

## Note

### New aliphatic ester and alcohol from the leaves of *Ziziphus mauritiana*<sup>†</sup>

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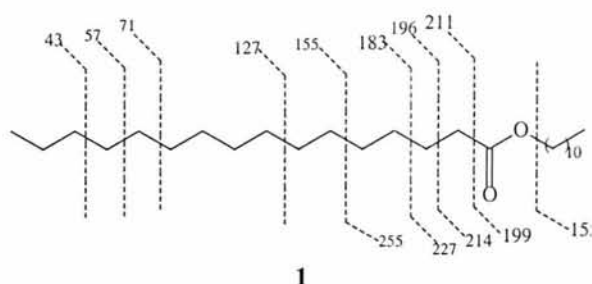
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The leaves of *Ziziphus mauritiana* yield two new long chain compounds characterised as undecyl-hexadecanoate **1** and 12-hydroxy-hentriacontane **2** using IR, <sup>1</sup>H NMR and mass spectral data.

The plant *Ziziphus mauritiana* Lam. (Rhamnaceae) is known for its medicinal importance<sup>1-3</sup>. In continuation to our work on *Z. mauritiana* leaves, we have further isolated new aliphatic ester and a long chain alcohol from its hexane extract<sup>4</sup>. In the present paper, we report the isolation and characterisation of these compounds.

The hexane extract of the leaves of *Z. mauritiana* on repeated silica gel column chromatography yielded compounds **1** and **2** named as undecyl-hexadecanoate **1** and 12-hydroxy-hentriacontane **2** and their structures were elucidated by physico-chemical data.

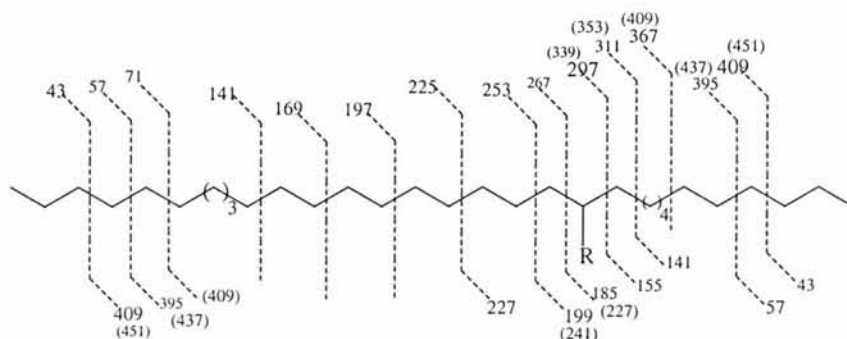
Compound **1** had a molecular formulae C<sub>27</sub>H<sub>54</sub>O<sub>2</sub> as indicated by its molecular ion at m/z 410 in its EIMS and elemental analysis. The presence of an ester carbonyl and aliphatic nature of the molecule were revealed by absorption bands at 1736 and 2920, 2850,



1465, 1375, 1178 and 725 cm<sup>-1</sup> respectively in its spectrum<sup>5</sup>.

The <sup>1</sup>H NMR spectrum of **1** depicted a triplet at 0.88 for two terminal methyl groups, a broad singlet at 1.25 for 44 protons of methylene group, a triplet at 2.25 for CH<sub>2</sub> adjacent to C=O and a two proton multiplet at δ 4.10 assigned for an oxymethylene group<sup>6,7</sup>.

The position of the ester group was established by its mass fragmentation pattern and its alkali hydrolysis<sup>8</sup> which afforded undecanol-1 a hexadecanoic acid (palmitic acid) identified by comparison with authentic samples. In mass spectrum the separation of most of the peaks by 14 mass units and appearance of C<sub>n</sub>H<sub>2n+1</sub><sup>+</sup>, C<sub>n</sub>H<sub>2n</sub><sup>+</sup> and C<sub>n</sub>H<sub>2n-1</sub><sup>+</sup> series confirmed its long chain aliphatic nature. Characteristic peak of ester group involving β-fission of McLafferty rearrangement ions were observed at m/z 196 and 214 and appearance of fragments at m/z 199, 211 and 155 were observed due to α-cleavage<sup>9</sup>, which confirmed the structure of compound **1** as undecyl-hexadecanoate.



**2**: R=OH

**2a**: R=Oac; The mass fragments given in parenthesis

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Compound **2**,  $C_{31}H_{64}O$  ( $M^+$ , 452) in its IR spectrum demonstrated bands at 3436 (OH) and 2922, 2848, 1465, 1380, 1064, 723  $cm^{-1}$  (a long aliphatic chain). Acetylation of **2** afforded a monoacetate **2a**,  $C_{33}H_{66}O_2$  ( $M^+$ , 494) which confirmed the presence of only one hydroxyl group in the molecule.

$^1H$  NMR spectrum of **2** showed a six proton triplet at  $\delta$  0.89 ( $J=6$  Hz) for two terminal methyl groups and a 56 proton broad singlet at  $\delta$  1.27 for 28 methylene units present in identical environment. A four proton multiplet at  $\delta$  1.56 was attributed to two methylene units present on either side of CHOH group and a triplet centred at  $\delta$  3.67 (1H,  $J=8$  Hz) corresponded to a hydroxy methine. All these data indicated **2** to be a long chain alcohol.

Appearance of a number of ion peaks at a regular difference of 14 mass units and the absence of  $[M-15]^+$  in the MS of **2** and **2a** confirmed the straight chain nature of the compound. The presence of  $\alpha$ -fission peak at  $m/z$  185, 267, 155 and 297 suggested the location of one hydroxyl group at C-12. This was finally confirmed by the presence of  $\alpha$ -fission peaks at  $m/z$  155, 279 (339-AcOH), 227 and 267 in the MS of **2a**. On the basis of above evidences, compound **2** was assigned as 12-hydroxy-hentriacontane.

### Experimental Section

Melting points were recorded with a Toshniwal apparatus and were uncorrected. The IR spectra were scanned with a Perkin Elmer spectrophotometer model 399B and  $^1H$  NMR spectra of **1** and **2** on a Bruker spectrometer (200 MHz) in  $CDCl_3$  with TMS as an internal standard and EIMS on a JEOL D-300 mass spectrometer at 70 eV. Column chromatography and thin layer chromatography (TLC) were done on silica gel (Ranbaxy). The spots were visualized by exposure to  $I_2$  vapours and/or by spraying with 1% ceric sulphate in 2N  $H_2SO_4$  solution followed by heating at 105° C for 5 min. The leaves of well identified *Z. mauritiana* tree were collected from Central Institute of Medicinal and Aromatic Plants (CIMAP) farms and again identified by the Botany Department, CIMAP, where a voucher specimen has been maintained.

**Extraction and isolation of compounds.** The air dried and ground leaves (1.0 kg) of *Z. mauritiana* were extracted with hexane (3 × 5 L) at room temperature. The hexane extract was concentrated to a dark green mass (8.5 g). This was chromato-

graphed on a silica gel (300 g) column eluting successively with hexane, hexane- $CHCl_3$  [(3:1), (2:1), (1:1), (1:2), (1:3) and (1:4) v/v]. The eluates were grouped into 7 fractions according to TLC.

Fraction No. 2 (1.64 g), eluted with hexane- $CHCl_3$  (3:1) was rechromatographed on a silica gel (50 g) column using hexane and increasing proportions of hexane- $CHCl_3$  (1%, 5%, 10%, 25%) yielding compound **1** (28.0 mg).

Fraction No. 3 (0.86 g), eluted with hexane- $CHCl_3$  (2:1) was rechromatographed on a silica gel (30 g) column using hexane and increasing proportions of hexane- $CHCl_3$  (5%, 10%, 25%, 50%) yielding compound **2** (22.4 mg).

**Undecyl-hexadecanoate 1:** colourless crystals, mp. 82° C,  $R_f$  0.4 (hexane- $CHCl_3$ , 9:1). IR (KBr) : 2920, 2850, (C-H str), 1736 (C=O), 1465, 1375, 1178, 725  $cm^{-1}$ .  $^1H$  NMR :  $\delta$  0.88 (6H, t,  $J=7$  Hz,  $2 \times CH_3$ ), 1.25 (44H, brs,  $22 \times CH_2$ ), 2.25 (2H, t,  $J=6$  Hz,  $CH_2-CO$ ), 4.10 (2H, m,  $COOCH_2$ ). EIMS (rel. int.) :  $m/z$  410  $[M]^+$  (3.6), 255 (5.5), 227 (3.2), 214 (4.3), 211 (2.5), 199 (7.8), 196 (6.4), 183 (11.0), 155 (12.3), 127 (11.4), 71 (55.2), 57 (82.4), 43 (100). Anal. Found: C, 79.23; H, 13.49. Calcd. for  $C_{27}H_{54}O_2$ : C, 79.02; H, 13.17 %.

**Alkaline hydrolysis of 1.** Compound **1** (5.0 mg) was refluxed with alc. KOH (5 %, 2.5 mL., 1 hr). At the end of the reaction the mixture was diluted with water (3.0 ml) and extracted with  $CHCl_3$  ( $2 \times 5$  mL). The  $CHCl_3$  layer was collected and dried with  $Na_2SO_4$ . It gave a viscous oil, which was identified as 1-undecanol. The aqueous hydrolysate was acidified with dil HCl and extracted with  $CHCl_3$ . The  $CHCl_3$  layer was separated, concentrated and dried over  $Na_2SO_4$  yielding a white crystalline acid hexadecanoic acid (palmitic acid) identified by direct comparison with authentic sample. 1-undecanol. EIMS :  $m/z$  172  $[M^+]$  (1.4) and other fragments, IR (KBr) : 3446, 2954, 2844, 1468, 1380, 1060, 730, 720,  $cm^{-1}$ .  $^1H$  NMR :  $\delta$  0.88 (3H, t,  $J=6$  Hz,  $CH_3$ ), 1.25 (18H, brs,  $9 \times CH_2$ ), 3.64 (2H, t,  $J=8$  Hz,  $CH_2OH$ ). Hexadecanoic acid : mp 62-64° C. EIMS:  $m/z$  256  $[M^+]$  (2.1), 196 (3.2), 183 (4.8), 155 (5.5), 127 (10.6), 101 (8.4), 73 (18.6), 71 (55.6), 60 (46.2), 57 (85.2), 43 (100). IR (KBr) : 2928, 2852, 1700, 1464, 1176, 724  $cm^{-1}$ .  $^1HNMR$  :  $\delta$  0.90 (3H, t,  $J=6$  Hz,  $CH_3$ ), 1.23 (26H, brs,  $13 \times CH_2$ ), 2.36 (2H, t,  $J=6$  Hz,  $CH_2COOH$ ).

**12-Hydroxy-hentriacontane 2:** White solid, mp 77° C,  $R_f$  0.4 (hexane- $CHCl_3$ , 1:1). IR (KBr): 3436 (OH), 2922, 2848, 1465, 1380, 1064, 723  $cm^{-1}$ .  $^1H$

NMR :  $\delta$  0.89 (6H, t,  $J=6$  Hz,  $2 \times \text{CH}_3$ ), 1.27 (56H, brs,  $28 \times \text{CH}_2$ ), 1.56 (4H, m,  $\text{CH}_2\text{-CHOH}$ ), 3.67 (1H, t,  $J=8$  Hz,  $\text{CHOH}$ ). EIMS (rel. int.) :  $m/z$  452  $[\text{M}]^+$  (2.9), 409 (3.9), 395 (3.3), 367 (3.4), 311 (3.7), 297 (4.9), 267 (5.3), 253 (4.8), 227 (3.8), 225 (4.7), 199 (1.2), 197 (3.2), 185 (2.4), 169 (3.4), 155 (4.1), 141 (4.7), 71 (66.4), 57 (100), 43 (80.5). Anal. Found : C, 82.68; H, 14.53. Calcd. for  $\text{C}_{31}\text{H}_{64}\text{O}$  : C, 82.30; H, 14.16 %).

**Acetylation of 2 (2a)** : Compound **2** (5.0 mg),  $\text{Ac}_2\text{O}$  and  $\text{C}_5\text{H}_5\text{N}$  (0.5 mL each) was allowed to stand overnight at room temperature. At the end of the reaction, the mixture was diluted with water (2 mL) and extracted with  $\text{CHCl}_3$  ( $2 \times 4$  mL). The  $\text{CHCl}_3$  extract was washed in sequence with 5%  $\text{HCl}$ , water,  $\text{NaHCO}_3$  and water. The extract was dried over  $\text{Na}_2\text{SO}_4$  and concentrated to get white crystals of **2a** (3.8 mg). TLC :  $R_f$  0.75 (hexane: $\text{CHCl}_3$ , 9:1).  $^1\text{H}$  NMR :  $\delta$  1.98 (3H, s,  $\text{OAc}$ ) and other proton signals. MS :  $m/z$  494  $[\text{M}]^+$  (2.1) for  $\text{C}_{33}\text{H}_{66}\text{O}_2$ , 451 (3.9), 437 (6.1), 409 (3.9), 353 (3.3), 339 (3.6), 279 (4.9), 267 (5.1), 253 (4.8), 241 (3.0), 227 (3.8), 225 (4.7), 197 (3.2), 169 (3.4), 155 (4.1), 141 (4.7), 71 (60.1), 57 (100), 43 (80.3).

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