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Diterpenoid Derivatives of Kenyan *Croton sylvaticus*Beth Ndunda^{a,b}, Moses K. Langat^b, Jacob O. Midiwo^a and Leonidah K. Omosa^a^aDepartment of Chemistry, School of Physical Sciences, University of Nairobi, PO Box 30197-00100, Nairobi, Kenya^bDepartment of Chemistry, FEPS, University of Surrey, Guildford, Surrey, GU2 7XH, United Kingdom

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Kenyan *Croton sylvaticus* Hochst. ex Krauss gave four clerodane diterpenoids, the new *ent*-3,13*E*-clerodadiene-15-formate (**1**), the known 15-acetoxy-*ent*-3,13*E*-clerodadiene (**2**), *ent*-3,13*E*-clerodadien-15-ol (**3**) and hardwickiic acid (**4**), two known halimane diterpenoids, penduliflaworosin (**5**) and crotohalimaneic acid (**6**) and one labdane diterpenoid, labda-13*E*-ene-8 α ,15-diol (**7**). The compounds, when tested for their anti-microbial activities against *Bacillus subtilis*, *Xanthomonas campestris* and *Candida albicans*, were found to be inactive.

Keywords: *Croton sylvaticus*, Euphorbiaceae, Clerodane, *ent*-3,13*E*-Clerodadiene-15-formate, Anti-microbial activity.

Croton sylvaticus Hochst. ex Krauss (Euphorbiaceae) is a tree growing to 3.5-24 m tall with its bark smelling of black pepper, found at an altitude of 350-1750 m and spread from the northern to the southern parts of Africa [1a, 1b]. In Kenya, it is found in the coastal regions and is used ethno-medicinally as a wash for body swellings caused by kwashiorkor, as a purgative (leaves), as an oral remedy for tuberculosis (stem bark), and as poultices for swellings (roots) [1a]. It is also used in other parts of Africa to treat gall-sickness in cattle, abdominal pains, indigestion, pleurisy, rheumatism, chest pains, inflammation and malaria, and as a fish poison [1a-1e]. *C. sylvaticus* is reported to contain toxalbumin crotin, a glycoprotein that is attached to crotin, a dihydrochalcone [1e], caryophyllene oxide, α -humulen-1,2-epoxide, penduliflaworosin, hardwickic acid, lupeol, sitosterol, stigmasterol and julocrotine [2a].

Eight compounds were isolated from the roots of *C. sylvaticus* including the new 15-formate-*ent*-3,13*E*-clerodadiene (**1**) (Fig. 1), and the known 15-acetoxy-*ent*-3,13*E*-clerodadiene (**2**) [2b], *ent*-3,13*E*-clerodadien-15-ol, commonly named kolavenol (**3**) [2b], hardwickiic acid (**4**) [2a-2c], penduliflaworosin (**5**) [2a-2c], crotohalimaneic acid (**6**) [2d], labda-13*E*-ene-8 α ,15-diol (**7**) [2e] and stigmasterol. The structures of the known compounds were determined using 2D NMR spectroscopy and confirmed by comparison with literature data, as referenced below. Compound **1** was identified as *ent*-3,13*E*-clerodadiene-15-formate whose spectroscopic data were similar to those of kolavenol (**3**), previously reported from *Solidago canadensis* [2b], except for the presence of a formyl group in **1**. The MS for **1** indicated a molecular formula of C₂₁H₃₄O₂ supporting a double bond equivalence of 5.

The ¹³C NMR spectrum for **1** displayed twenty-one carbon resonances including those of a carbonyl at δ 161.3, four double bonds at δ 144.5, 127.0, 120.5 and 117.1, an oxymethylene at δ 60.9 and five methyls at δ 20.2, 18.9, 18.2, 16.8 and 16.0. The ¹H NMR spectrum showed a formate proton resonance at δ 8.07 (s), two double bond proton resonances at δ 5.35 (t, *J*=7.1 Hz) and 5.19 (br s), an oxymethylene proton resonance at δ 4.69 (m), a doublet methyl proton resonance at δ 0.87 (d, *J* = 6.2 Hz), two allylic methyl group proton resonances at δ 1.72 (s) and 1.57 (s) and two singlet methyl proton resonances at δ 0.98 (s) and 1.57 (s). The

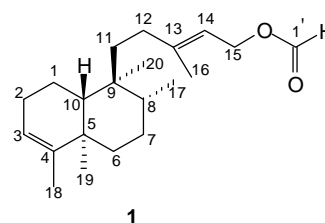


Figure 1: Structure of compound **1**, 15-formate-*ent*-3,13*E*-clerodadiene.

above ¹³C and ¹H NMR spectroscopic data were consistent with a clerodane diterpenoid containing a formate group. Correlations in the HMBC spectrum between a methyl proton resonance at δ 1.72 (s) for 3H-16 and carbon resonances at δ 32.9 (C-12), 117.1 (C-14) and 127.0 (C-13) were observed.

The C-14 carbon resonance corresponded in the HSQC-DEPT spectrum with a triplet double bond proton resonance at δ 5.35 for H-14. The H-14 proton resonance, in turn, was coupled with the oxymethylene group resonance at δ 4.69 assigned to 2H-15 in the COSY spectrum. The 2H-15 showed a correlation in the HMBC spectrum with the formate carbonyl at δ 161.3, which, in turn, corresponded with a proton resonance at δ 8.07 (s) in the HSQCDEPT spectrum. The doublet methyl proton resonance at δ 0.87 (d, *J* = 6.2 Hz) was assigned as 3H-17, whereas a double bond was placed between C-3 and C-4, as in kolavenol. The 3H-18 (δ 1.57, s) showed correlation in the HMBC spectrum with C-3 (δ 120.5), C-4 (δ 144.5) and C-5 (δ 38.4). The C-5 further showed correlation in the HMBC spectrum with 3H-19 (δ 0.98, s). The relative configuration for this compound was assigned using NOESY experiment where H-10 showed correlations with H-8 and 2H-11. Other correlations observed in the NOESY were between 3H-19 with 3H-20 and 3H-19 with 3H-17. The specific rotation of **1** was determined to be -39.2° , which is similar to that of kolavenol allowing for the identification of this compound as *ent*-3,13*E*-clerodadiene-15-formate, a new formate derivative of kolavenol.

Compounds (**1-7**) were tested for their anti-microbial activities against *Bacillus subtilis*, *Xanthomonas campestris* and *Candida albicans* and found to be inactive.

Experimental

General: The optical rotations were measured on a JASCO P-1020 polarimeter and the 1D and 2D NMR spectra were recorded in CDCl₃ on a 500 MHz Bruker AVANCE NMR instrument at room temperature. Chemical shifts, δ , were expressed in ppm and referenced against the solvent resonances at 7.26 and 77.23 ppm for ¹H and ¹³C NMR respectively. The ESIMS were recorded on a LCMS Bruker Micro ToF mass spectrometer by direct injection using a Bruker Bioapex-FTMS with electrospray ionization (University of Oxford). GCMS were recorded on an Agilent 7890A instrument. For column chromatography, Merck silica gel 60 (0.063-0.200 mm) and Fluka Sephadex LH-20 were used as stationary phases. Analytical TLC was carried out using aluminium plates (0.25 mm) coated with silica gel (60 F254, Merck). Compounds were visualized by observing under UV light at 254 or 365 nm, followed by spraying with 1% vanillin-H₂SO₄ spray reagent and heating.

Plant material: The root barks of *C. sylvaticus* were collected from Taita Hills in Coast province, Kenya (May 2008) and identified at the University of Nairobi herbarium where a voucher specimen, BN 2008/6 was deposited.

Extraction and isolation: The air-dried and powdered root bark (460g) was extracted by cold percolation at room temperature using MeOH: CH₂Cl₂ (1:1, v/v) solvent mixture (3 x 1L, 24 h each). The filtrates were then concentrated under reduced pressure using a rotary evaporator and combined to give 126.9 g (27.6% yield) of extract. From this, 50 g was absorbed on 50 g silica gel, chromatographed over silica gel (500 g, 10 x 60 cm) and eluted with *n*-hexane containing increasing amounts of CH₂Cl₂ to afford compounds **1** - **7**. Fractions (75 mL each) obtained were combined based on their TLC profiles and purified by chromatographic analysis over silica gel using CH₂Cl₂: diethyl ether (34:1 v/v) giving the compounds as follows: Fractions 3-4, *ent*-3, 13*E*-clerodadiene-15-formate (**1**) (< 2 mg), fractions 6-8, 15-acetoxy-*ent*-3, 13*E*-clerodadiene (**2**) (< 2 mg), fractions 12-20, penduliflaworosin (**5**) (12.4 mg), fractions 22-25, *ent*-3,13*E*-clerodadiene-15-ol (**3**) (10.4 mg), fraction 37-42, stigmaterol (5 mg), fractions 45-51, hardwickiic acid (**4**) (20.5 mg) and fractions 56-78, crotohalimaneic acid (5.8 mg). Increasing the polarity of the solvent system of the former column to CH₂Cl₂: *n*-hexane (1:3 v/v) produced fractions 10-19 (75 mL each) that were purified by crystallization in *n*-hexane to give, labda-13*E*-ene-8*a*, 15-diol [2*e*] (10.1mg).

Ent-3,13*E*-Clerodadiene-15-formate (**1**)

Clear oil

[α]_D²⁴: -39.2 (*c* 1.34x10⁻³, CHCl₃).

¹H NMR (500 MHz, CDCl₃): 0.72 (1H, s, H-1 α), 0.87 (3H, d, *J* = 6.2 Hz, H-17), 0.98 (3H, s, H-19), 1.17 (1H, m, H-1 β), 1.33 (1H, m, H-10), 1.35 (1H, m, H-6 β), 1.45 (1H, m, H-8), 1.57 (3H, s, H-18), 1.57 (3H, m, H-20), 1.69 (1H, m, H-6 α), 1.69 (1H, m, H-11A), 1.70 (1H, m, H-11B), 1.72 (3H, s, H-16), 1.83 (1H, m, H-12A), 1.90 (1H, m, H-12B), 2.02 (1H, m, H-7 α), 2.04 (1H, m, H-7 β), 4.69 (2H, m, H-12), 5.35 (1H, t, *J* = 7.1 Hz, H-14), 5.91 (1H, br s, H-3), 8.07 (1H, s, COOH).

¹³C NMR (125 MHz, CDCl₃): 16.0 (C-17, CH₃), 16.8 (C-16, CH₃), 18.2 (C-20, CH₃), 18.3 (C-1, CH₂), 18.9 (C-18, CH₃), 20.2 (C-19, CH₃), 27.6 (C-2, CH₂), 32.9 (C-12, CH₂), 36.3 (C-8, CH), 38.1 (C-11, CH₂), 38.4 (C-5, C), 38.8 (C-9, C), 46.5 (C-10, CH), 117.1 (C-14, CH), 120.5 (C-3, CH), 127.0 (C-13, C), 144.6 (C-4, C), 161.3 (COOH, CH).

HRMS: [M-H]⁺ *m/z*: 317.2121 for C₂₀H₃₄O₂ (calculated for C₂₀H₃₄O₂: 318.2559).

Antimicrobial assays: The modified CLSI (NCCLS 1998 and 2000) method described by Samoylenko *et al.* [2f] was used for the antimicrobial assays. Ciprofloxacin (ICN Biomedicals, Ohio) for bacteria and amphotericin B (ICN Biomedicals, Ohio) for fungi were used as positive controls. *Candida albicans* was from the American Type Culture Collection, Manassas, VA, (ATCC 90028) while, *Bacillus subtilis* and *Xanthomonas campestris* were local isolates. To obtain extracts for preliminary screening, 10 g of the powder was extracted with distilled water by boiling for 3 x 20 min, cooled, filtered and freeze dried. A similar quantity was extracted using methanol by maceration for 3 x 72 h at room temperature, filtered and concentrated under reduced pressure below 50°C using a rotary evaporator.

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