

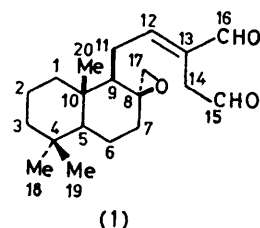
The Structure of a Labdane Dialdehyde from *Afromomum daniellii* (Zingiberaceae)

By Samuel F. Kimbu, Thomas K. Njimi, and B. Lucas Sondengam, Department of Chemistry, University of Yaounde, Cameroon

John A. Akinniyi and Joseph D. Connolly,* Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

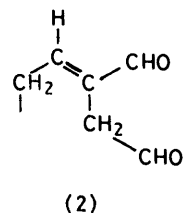
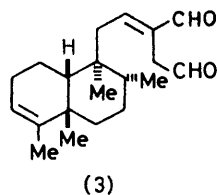
A diterpenoid dialdehyde isolated from the seeds of *Afromomum daniellii* has been shown to be (*E*)-8 β ,17-epoxy-labd-12-ene-15,16-dial (1) by its spectroscopic properties and by correlation with *cis*-12-norambreinolide (6).

THE plant *Afromomum daniellii* (Zingiberaceae) grows in many regions of Cameroon. It is known locally as 'Achoh' and the seeds produce a hot taste on chewing. The roots are used as a purgative. Extraction of the seeds with hexane afforded a diterpenoid dialdehyde $C_{20}H_{30}O_3$ which has been assigned the structure (*E*)-8 β ,17-epoxylabd-12-ene-15,16-dial (1).



RESULTS AND DISCUSSION

The 1H n.m.r. spectrum of (1) had signals for three tertiary methyls [δ 0.9, 0.87, and 0.84], an epoxide methylene [δ 2.27 and 2.42 (AB quartet, J 3.5 Hz)], an allylic methylene [δ 3.38 (br s)], a saturated aldehyde [δ 9.58 (t, J 1 Hz)] and an $\alpha\beta$ -unsaturated aldehyde [δ 9.36 (s); 6.64 (br t, J 7 Hz, vinyl H-12)]. The i.r. [ν_{max} . 2712, 1731, 1690, and 1640 cm^{-1}] and u.v. [λ_{max} . 234 nm (ϵ 14 400)] spectra confirmed the presence of two aldehyde groups. The above data account for the functionality of (1) which is, therefore, bicarbocyclic. The relationship between the two aldehyde groups was established by double-resonance experiments. Irradiation of the allylic methylene resonance at δ 3.38 caused the collapse of the saturated aldehyde triplet at δ 9.58 to a singlet and simultaneous sharpening of the vinyl proton triplet at δ 6.64. This suggested the partial structure (2). Irradiation at δ 6.64, the resonance



frequency of the vinyl proton, resulted in a 20% increase in the integrated intensity of the unsaturated aldehyde proton and thus established the (*E*)-configuration of the

double bond. The partial structure (2) corresponds to the side chain of linaridial (3), a *cis*-clerodane from *Linaria japonica*,¹ and there is good agreement between the above spectroscopic data and those reported for linaridial. The remaining features of the dialdehyde were readily accommodated in a labdane skeleton, leading to structure (1). The ^{13}C resonances of rings A and B of (1) (see Table) were similar to published data.²

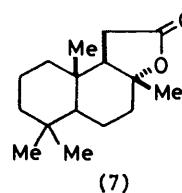
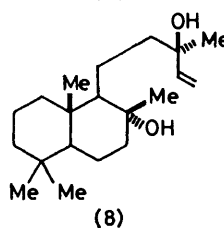
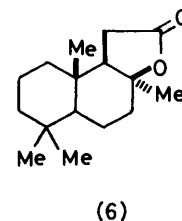
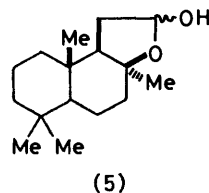
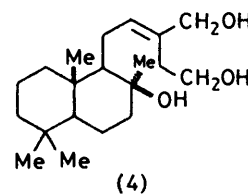
Carbon-13 n.m.r. spectrum of the dialdehyde (1)

Carbon	δ	Carbon	δ	Carbon	δ
1	39.6	8	57.6	15	198.0
2	18.4	9	55.2	16	194.0
3	42.0	10	40.0	17	48.8
4	33.6	11	22.4	18	33.6
5	52.8	12	161.2	19	21.6
6	20.0	13	136.0	20	14.8
7	39.6	14	36.0		

Assignments are based on chemical-shift rules, multiplicity in off-resonance spectra, and comparison with published data.²

Confirmation of the structure and absolute stereochemistry was obtained as follows.

Reduction of (1) with $LiAlH_4$ afforded the triol (4) whose 1H n.m.r. spectrum fully supported its structure (see Experimental section). Reaction of (4) with OsO_4 and periodate cleavage of the resulting pentaol



yielded the non-crystalline hemiacetal (5) [δ 4.95 (t, J 5 Hz, H-12)]. This was converted by Jones oxidation into *cis*-12-norambreinolide (6) ($[\alpha]_D -28^\circ$). *trans*-12-Norambreinolide (7)⁴ was obtained by chromium trioxide oxidation of sclareol (8)⁵ and was epimerised under acidic conditions³ to *cis*-12-norambreinolide (6) ($[\alpha] -33^\circ$), identical in all respects with the degradation product of (1).

EXPERIMENTAL

N.m.r. spectra were obtained on a Varian XL-100 instrument with VFT-100 accessory or a Perkin-Elmer R32 spectrometer, using solutions in deuteriochloroform with tetramethylsilane as internal standard. I.r. spectra were run in carbon tetrachloride solution on a Perkin-Elmer 58 and u.v. spectra in ethanol on a Pye-Unicam SP 800B. Mass spectra were obtained on an AEI MS12 single focusing instrument. Specific rotations refer to chloroform solutions and were run on a PE 141 polarimeter.

Extraction.—Dried seeds (1 kg) of *A. daniellii*, collected from Evodoula in the Central South Province of Cameroon in December, were powdered and Soxhlet-extracted with hexane for 24 h. The extract was concentrated and set aside for several days. The solid which was deposited was filtered off through a column of alumina in hexane to give (1) (20 g). Recrystallisation from chloroform–light petroleum afforded the pure *dialdehyde* (1), m.p. 90–92 °C; $[\alpha]_D +28.1^\circ$ (c 1.41) (Found: C, 73.65; H, 9.65. $C_{20}H_{30}O_3 \cdot 0.5H_2O$ requires C, 73.4; H, 9.55%).

Reduction of (1).—The dialdehyde (1) (300 mg) in dry ether (20 ml) was treated with excess of $LiAlH_4$ (500 mg) and the solution refluxed for 4 h. The excess of $LiAlH_4$ was destroyed by dropwise addition of saturated brine and the inorganic residue removed by filtration. Evaporation of the ether afforded the *triol* (4) which was crystallised from light petroleum as needles, m.p. 98–99 °C [δ 0.83, 0.86, 0.96, 1.09 (C-Me), 2.44 (t, J 6 Hz, H₂-14), 3.73 (t, J 6 Hz, CH₂OH), 4.0 (br s, CH₂OH), and 5.48 (t, J 6 Hz, H-12)]. (Found: C, 74.3; H, 11.10. $C_{20}H_{36}O_3$ requires C, 74.0; H, 11.2%).

Hemiacetal (5).—The triol (4) (100 mg) was dissolved in

ether (40 ml) containing a few drops of pyridine, and osmium tetroxide (100 mg) was added. The reaction mixture was set aside in the dark for 24 h, stirred with saturated aqueous sodium metabisulphite solution, and extracted with ethyl acetate. The product, a single polar spot on analytical t.l.c., was stirred overnight in aqueous methanol (20 ml) with excess of $NaIO_4$. Addition of water and extraction with ethyl acetate afforded the *hemiacetal* (5) as a gum; m/e 234; δ 0.86 (6 H), 0.88, 1.27 (C-Me), and 4.95 (t, J 5 Hz, H-12).

Lactone (6).—The hemiacetal (5) (20 mg) in acetone was oxidised with Jones reagent. The lactone (6) was recrystallised from light petroleum as needles, m.p. 94–96 °C; $[\alpha]_D -28^\circ$ (c 0.61); ν_{max} (CCl₄) 1780 cm^{-1} ; δ 0.87, 0.91 (6 H), and 1.32 (C-Me).

Oxidation of Sclareol (8).—A stirred solution of sclareol (8) (2 g) in glacial acetic acid (20 ml) was treated with CrO_3 (4.4 g) in 10% aqueous acetic acid (20 ml), during 30 min, and stirring was continued for 24 h. Extraction with ether and removal of acidic products with aqueous Na_2CO_3 afforded *trans*-12-norambreinolide (7), m.p. 123–125 °C (from light petroleum) (lit.⁴ 123–125 °C); ν_{max} (CCl₄) 1778 cm^{-1} ; δ 0.85, 0.88, 0.92, and 1.33 (C-Me).

***cis*-12-Norambreinolide (6).**—The *trans*-lactone (7) (51 mg) was heated at 70 °C in glacial acetic acid (2 ml) containing 50% H_2SO_4 (0.2 ml) for 6 h and set aside overnight. Addition of water and extraction with ether gave *cis*-12-norambreinolide (6) which crystallised from light petroleum as needles, m.p. 93–94.5 °C (lit.³ 95 °C); $[\alpha] -33^\circ$ (c 0.57), identical in all respects with the degradation product of the natural dialdehyde (1).

[8/1177 Received, 26th June, 1978]

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