the functional groups in position 1 or 7. It can be seen that there is a good agreement with the proposed structure. The assignments are made with th help of "off resonance" spectra of I and II.

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
I^a	41.3	18.4	41.9	33.1	55.9	19.7	36.7	40.3	60.2	38.9
II^a	41.4	18.4	42.0	33.1	56.0	19.7	36.8	40.2	60.3	38.9
IV^a	39.3	18.7	42.2	33.3	56.1	20.3	37.4	39.1	53.6	37.4
	C-11	**C-12**	**C-13**	**C-14**	**C-15**	**C-16**	**C-17**	**C-18**	**C-19**	**C-20**
I^a	71.4	50.0	126.7	143.8	51.2	82.8	75.0	34.1	22.2	17.9
II^a	71.5	48.0	127.3	142.1	49.2	75.6	69.3	34.1	22.2	17.9
IV^a	22.6	40.0	---	---	50.0	83.9	70-80	33.8	22.0	15.1

a) The spectra are performed in $CDCl_3$ as solvent and TMS as internal standard in a Varian XLFT-1C

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