

A NEW LABDANE DITERPENOID FROM THE SEEDS OF
AFRAMOMUM DANIELLII

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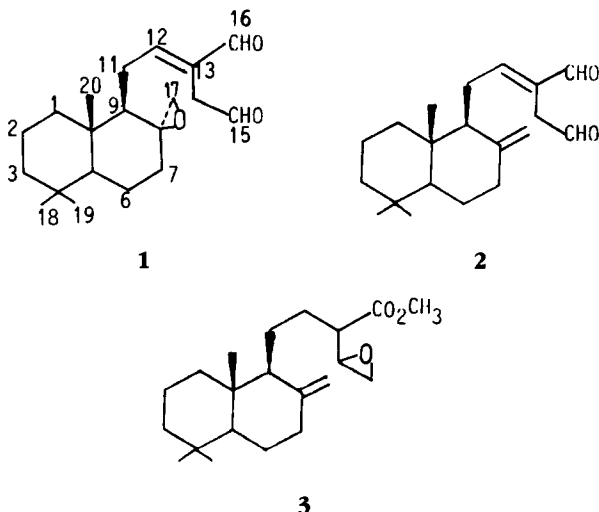
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The plant *Aframomum daniellii* (Hook. f.) K. Schum (Zingiberaceae) is a perennial herb that grows in many regions of Cameroon. It is known locally as "Achoh," and the seeds produce a hot taste on chewing. As with other members of the family that have been found useful, the roots are used as a purgative and the seeds are believed to be eaten by snakes to facilitate sloughing. The major diterpenoid component, 8 β ,17-epoxy-12*E*-labdene-15,16-dial [1], whose structure and absolute configuration were previously reported by us (1) exhibits potent antifungal properties (2).

Analytical tlc of the oily nonpolar fraction obtained by column chromatography of the crude extract revealed the presence of two minor uv-active compounds. These were isolated as amorph-

ous gums by preparative tlc and have been shown to be the diterpenoids 8(17),12*E*-labdadiene-15,16-dial [2] and methyl 14 ξ ,15-epoxy 8(17),12*E*-labdadiene-16-oate [3] on the basis of the following evidence.

The more polar component, 8(17),12*E*-labdadiene-15,16-dial [2], was identified from its spectroscopic properties, which were very similar to those reported in the literature (3). The less polar component, methyl 14 ξ ,15-epoxy 8(17),12*E*-labdadiene-16-oate [3], was present in a minor amount. In addition to the presence of tertiary methyl groups (δ_{H} 0.71, 0.80, 0.85) and an exomethylene moiety [δ_{H} 4.84 and 4.47 (both br s)], it exhibited resonances for a vinyl proton [δ_{H} 6.87 (t, $J=7$ Hz)] attached to the β -position of an α,β -unsaturated methoxy-carbonyl moiety (δ_{H}



3.71) and a monosubstituted epoxide [3.65 (br m), 2.98 (dd, $J=4, 6$ Hz), 2.78 (dd, $J=3, 6$ Hz)] which can only be situated at C-14 of a normal labdane nucleus. Irradiation of the broad multiplet at δ 3.65 caused collapse of the C-15 methylene protons to an AB quartet ($J=6$ Hz). The above spectroscopic data led to structure **3** for the new methyl ester. The configuration of the 12,13 double bond was assumed to be the same as in compounds **1** and **2**. Confirmation of the structure proposed was obtained by comparison of the ^{13}C -nmr chemical shifts of **3** with those of **1** and **2** (Table 1).

TABLE 1. Carbon-13 Chemical Shifts of the Labdanes **1**, **2**, and **3**

Carbon	Compound		
	1	2	3
1	39.6	39.6	39.2
2	18.4	19.3	19.4
3	42.0	42.0	42.1
4	33.6	33.6	33.6
5	52.8	55.4	55.5
6	20.0	24.1	24.2
7	39.6	39.3	38.0
8	57.6	148.0	148.4
9	55.2	56.5	56.9
10	40.0	40.0	39.7
11	22.4	24.7	23.6
12	161.2	159.7	149.9
13	136.0	135.0	127.3
14	36.0	37.9	48.8
15	198.0	197.0	47.7
16	194.0	193.3	166.6
17	48.8	107.9	107.7
18	33.6	33.6	33.6
19	21.6	21.7	21.8
20	14.8	14.4	14.4
OCH ₃	—	—	51.7

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined on a Kofler hot plate and are uncorrected. Spectra were recorded with the following instruments and conditions; uv, Pye Unicam SP 800 B spectrophotometer in

EtOH solution; ir, Perkin-Elmer 580 instrument in CCl_4 solutions; ms, MS 902 S instrument (high resolution); ^1H nmr, Perkin-Elmer R32 (90 MHz) in CDCl_3 ; ^{13}C nmr Varian XL 100 with a VFT-100 accessory; optical activity was determined on the AA-100 polarimeter in CHCl_3 solution.

PLANT MATERIAL.—The seeds of *A. daniellii* were collected at Bertoua in the East Province of Cameroon in January 1983, and identified by Mr. J. Asonganyi of the National Herbarium, Yaounde. A voucher specimen of this plant has been deposited in the National Herbarium, Yaounde.

EXTRACTION AND CHROMATOGRAPHY.—Dried seeds (1 kg) were powdered and extracted with hexane in a Soxhlet apparatus for 24 h. The hexane extract was concentrated and the residue purified on a column of silica gel (Merck Kieselgel 0.063-0.200 mg). Elution with hexane-EtOAc (9:1) mixture afforded an oil (1 g). Further purification of this oil by preparative tlc using silica gel (Merck Kieselgel GF 254 with 1% EtOAc in hexane) gave two oily compounds (Rf 0.6, 0.7).

8(17),12E-Labdadiene-15,16-dial.—Compound **2** (200 mg) was identified by comparison of the uv, ir, ms, ^1H - and ^{13}C -nmr spectroscopic data with literature values (3).

Methyl 14 ξ ,15-epoxy-8(17),12E-labdadiene-16-ate.—Compound **3** (60 mg), $[\alpha]^{21\text{D}} + 10$ (c 0.6 CHCl_3); ms, m/z (%) 332 (M^+ , 8), 303 (19), 300 (47), 285 (21), 137 (100) and 123 (40); ir (CCl_4) 1715, 1725, 1643, 893 cm^{-1} ; uv λ_{max} (EtOH) 225 nm (ϵ 8,000); ^1H nmr 4.84 and 4.47 (both br s, H_2 -17), 6.87 (t, $J=7$ Hz, H-12), 3.71 (s, CO_2Me), 3.65 (br m, H-14), 2.98 (dd, $J=4, 6$ Hz) and 2.78 (dd, $J=3, 6$ Hz, H_2 -15), 0.71, 0.80, 0.85 (3 \times CCH₃); ^{13}C nmr (Table 1).

8 β ,17-Epoxy-12E-labdadiene-15,16-dial [**1**].—Further column chromatography of the residue gave the labdane dialdehyde **1** (20 g) which was recrystallized from CHCl_3 /light petroleum, mp 90-92° (1).

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Received 1 November 1985