

Notes

Two new long chain compounds from *Bauhinia variegata* Linn.

R S Singh*, H S Pandey[†] & Ghanshyam

Natural Products Research Laboratory, Department of Chemistry
DDU Gorakhpur University, Gorakhpur 273 009, India
and

[†]Department of Chemistry, Buddha P G College,
Kushinagar 274 403, India
E-mail: rssingh_chem@yahoo.com

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Two new long chain compounds, heptatriacontan-12,13-diol **1** and dotetracont-15-en-9-ol **2** have been isolated from the leaves of *Bauhinia variegata*. Structures of these compounds have been elucidated by spectral data analyses and chemical studies.

Keywords: *Bauhinia variegata* Linn., snake-antivenom, antifungal, aphrodisiac, heptatriacontan-12, 13-diol, dotetracont-15-en-9-ol

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Bauhinia variegata Linn. (Caesalpiniaceae), a woody deciduous tree has snake-antivenom, antifungal, antitumour, anti-inflammatory and aphrodisiac properties¹. Presence of some flavonoids, amino acids, sterols, triterpenoids and anthocyanins has been reported from different parts of this plant²⁻⁶. The present paper describes the isolation and structure elucidation of two new long chain compounds from the leaves of this plant.

Compound **1**, m.p. 65°C, $C_{37}H_{76}O_2$ (M^+ at m/z 552) showed characteristic IR absorption bands at 3436 (-OH groups) and 723 cm^{-1} (a long aliphatic chain). On acetylation it yielded an acetate derivative **1a**, m.p. 54-55°C, IR 1737 cm^{-1} (C=O). Its ¹H NMR spectrum displayed a six proton triplet at δ 0.88 ($J=11$ Hz) for two terminal methyl groups and a 62 proton broad singlet at δ 1.25 for 31 identical methylene groups. Two proton multiplet at δ 3.60 for protons attached to carbinolic carbons showed the presence of two hydroxyl groups. A four proton signal at δ 1.54 was characteristic of two methylene groups attached to carbinolic carbon⁷. This showed two hydroxyl groups on vicinal carbon atoms. On the basis of IR and ¹H NMR spectra it was inferred to be 37 carbon aliphatic compound with two hydroxyl at vicinal positions.

The mass spectrum of **1** showed a number of ion peaks at a regular difference of 14 amu which supported the long chain skeleton of the molecule. Further, unramified nature of the skeleton was suggested by the absence of a $[M-15]^+$ peak. The prominent α -fission peaks at m/z 155, 397, 185, 367, 215 and 337 can only be explained if the two hydroxyl groups are located at C-12 and C-13. The positions of hydroxyl group were confirmed by the appearance of β -fission peaks of m/z 411 and 229. Appearance of a peak at m/z 516 corresponding to (M^+-36) is due to the elimination of two water molecules from the parent ion. Thus, on the basis of above studies, **1** was characterized as heptatriacontan-12, 13-diol (**Figure 1**).

Compound **2**, m.p. 95-96°C, $C_{42}H_{84}O$ (M^+ , 604) displayed important IR absorption bands at 3418 (OH), 1630 (>C=C<) and 722 cm^{-1} (a long aliphatic chain)⁸. Acetylation of **2** afforded a monoacetate derivative **2a**, m.p. 85-86°C, $C_{44}H_{86}O_2$ (M^+ , 646), IR 1752 cm^{-1} (C=O). High resolution ¹H NMR spectrum of the compound showed a six proton triplet at δ 0.87 ($J=9$ Hz) for two terminal methyl groups and a 66 proton broad singlet at δ 1.20 for 33 methylene units present in identical environment. A four proton signal at δ 1.50 was attributed to two methylene units present on either side of carbinolic carbon. Four protons of two methylene units adjacent to double bond resonated as a triplet⁹ at δ 2.26 ($J=7.5$ Hz). The lone methine proton of carbinolic carbon appeared as a triplet at δ 3.50 ($J=7.2$ Hz). A one proton singlet at δ 3.8 was attributed to the alcoholic proton. A two proton multiplet at δ 4.90 was assigned to two olefinic protons. Thus, **2** was indicated to be a long chain aliphatic alcohol with a double bond.

Appearance of a number of ion fragments with systematic difference of 14 amu and the absence of peak corresponding to $[M-15]^+$ in the MS of **2** and **2a** confirmed the straight chain nature of the compound. A characteristic pattern of more intense clusters of peaks corresponding to C_nH_{2n-1} appeared at m/z 391, 405, 461 which are formed from alkene end of the molecule. Another set of intense ion peaks at m/z 213, 199, 143 might be originating from the methyl end containing hydroxyl group. The formation of these

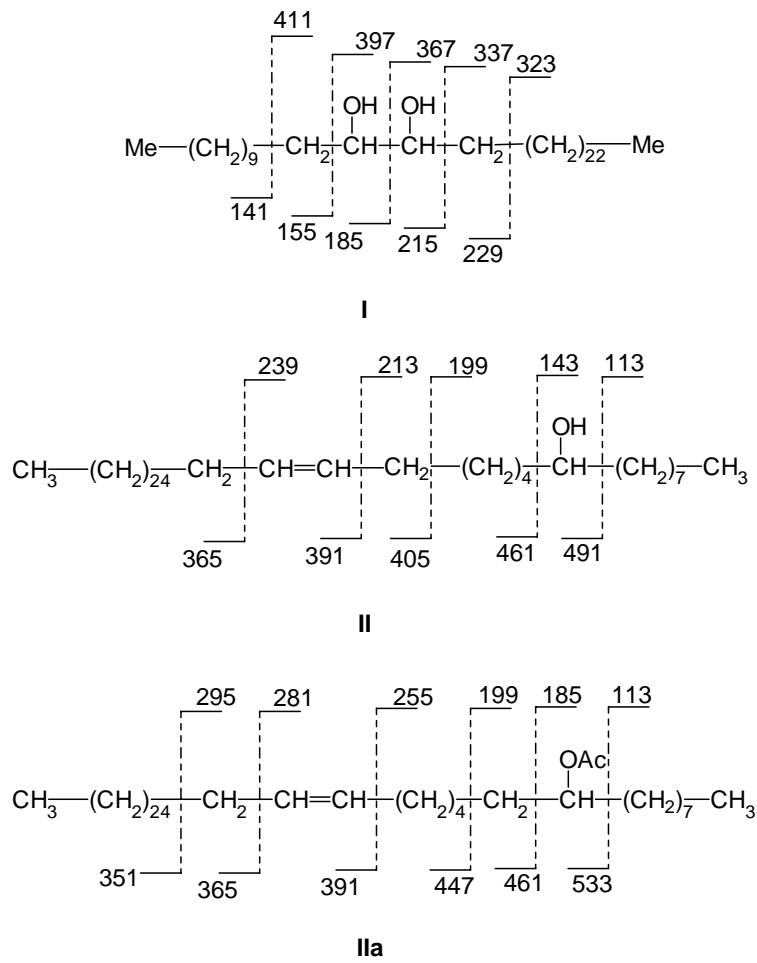


Figure 1

ion peaks can be only explained if the double bond is located at C-15. Occurrence of α -fission peaks at m/z 491, 461 suggested the presence of hydroxyl group at C-9. This assignment was ably supported by the formation of α -fission peaks at m/z 533, 461, 185, 113 and β -fission peaks at m/z 447 and 199 in the MS of **2a**. Thus, compound **2** was characterized as dotetracont-15-en-9-ol (Figure 1).

Experimental Section

All reported m.p.s are uncorrected. IR (KBr) spectra were recorded on a Perkin-Elmer 177 spectrometer; ^1H NMR spectra in CDCl_3 on a WM-300 (Bruker-FT) instrument using TMS as internal standard and FAB (positive ion) mass spectra on a Jeol D-300 mass spectrometer. Silica gel (Qualigens) was used for TLC and column chromatography. Spots on TLC plates were visualized by UV light, I_2 vapours as well as by heating the plates after spraying with 10% H_2SO_4 .

Plant Material. Leaves of *Bauhinia variegata* were collected from nearby area of Gorakhpur in February-March 2002 and identified by Prof. S. K. Singh, (Department of Botany, DDU Gorakhpur University, Gorakhpur). A voucher specimen (No. 16) has been deposited in the laboratory.

Extraction and Isolation. Air dried and powdered leaves (6.0 kg) were exhaustively extracted with ethanol. The extract was filtered and solvent removed under reduced pressure to yield a dark brownish semi-solid mass (560 g). Its hexane soluble fraction (105 g) was chromatographed over a Si-Gel (1.5 kg) column. The column was eluted with *n*-hexane. The elution of the column was monitored by TLC. Chromatographically similar fractions were mixed and solvent removed under reduced pressure.

Heptatriacont-12,13-diol 1. Fractions 1-4 of the hexane eluate yielded white solid which was purified by recrystallization from acetone as colourless crystals (61 mg), m.p. 65°C, TLC: R_f 0.75 (*n*-hexane);

IR(KBr): 3436, 2920, 2851, 1467, 1027, 802 and 723 cm^{-1} ; ^1H NMR (CDCl_3): δ 0.88 (6H, t, $J=11$ Hz, 2- CH_3), 1.25 (62H, brs, 31> CH_2), 1.54(4H, s, CH_2 - CHOH-CHOH-CH_2); 3.60(2H, m, - CHOH); MS: m/z 552 (M^+ , 12.5%) for $\text{C}_{37}\text{H}_{76}\text{O}_2$, 516(5), 453(5), 411(5), 397(5), 367(5), 337 (12.5), 268 (77.5), 243 (28), 229 (12.5), 215 (20), 185 (12.5) and 155 (62.5).

Acetylation of 1. A mixture of **1** (10 mg), Ac_2O and pyridine (1 mL each) was allowed to stand overnight at RT. On usual work-up, the mixture afforded white crystals of **1a** (7 mg), m.p. 54-55°C; TLC: R_f 0.60 (*n*-hexane); IR (KBr): 2920, 2850, 1737, 1467, 1375, 1243, 1174, 1087, 803 and 723 cm^{-1} .

Dotetracont-15-en-9-ol 2. Fractions 38-60 of *n*-hexane eluate yielded a solid mass on addition of methanol. On repeated recrystallization from methanol it afforded white crystals of **2** (234 mg), m.p. 95-96°C; TLC: R_f 0.35 (hexane : benzene, 1:1); IR (KBr): 3418, 2920, 2850, 1630, 1466, 1126 and 722 cm^{-1} ; ^1H NMR (CDCl_3): δ 0.87 (6H, t, $J=9$ Hz, 2- CH_3), 1.20 (66H, brs, 33> CH_2), 1.50 (4H, s, - CH_2 - CHOH-CH_2), 2.26 (4H, t, $J=7.5$ Hz, $\text{CH}_2\text{-C=C-CH}_2$), 3.50 (1H, t, $J=7.2$ Hz, > CH-OH), 3.80(1H, s, > CH-OH); 4.90 (2H, m, - CH=CH-); MS : m/z 604 (M^+ , 5%) for $\text{C}_{42}\text{H}_{84}\text{O}$, 491 (5), 490 (12), 461 (2), 460 (5), 419 (5), 405 (5), 391 (25), 365 (12), 239 (20), 213 (22), 199 (15), 185 (12.5), 143 (30), 113 (25).

Acetylation of 2. A mixture of **2** (20 mg), Ac_2O and pyridine (2 mL each) was left overnight at RT. On usual work-up it afforded white crystals of **2a** (15 mg); m.p. 85-86°C, TLC: R_f 0.26 (hexane : benzene, 1:1); IR (KBr): 2904, 2856, 1752, 1638,

1460, 1452, 1248, 1260, 1240, 1096, 1024, 824 and 728 cm^{-1} ; MS: m/z 646 (M^+ , 11%) for $\text{C}_{44}\text{H}_{86}\text{O}_2$, 611(8), 582(15), 557(10), 533(8), 526(10), 498 (12), 472 (10), 461 (12), 449 (14), 447 (12), 391 (18), 365 (12), 352 (18), 351 (15), 328 (28), 295 (20), 287 (30), 281 (25), 263 (29), 255 (28), 252 (32), 202 (40), 199 (18), 185 (22), 178 (45), 165 (65), 113 (62), 105 (100).

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