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# FUSICORRUGATOL FROM THE VENEZUELAN LIVERWORT *PLAGIOCHILA CORRUGATA*

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Fusicorrugatol, a new fusicoccane-type diterpene alcohol, has been isolated from the Venezuelan liverwort *Plagiochila corrugata* and its structure determined on the basis of spectroscopic evidence and X-ray crystallography.

**KEYWORDS** Fusicorrugatol; fusicoccane-type diterpene; liverwort; *Plagiochila corrugata*; X-ray crystallography

We have recently reported interesting chemical constituents from the liverworts *Frullanoides*,[1] *Porella*,[2] and *Marchantia*[3] species collected in South America, and they are interesting from the chemical point of view.[4] *Plagiochila* species have also been extensively studied, and many fusicoccane- and sacculatane-type diterpenoids have been isolated.[5,6] Recently we have reported isolation and structures of fusicogigantones A (**2**), B (**3**) and fusicogigantepoxide (**6**) from *Pleurozia gigantea*.[7] Fusicogigantepoxide has quite recently been isolated from Panamanian *Bryopteris firicina*, and its structure was fully established by X-ray analysis.[8] We have now investigated the chemical constituents of the Venezuelan liverwort *Plagiochila corrugata* and found a diterpenoid, named fusicorrugatol (**1**), which is closely related to the above-mentioned diterpenoids. Due to difficulties in determination of stereochemistries of the epoxides of fusicoccane diterpenoids by use of NMR spectroscopy alone, the relative stereostructure of **1** has been established by X-ray analysis.

The ether extracts (759 mg) of the dried *P. corrugata* (27 g) were subjected to Sephadex LH-20 and silica gel column chromatography to afford fusicorrugatol (**1**) (8.8 mg).[9] The molecular formula of **1** was determined as $C_{20}H_{30}O_3$ by HRMS. The $^{13}C$ NMR and DEPT spectra showed the presence of five methyls, three methylenes, eight methines (including two $sp^2$ carbons) and four quaternary carbons. The $^{13}C$ NMR spectrum also showed five carbons attached to oxygen functions ($\delta$ 75.0, 74.7, 67.7, 66.8, 59.5). Since the IR spectrum indicated the presence of a hydroxyl group (3500 $cm^{-1}$), at least one of the three oxygen atoms in the formula was explained as a hydroxyl group. From the HMBC spectrum (Fig.1), the fusicoccane skeleton was demonstrated for compound **1**. Therefore, the other two oxygens must be assigned as epoxides attached to the C-2,3 and C-5,6 positions, which is supported by six degrees of unsaturation for this molecule. The stereochemistries were deduced by the PSNOESY spectrum (Fig.2). Since correlations between H-7 and H-10, H-10 and H-14, and H-13 and H-14 were observed, C-10 and C-11 must be *trans*, and the stereochemistries were determined as depicted in the formula, except for those of epoxides. Fortunately good crystals

were made from EtOAc solution, and X-ray crystallographic analysis has been carried out. Figure 3 displays an ORTEP drawing, showing *cis* relationship of two epoxides, both being α-oriented.[10]

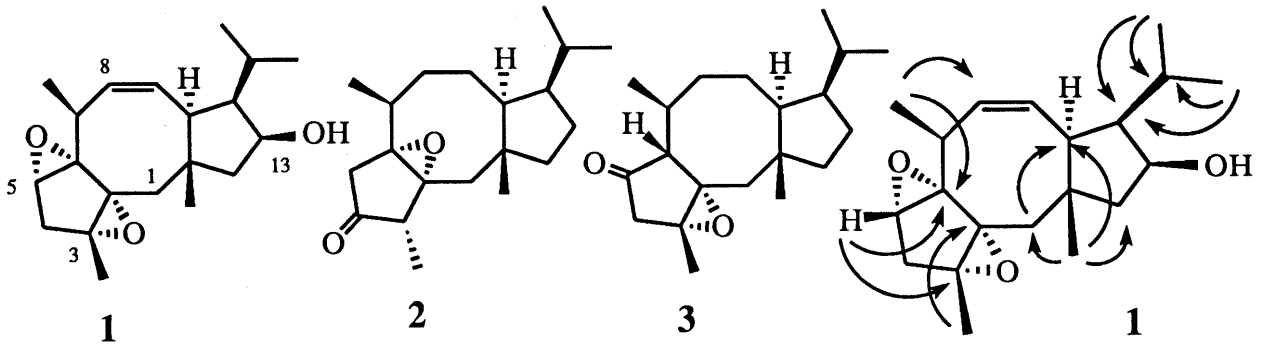


Fig.1. HMBC Correlations for **1**

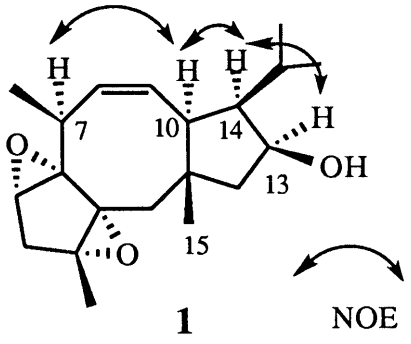


Fig.2. NOE Correlations for **1**

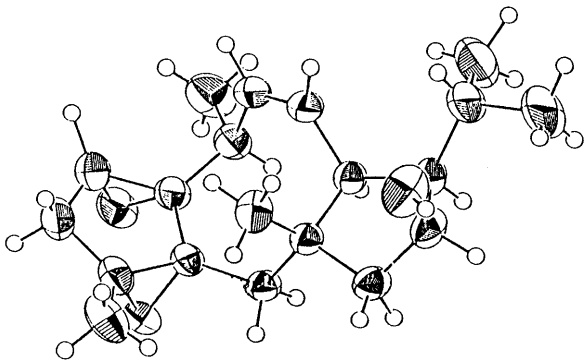

Fig.3. ORTEP Drawing of **1**

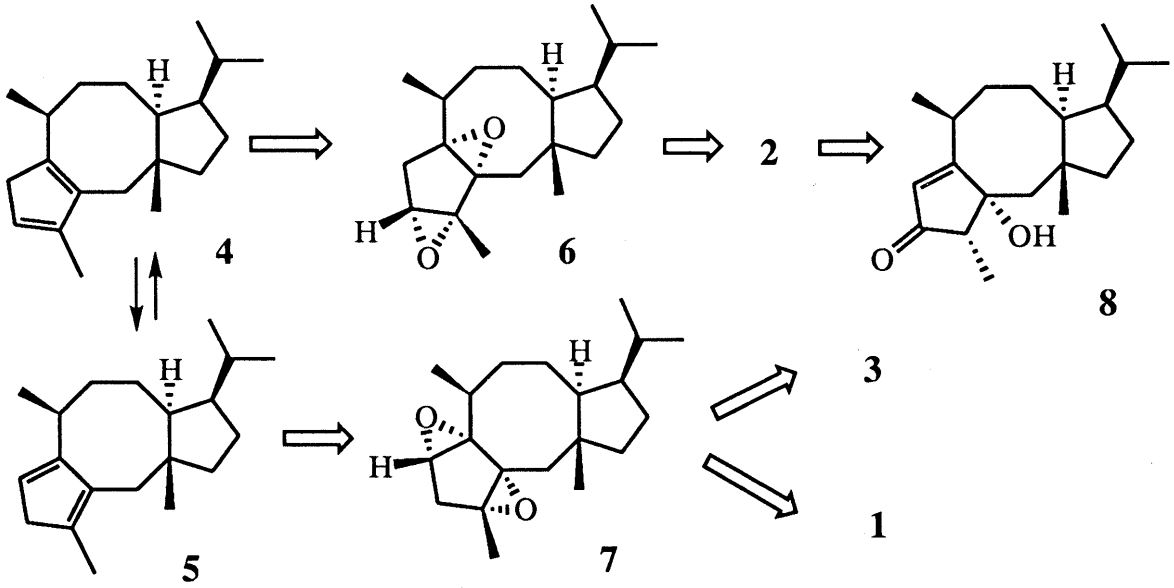


Fig.4. Plausible Biogenetic Pathways for **1**, **2**, **3**, and **8**

This class of compounds, *e.g.* **6** and **7**, are presumably derived from dienes, **4** and **5**, by oxidation *via* endoperoxides through rearrangement. Quite recently Takeshita and Kato synthesized both fusicogigantones A (**2**) and B (**3**) by oxidation of the diene mixture.[11] Therefore the structure of **3** has now fully been established to have the α-oriented epoxide, as depicted in the formula.[7] Anadensin (**8**)[12] may be derived from **2** as shown in Fig.4.

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9) $[\alpha]_D$ -10.9 ° (*c* 0.8, $CHCl_3$); IR (KBr) 3500, 1460, 1400, 1140, 1100, 1040, 940, 800, 760 $cm^{-1}$; MS (EI) *m/z* : 318 ($M^+$), 275, 257, 243, 220, 193, 175, 149 (base), 137, 121, 95, 81, 55, 43; HRMS (EI) Obs. 318.2193. $C_{20}H_{30}O_3$ requires 318.2194; $\delta_H$ ($CDCl_3$) 5.77 (1H, t, *J* = 10), 5.21 (1H, t, *J* = 10), 4.32 (1H, t, *J* = 4.0), 3.44 (1H, d, *J* = 2.9), 3.37 (1H, m), 3.19 (1H, t, *J* = 11), 2.31 (1H, d, *J* = 15), 2.08 (1H, d, *J* = 16), 1.9 (2H, m), 1.7 (2H, m), 1.67 (1H, d, *J* = 15), 1.56 (1H, dd, *J* = 16, 2.9), 1.27 (3H, s), 1.07 (3H, s), 1.05 (2H, d, *J* = 6.1), 0.94 (3H, d, *J* = 6.1), 0.82 (3H, d, *J* = 6.8); $\delta_C$ ($CDCl_3$) 45.1 (C-1), 67.7 (C-2), 75.0 (C-3), 32.3 (C-4), 59.5 (C-5), 66.8 (C-6), 29.4, (C-7) 30.4 (C-8), 31.5 (C-9), 48.7 (C-10), 46.6 (C-11), 50.7 (C-12), 74.7 (C-13), 55.5 (C-14), 24.1 (C-15), 18.5 (C-16), 16.1 (C-17), 25.4 (C-18), 22.4 (C-19 or 20), 22.7 (C-20 or 19).
10) Crystal data for **1**; monoclinic, *a*=23.204(7), *b*=5.809(4), *c*=15.047(4) Å, β=104.85(2)°, space group C2, μ(Cu-Kα)=1.54178. The structure was solved by using direct methods, and the refinement was carried out by using the full-matrix least squares to R=0.0457, Rw=0.0464.
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