

Note

Two new aliphatic compounds from the leaves of *Ziziphus mauritiana*

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Received 10 June 1999; accepted (revised) 10 December 1999

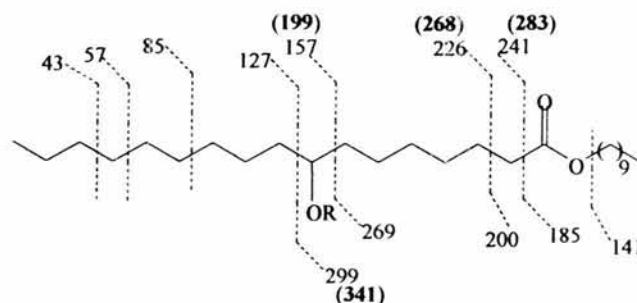
Chemical investigation of the leaves of *Ziziphus mauritiana* yields two new compounds characterised as decyl-8-hydroxy-heptadecanoate **1** and 12-hydroxy-tetratriacontan-9-one **2** using IR, ¹H NMR and mass spectral data.

Ziziphus mauritiana Lam. syn. *Ziziphus jujuba* Lam. (Indian Jujube) is found both wild and cultivated throughout India. The leaves are astringent, diaphoretic and are prescribed for typhoid¹. In Iran, its leaves are said to be used to decrease the intake of sweets and *Z. jujuba* leaf extract elevates human taste thresholds to sucrose solutions². The anti-sweet principle of *Z. jujuba* is ziziphin, a dammarane triterpene glycoside. The extract of *Z. jujuba* leaves also suppresses sweet taste sensation in the fly *Phormia regina* and in the rat and hamster^{3,4}. Due to all these biological properties specially antidiabetic property, the leaves of *Indian jujube* has been taken for biochemical studies. The present note describes the isolation and characterisation of two new long chain compounds from the non-polar fraction of its MeOH extract.

The hexane extract of the leaves of *Z. mauritiana* on repeated silica gel column chromatography yielded two compounds named as decyl-8-hydroxy-heptadecanoate **1** and 12-hydroxy-tetratriacontan-9-one **2** and their structures were elucidated by physico-chemical data.

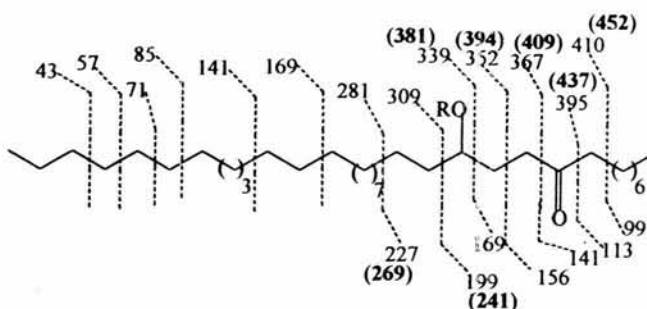
Compound **1** had a molecular formula C₂₇H₅₄O₃ as indicated by its molecular ion at m/z 426 in its EIMS and elemental analysis. The presence of hydroxyl, ester carbonyl and aliphatic nature of molecule were revealed by absorption bands at 3486, 2918, 1740, 1450, 1380, 725 and 715 cm⁻¹, respectively in its IR spectrum^{5,6}.

Acetylation of **1** afforded a monoacetate **1a**,



1 : R=H

1a : R=Ac ; its mass fragments given in paranthesis



2 : R=H

2a : R=Ac ; its mass fragments given in paranthesis

C₂₉H₅₆O₄ (M⁺, 468) which confirmed the presence of only one acetylatable hydroxyl group in the molecule.

¹H NMR spectrum of **1** depicted a triplet at δ 0.90 for two methyl groups, a broad singlet at δ 1.26 for 38 methylene protons, a multiplet at δ 1.61 for four -CH₂ protons adjacent to -CHOH group, a triplet at δ 2.29 for CH₂ next to C=O, triplet at δ 3.59 for hydroxymethine proton and a multiplet at δ 4.05 for -CH₂ group attached to CH₂OCO group^{7,8}.

The position of the ester group was determined by its mass fragmentation pattern and its alkaline hydrolysis⁹ which afforded decanol-1. In mass spectrum the separation of most of the peaks by 14 mass units and appearance of (C_nH_{2n+1})⁺, C_nH_{2n} and C_nH_{2n-1} ion series confirmed its long chain aliphatic nature¹⁰. Abundant fragments involving β-fission ions at m/z 226 and 200 formed by Mc-Lafferty rearrangement indicated the position of the ester group at C-17 and formation of fragments at m/z 127, 299, 157 and 269 by α-cleavage^{10,11} indicated the

position of hydroxyl group at C-8, which confirmed the structure of compound **1** as decyl-8-hydroxy-heptadecanoate.

Compound **2**, mp 82-84°, C₃₄H₆₈O₂ (M⁺, 508) gave a positive test with 2,4-dinitrophenylhydrazine for carbonyl group. Its IR spectrum demonstrated bands at 3464 (OH), 1706 (C=O) and 2922, 1460, 1388, 724, 715 cm⁻¹ (a long aliphatic chain).

Acetylation of **2** afforded a monoacetate **2a**, C₃₆H₇₀O₃ (M⁺, 550) which confirmed the presence of only one acetylatable hydroxyl group in the molecule.

¹H NMR spectrum of **2** showed a six proton triplet at δ 0.89 (*J*=6 Hz) for two terminal methyl groups and a 52 proton broad singlet at δ 1.24 for 26 methylene units present in identical environment. A four proton multiplet at δ 1.59 was attributed to two methylene units present on either side of carbinolic carbon. The presence of a four proton triplet at δ 2.35 (*J*=6 Hz) was attributed to two methylene units α to carbonyl group. A triplet centred at δ 3.64 (1H, *J*=10 Hz) corresponded to a hydroxy methine. All these data indicated **2** to be a long chain keto 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 α-fission peak at *m/z* 199, 309, 169 and 339 suggested the location of one hydroxyl group at C-12. This was finally confirmed by the presence of α-fission peaks at *m/z* 169, 321 (381-AcOH), 241, 309 in the MS of **2a**. Location of carbonyl group at C-9 was deduced from the presence of α-fission peaks at *m/z* 113, 141 and 367 and the presence of β-fission ion peaks at *m/z* 98 and 410 involving Mc-Lafferty rearrangement in the mass spectrum of **2**. This assignment was ably supported by the formation of α-fission peaks at *m/z* 349 (409-AcOH), 141, 377 (437-AcOH), 113 involving Mc-Lafferty rearrangement in the MS of **2a**. On the basis of above evidences, compound **2** was assigned the structure as 12-hydroxy-tetratriacontan-9-one.

Experimental Section

Mps were uncorrected on a Toshniwal apparatus. The IR spectra were recorded on a Perkin Elmer 399B, ¹H NMR spectra on a Bruker spectrometer (300 MHz) in CDCl₃ with TMS as internal standard and EIMS on a JEOL D-300 mass spectrometer at 70 eV. CC and TLC was done on Si gel (Ranbaxy). The

spots were visualized by exposure to I₂ vapours and/or by spraying with 5% vanillin-H₂SO₄ solution followed by heating at 105° for 5 min.

The leaves of well-identified *Z. mauritiana* tree were collected from the farms of Narendra Dev University of Agriculture and Technology, Faizabad, U.P. and were again identified by Botany Department, CIMAP, where a voucher specimen has been maintained.

Extraction and Isolation

The air dried and grounded leaves (500 g) of *Z. mauritiana* were extracted in MeOH (3×1.5L) at room temperature. The MeOH extract was concentrated to get brown coloured mass (55 g) which was extracted successively with hexane (4×500 mL, 13.17 g), CHCl₃ (4×500 mL, 18.13 g) and *n*-BuOH (4×500 mL, 14.00 g). The hexane extract (13.17 g) was chromatographed on a Si gel (300 g) column eluting successively with hexane, hexane-CHCl₃ [(3:1), (2:1), (1:1), (1:2) and (1:3) v/v]. The eluates were grouped into 6 fractions according to TLC.

Fraction no. 3 (1.56 g) eluted with hexane-CHCl₃ (2:1) was rechromatographed on a Si gel column using hexane and increasing proportions of hexane-CHCl₃ yielding compounds **1** (38 mg) and **2** (44 mg).

Decyl-8-hydroxy-heptadecanoate 1. Colourless crystals, mp 94-96°, yield 38 mg, IR (KBr): 3486 (OH), 2918, 1740 (C=O), 1450, 1380, 725, 715 cm⁻¹. ¹H NMR: δ 0.90 (6H, t, *J*=6 Hz, 2 × CH₃), 1.26 (38H, brs, 19 × CH₂), 1.61 (4H, m, 2 × CH₂-CHOH), 2.29 (2H, t, *J*=6 Hz, CH₂-CO), 3.59 (1H, t, *J*=8 Hz, CHOH), 4.05 (2H, m, COOCH₂). EIMS (*m/z*) (rel. int.): 426 [M]⁺ (2.8), 299 (12.6), 269 (12.2), 241 (3.2), 226 (2.5), 200 (1.2), 185 (3.7), 157 (12.4), 141 (2.7), 127 (10.5), 85 (45.6), 57 (100), 43 (80). R_f 0.9 (hexane-CHCl₃, 1:1). Found: C, 76.23; H, 12.89. C₂₇H₅₄O₃ requires C, 76.05; H, 12.67 %).

Alkaline hydrolysis of 1. Compound **1** (10 mg) was refluxed with alcoholic KOH (5%, 2.5 mL, 1 hr). At the end of the reaction the mixture was diluted with water 3.0 mL and after usual work-up it afforded a viscous oil, identified as 1-decanol (MS: M⁺ 158 and other fragments, IR, ¹H NMR).

Acetylation of 1 (1a). Compound **1** (5 mg), Ac₂O and C₅H₅N (0.5 mL each) was allowed to stand overnight at room temperature. On usual work-up, the mixture afforded white crystals of **1a** (4 mg). TLC:

R_f 0.95 (hexane); MS : m/z 468 [M]⁺ (3.8) for C₂₉H₅₆O₄, 341 (2.8), 283 (1.5), 269 (4.5), 268 (10.6), 200 (1.8), 199 (9.8), 185 (4.8), 141 (3.2), 127 (12.6), 85 (42.8), 57 (100), 43 (70.5).

12-Hydroxy-tetratriacontan-9-one 2. Colourless crystals, mp 82-84°, yield 44 mg, IR (KBr): 3464 (OH), 2922, 1706 (C=O), 1460, 1388, 1040, 725, 715 cm⁻¹; ¹H NMR : δ 0.89 (6H, t, J=6 Hz, 2×CH₃), 1.24 (52H, brs, 26×CH₂), 1.59 (4H, m, 2×CH₂-CHOH), 2.35 (4H, t, J=6 Hz, 2×CH₂-CO), 3.64 (1H, t, J=10Hz, CHOH), EIMS m/z (rel. int.) : 508 [M]⁺ (2.4), 479 (7.8), 451 (18.4), 423 (9.9), 410 (2.0), 395 (5.0), 367 (1.7), 352 (2.2), 339 (1.5), 309 (1.6), 281 (1.7), 227 (1.8), 199 (2.1), 169 (2.0), 156 (2.9), 141 (2.7), 113 (19.6), 98 (25.8), 85 (43.0), 71 (45.6), 57 (100), 43 (80.5). R_f 0.4 (hexane-CHCl₃, 1:1) (Found: C, 80.68; H, 13.53; C₃₄H₆₈O₂ requires C, 80.31; H, 13.38%).

Acetylation of 2 (2a). Compound 2 (8 mg), Ac₂O and C₅H₅N (0.5 mL each) was allowed to stand overnight at room temperature. On usual work-up, the mixture afforded white crystals of 2a (4 mg). TLC: R_f 0.75 (hexane); MS: m/z 550 [M]⁺ (0.7) for C₃₆H₇₀O₃, 521 (2.3), 493 (5.4), 465 (7.9), 452 (15.6), 437 (10.8), 409 (3.9), 394 (8.5), 381 (5.0), 377(4.8), 349 (3.4),

321 (2.6), 309 (2.2), 281 (1.6), 269 (1.6), 241 (1.9), 169 (2.4), 156 (3.6), 141 (4.5), 113 (14.5), 98 (30.5), 85 (42.8), 71 (32.1), 57 (100), 43 (70.6).

Acknowledgements

The authors are grateful to Mr M S Siddiqui, for his help in collection of leaves and to Head, RSIC at CDRI, Lucknow for recording the spectral data.

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