

Note

Identification of novel aliphatic compounds from *Artabotrys odoratissimus* (leaves)

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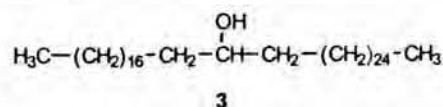
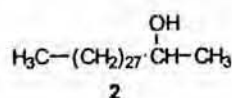
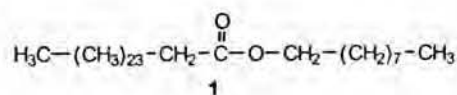
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Three novel aliphatic compounds have been isolated and identified from the leaves of *Artabotrys odoratissimus*. The compounds have been characterised as nonacosanyl hexacosanoate **1**, 2-hydroxytricontane **2**, and pentatetracontan-19-ol **3** by spectral and chemical analyses.

In earlier communications^{1,2} we have reported isolation and characterisation of pentadecyl-7-hydroxydodecanoate, pentadecyl tritriacontanoate and 4, 5-epoxy-dopentacontan-26-ol, β -sitosterol, aplysterol, aliphatic esters and alcohols. Further investigation of hexane and benzene extracts yielded three novel compounds characterised as nonacosanyl hexacosanoate **1**, 2-hydroxytricontane **2**, and pentatetracontan-19-ol **3**.

Compound 1. Nonacosanyl hexacosanoate ($C_{35}H_{70}O_2$, M^+ 522), mp 83°C (benzene). IR spectrum showed the presence of an ester group (1730 and 1190 - 1180 cm^{-1})³ and aliphatic nature of the molecule. 1H NMR spectrum (400 MHz, TMS, $CDCl_3$) showed signals at δ 0.90 (t, 6H, $2-CH_3$, $J=8$ Hz), due to two terminal methyl groups³, 1.25 (bs, 64H, $32-CH_2$), 4.08 (t, 2H, $-CH_2$, $J=6$ Hz), due to methylene protons directly attached to the ester group⁴, 2.28 (t, 2H, $-CH_2$), due to methylene protons attached to the carbonyl group and 1.62 (t, 4H, $-CH_2$), due to methylene protons- β to ester group.

Position of the ester group was determined by its mass fragmentation pattern. In mass spectrum abundant fragments were found at m/z 396 and 126 formed by α -cleavage and H rearrangement. The abundant fragments at m/z 336 and 186 were formed by McLafferty rearrangement and indicated the position of the ester group. Compound **1** on alkaline hydrolysis furnished a mixture of acid and alcohol, identified as hexacosanoic acid and 1-nonanol^{6,9} respectively, which confirmed the structure of the



compound **1** as nonacosanyl hexacosanoate. It is being reported for the first time in the literature.

Compound 2. 2-Hydroxytricontane ($C_{30}H_{62}O$, M^+ 438), mp 91°C (benzene). IR spectrum showed the presence of hydroxyl group (3400 cm^{-1})¹⁰ and aliphatic nature of the molecule. 1H NMR spectrum (400 MHz, TMS, $CDCl_3$) showed a triplet at δ 0.83 ($J=7.5$ Hz) for three protons for terminal methyl group. The methine proton resonated at δ 3.59 as multiplet. The hydroxyl proton (D_2O exchangeable) appeared at δ 1.39 as singlet. The methyl group attached to carbinolic carbon resonated at δ 1.52 as doublet ($J=6$ Hz). The remaining methylenes were merged into a broad singlet appearing at δ 1.25 for 54 protons.

Mass spectrum of the compound **2** suggested it to be an aliphatic alcohol, as most of the fragments were separated by 14 mass units. The appearance of abundant fragments at m/z 393 ($M-C_2H_5O$) and 423 ($M-CH_3$) indicated the position of OH group at C-2. On acetylation with acetic anhydride and pyridine compound **2** gave a monoacetate, IR 1735 cm^{-1} . These data were in full agreement with the proposed structure.

Compound 3. Pentatetracontan-19-ol ($C_{45}H_{92}O$, M^+ 648), mp 93°C (hexane-benzene). IR, 1H NMR and mass spectra confirmed the aliphatic nature of the molecule. 1H NMR spectrum (400 MHz, TMS, $CDCl_3$) showed a triplet at δ 0.89 ($J=7.5$ Hz) for six protons due to terminal methyl groups. The methine and hydroxyl protons resonated at δ 3.60 and 1.6 as triplet and singlet (D_2O exchangeable), respectively. The remaining methylenes were merged into a broad

singlet appearing at δ 1.20 for 80 protons. In mass spectrum, most of the peaks were separated by 14 mass units and appearance of fragments corresponding to ion series $C_nH_{2n}+1$, C_nH_{2n} and $C_nH_{2n}-1$, confirmed the aliphatic nature. Position of the hydroxyl group was determined by the appearance of abundant fragments at m/z 364 and 284 formed by α -cleavage and H rearrangement at C-19. This was further confirmed by the appearance of abundant fragments at m/z 253 and 395. Compound **3** on acetylation with acetic anhydride and pyridine gave a monoacetate, IR 1735 cm^{-1} . Thus, the compound was identified as pentatetracontan-19-ol. It is being reported first time in the literature.

Experimental Section

General. All mp's are uncorrected. IR spectra were recorded in KBr on a Perkin Elmer- 377 infracord spectrophotometer, ^1H NMR spectra (400 MHz) on Jeol GSX 400 and Bruker WM -400 FT NMR spectrometers using TMS as internal standard, and mass spectra on Jeol D 300 mass spectrometer. Silica gel G was used for TLC and spots were visualised by exposure to iodine vapours.

Leaves of *A. odoratissimus* were collected from the nearby area of Ujjain city and identified by the School of Studies in Botany, Vikram University, Ujjain. These were washed with clean water, air-dried and ground to coarse powder.

Extraction and isolation. Powdered leaves (8 kg) were exhaustively extracted successively in soxhlet with hexane and benzene. Solvent was removed by rotatory vacuum evaporator. The hexane extract was separated by column chromatography using alumina grade-III as an adsorbent. The column was eluted with solvents of increasing polarity starting with *n*-hexane. Fractions were checked by TLC and those of similar compositions were combined and solvent was removed. Compound **1** was obtained from the rechromatography of the hexane eluate of hexane extract, while compounds **2** and **3** were obtained from the rechromatography of hexane eluate of benzene extract.

Compound 1. Recrystallised from benzene, mp 83°C ; IR: 2920, 2860, 1730, 1465, 1190-1180, 730-720 cm^{-1} ; ^1H NMR: δ 0.90 (6H, t, terminal 2 $-\text{CH}_3$, $J=8\text{ Hz}$), 1.25 (bs, 64H, 32 $-\text{CH}_2$), 1.62 (4H, t, 2x- CH_2 , $J=6\text{ Hz}$), 2.28 (2H, t, $-\text{CH}_2\text{CO}$, $J=6\text{ Hz}$) and 4.08 (2H, t, $-\text{CH}_2\text{OCO}$, $J=6\text{ Hz}$); EIMS: m/z 522

(M^+ 10.0%), 508(20.0), 493(1.3), 476(1.0), 465(2.2), 448(2.3), 437(4.1), 409(5.1), 396(40.0), 369(32.0), 365(18.0), 341(33.3), 336(6.0), 323(4.0), 297(4.2), 257(16.0), 237(4.3), 223(4.7), 209(4.8), 195(5.2), 186(6.0), 167(6.7), 153(10.3), 126(22.0), 112(38.0), 98(65.0), 83(64.0), 71(70.0), 57.0(100) etc.

Hydrolysis of compound 1. Compound **1** (40 mg) was refluxed with ethanolic KOH (50 mL, 5%) for 4 hr. Usual workup afforded a semisolid, which showed two spots on TLC. These compounds were separated by preparative TLC on silica gel H and identified as hexacosanoic acid and 1-nonanol.

Hexacosanoic acid, $C_{26}H_{52}O_2$, M^+ 396, mp 89°C ; IR: 3436, 2940-2850, 1710, 1430-1380, 1290, 1110, 830, 730-725 cm^{-1} . EIMS: m/z 396 (M^+ 3.2%), 382(2.8), 368(2.9), 354(2.9), 351(9.1), 340(3.0), 337(4.0), 336(6.3), 309(4.3), 281(3.9), 97(31.5), 83(52.2), 69(62.4), 55(100), etc.

1-Nonanol; $C_9H_{20}O$; fragrant liquid, IR: 3425-3360, 2920-2840, 1426-1385, 1290, 1275, 1080, 730 cm^{-1} . EIMS: m/z 144 (M^+ 10.28%), 130(3.8), 126(18.8), 113(14.2), 112(10.9), 98(32.3), 84(37.5), 70(42.1), 56(100) and 43(89.0).

Compound 2. Recrystallised from benzene, mp 91°C , IR: 3400, 2920, 2860, 1730, 1465, 1060, 750, 730-720 cm^{-1} ; ^1H NMR: δ 0.83 (3H, t, terminal $-\text{CH}_3$, $J=7.5\text{ Hz}$), 1.25 (bs, 54H, 27 $-\text{CH}_2$), 1.39 (1H, s, $-\text{OH}$, D_2O exchangeable), 1.52 (3H, d, $-\text{CH}_3$ CHOH , $J=6\text{ Hz}$) and 3.59 (1H, m, $-\text{CHOH}$). EIMS: m/z 438 (M^+ 2.1%), 423(2.3), 395(3.0), 393(6.8), 365(4.5), 337(6.1), 309(5.2), 98(34.2), 97(45.0), 85(53.0), 83(54.0), 71(67.0), 69(72.3), 57(94.0), 55(86.0), 45(62.3), 43(100), 41(89.8) etc.

Compound 3. Recrystallised from hexane-benzene, mp 93°C , IR: 3400, 2920, 2860, 1465, 1060-1050, 730-720 cm^{-1} ; ^1H NMR: δ 0.89 (6H, t, terminal 2- CH_3 , $J=7.5\text{ Hz}$), 1.20 (bs, 80H, 40 $-\text{CH}_2$), 1.60 (1H, s, $-\text{OH}$, D_2O exchangeable), 1.52 (4H, t, 2- CH_2 , $J=7\text{ Hz}$) and 3.60 (1H, t, $-\text{CHOH}$, $J=7\text{ Hz}$). EIMS: m/z 648 (M^+ , 1.0%), 624(0.4), 598(0.4), 575(0.3), 533(0.2), 504(1.0), 476(2.1), 448(2.6), 420(3.3), 395(4.6), 392(9.8), 365(4.6), 364(15.6), 336(5.1), 293(5.2), 284(3.0), 282(1.2), 265(4.2), 253(3.2), 240(6.2), 209(5.2), 181(8.0), 153(11.3), 125(29.0), 112(51.5), 97(84.2), 83(94.0), 57(100) etc.

Acetylation of compounds 2 and 3. Compounds 2 and 3 (16 and 15 mg) were treated with acetic anhydride and pyridine, and left overnight at room temperature. Usual work-up gave solid residues, mp's 67 and 69°C respectively; IR: 1735 cm⁻¹.

Acknowledgement

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