Asian Journal of Chemistry Vol. 20, No. 7 (2008), 5455-5460

New Aliphatic Alcohol from *Ailanthus excelsa* Roxb Bark

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A rare fatty acids, phytosterol and new aliphatic alcohol were isolated from the ethanolic extracts of the stem bark of *Ailanthus excelsa* Roxb. The structures of these compounds were established on the basis of the chemical reaction and spectral analysis as *n*-octanyl decasanoate, *n*-eintriacontane, stigmast-5,22-dien-3β-ol, *n*-tetratriacontanoic acid and *n*-eintriacontan-8β-ol.

Key Words: *Ailanthus excelsa*, Simaroubaceae, Aliphatic alcohol, Sterol and Fatty acids.

INTRODUCTION

Ailanthus excelsa Roxb. (Simaroubaceae), commonly called tree of the Heaven or Maharukh, has been used as a bitter, astringent, anthelmintic, febrifuge, antiseptic and to treat diarrhoea and dysentery[1-4]. This species is a rich source of quassonoids, alkaloids, terpenes and steroids[5-10]. In the present paper, the isolation and structure elucidation of new aliphatic alcohol along with a phytosterol and few rare fatty acids from the stem bark of the plant are described.

EXPERIMENTAL

Melting points, uncorrects on a complab melting point apparatus. IR spectra (KBr) were recorded on a Perkin-Elmer spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were run on a Bruker DPX 300 MHz and 75 MHz instrument, respectively. FAB mass were scanned on Jeol-102 mass spectrometer. Column chromatography was performed using neutral alumina; TLC: precoated silica gel G plates (Qualigens).

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The barks of *Ailanthus excelsa* Roxb. were collected during the month of June 2005 from roadside at Bhathera, Rewari, (Haryana) North India. The plant materials was taxonomically identified and authenticated by Dr. H.B. Singh, Raw Materials Herbarium and Museum division, NISCAIR, New Delhi with ref. no. NISCAIR/RHM/F-3/2005/conslt/590/70.

Extraction and isolation: The powdered bark of the plant (5 kg) was subjected to hot extraction process with ethanol for 72 h. The extract was concentrated by distillation followed by drying and kept in desiccators. The extract (190 g) obtained was a thick dark brownish viscous mass. The extract was dissolved in minimum amount of methanol and adsorbed on silica gel to form a slurry. The air-dried slurry was chromatographed on neutral alumina column loaded in petroleum ether (b.p. 60-80 ºC). The column was eluted petroleum ether, ethyl acetate, chloroform and methanol to get the following compounds:

***n*-Octanyl decasanoate (1):** Elution of the column with petroleum ether gave colourless crystals of compound **1**, recrystallized from alcohol, 250 mg (1.25 % yield), m.p. 65-66 ºC, IR (KBr, ν_{max}, cm^{-1}): 2921, 2850, 1737, 1463, 1376, 1249, 1177, 1033, 720; ^{1}H NMR (DMSO-d_6) δ: 4.07 (1H, d, J = 6.6 Hz, H_2-1′α), 4.04 (1H, d, J = 6.6 Hz, H_2-1′b), 2.75 (1H, d, J = 7.5 Hz, H_2-2a), 2.73 (1H, d, J = 7.5 Hz, H_2-2b), 2.27 (2H, m, H_2-2), 2.01 (2H, m, H_2-3), 1.54 (2H, m, CH_2), 1.29 (30H, br s, 15 × CH_2), 1.25 (14H, br s, 7 × CH_2), 0.87 (6H, br s, Me-8′, Me-22); ^{13}C NMR (DMSO-d_6) δ: 171.16 (C-1), 60.13 (C-1′), 33.32 (CH_2), 30.92 (CH_2), 28.59 (21 × CH_2), 26.29 (CH_2), 24.12 (CH_2), 21.66 (CH_2), 18.78 (Me-22), 13.43 (Me-9′); MS m/z (rel. int.) 452 $[M]^+$ ($C_{30}H_{60}O_2$), 323 (13.6).

***n*-Eintriacontane (2):** Elution of the column with ethyl acetate yield colourless crystals of compound **2**, recrystallized from ethanol, 355 mg (1.7 % yield), m.p. 63-65 ºC; IR (KBr, ν_{max}, cm^{-1}): 2917, 2850, 1463, 1379, 1243, 1174, 1105, 720; ^{1}H MMR (DMSO-d_6) δ: 1.50 (2H, br s, CH_2), 1.25 (56H, br s, 28 × CH_2), 0.84 (6H, br s, Me-1, Me31); ^{13}C NMR (DMSO-d_6) δ: 33.30 (CH_2), 30.93 (CH_2), 28.60 (CH_2), 24.14 (26 × CH_2), 13.46 (Me-1), 13.01 (Me-31); MS m/z: (rel. int.) 436 $[M]^+$ ($C_{31}H_{64}$), 45.3.

Stigmasterol (3): Elution of the column with chloroform furnished colourless crystals of **3**, recrystallized from ethanol 650 mg (3.25 % yield), m.p. 168-170 ºC; IR (KBr, ν_{max}, MeOH nm): (log ε 268 (1.631), 279 (log ε 1.6); IR (KBr, ν_{max}, cm^{-1}): 3434, 2918, 2850, 1637, 1463, 1382, 1254, 1172, 1059; ^{1}H NMR (DMSO-d_6) δ: 5.32 (1H, br s, H-6), 5.26 (1H, m, H-22), 5.09 (1H, m, H-23), 4.06 (1H, br m, w½ = 18.5 Hz, H-3α), 1.25 (3H, br s, Me-19), 0.96 (3H, d, J = 6.0 Hz, Me-21), 0.86 (3H, d, J = 6.1 Hz, Me-26), 0.84 (3H, d, J = 6.3 Hz, Me-27), 0.82 (3H, d, J = 6.2 Hz, Me-29), 0.68 (3H, br s, Me-18). MS m/z: (ref. int.) 412 $[M]^+$ ($C_{29}H_{48}O_2$), 42.5.

^{13}C NMR (DMSO-d_6)

C	δC	C	δC	C	δC	C	δC
1	38.96	9	50.28	17	55.37	25	28.66
2	31.13	10	36.74	18	13.40	26	21.65
3	69.82	11	21.09	19	19.97	27	22.52
4	41.96	12	39.22	20	39.77	28	23.57
5	137.46	13	41.96	21	18.76	29	11.55
6	119.92	14	56.04	22	128.73	–	–
7	31.09	15	24.12	23	127.42	–	–
8	31.13	16	28.61	24	45.13	–	–

***n*-Tetratriacontanoic acid (4):** Elution of the column with methanol afforded colourless amorphous mass of compound **4**, recrystallized from ethanol, 225 mg (1.1 % yield), m.p. 82-85 ºC; IR (KBr, ν_{max}, cm^{-1}): 3391, 2921, 2851, 1669, 1384, 1078, 1038, 825, 719; ^{1}H NMR (DMSO-d_6) δ: 2.25 (1H, d, J = 6.6 Hz, H_2-2a) 2.19 (1H, d, J = 6.6 Hz, H_2-2b), 1.99 (2H, br m, H_2-3), 1.49 (2H, m, H_2-4), 1.23 (58H, br s, 25 × CH_2), 0.82 (3H t, J = 5.4 Hz, Me-34); ^{13}C NMR (DMSO-d_6) δ: 180.11 (C-1), 31.13 (C-2), 28.61 (25 × CH_2), 24.18 (CH_2), 22.33 (CH_2), 14.37 (CH_3-34); MS m/z: (rel. int.) 508 $[M]^+$ ($C_{34}H_{68}O_2$), 56.9.

***n*-Eintriacontan-8β-ol (5):** Further elution of the column with methanol gave colourless crystals of compound **5**, recrystallized from ethanol, 225 mg (1.12 % yield), m.p. 73-75 ºC; IR (KBr, ν_{max}, cm^{-1}): 3397, 2921, 2851, 1640, 1399, 1385, 1078, 1034, 825, 720; ^{1}H NMR (DMSO-d_6) δ: 3.15 (1H, br, m, w½ = 16.5 Hz, H-8α), 1.47)4H, br s, 2 × CH_2), 1.23 (52H, br s, 26 × CH_2), 0.85 (6H, br s, Me-1, Me-31); ^{13}C NMR (DMSO-d_6) δ: 77.89 (C-8), 33.95 (C-7), 31.33 (C-9), 29.49 (21 × CH_2), 29.16 (3 × CH_2), 24.49 (CH_2), 22.71 (CH_2), 13.95 (Me-1, Me-31); MS m/z: (rel. int.) 452 $[M]^+$ ($C_{31}H_{64}O$) (12.3), 323 (8.9).

RESULTS AND DISCUSSION

The petroleum ether eluents of the ethanolic extracts of *A. excelsa* bark gave a colourless crystalline mass of **1** which did not decolourize bromine water indicating saturated nature of the molecule. IR spectra showed characteristics absorption bands for the ester groups at 1737 cm^{-1} and long aliphatic chain (720 cm^{-1}). The mass spectrum gave molecular ions peaks at m/z 452 corresponding to aliphatic ester of the C-22 acid. A prominent ions peak at m/z 323 generated due to cleavage of the C_1-O linkage indicated that *n*-octyl alcohol was esterified with C-22 acids. ^{1}H NMR spectrum of **1** exhibited two one-proton doublet at δ 4.07 (J = 6.6 Hz) and 4.04 (J = 6.6 Hz) assigned to oxygenated methylene protons H_2-1, another of two one-proton doublets at δ 2.75 (J = 7.5 Hz) and 2.73 (J = 7.5 Hz) was ascribed to C-2 methylene

protons adjacent to the ester group. Three multiplets at δ 101 (2H), 2.01 (2H) and 1.54 (2H) and two broad signals at δ 1.29 (30H) and 1.25 (14H) were attributed to the remaining methylene protons. A six proton broad signal at δ 0.87 was accounted to C-22 and C-8 primary, methyl protons. The ^{13}C NMR spectrum of **1** showed signals for ester carbon at δ 171.16 (C-1) oxygenated methylene carbon at δ 60.13 (C-1), methylene carbon between δ 33.32-21.66 and methyl carbons at δ 18.78 (Me-22) and 13.43 (Me-8). The absence of any signal beyond δ 4.07 in the ^{1}H NMR spectrum and between δ 171.16-60.13 in ^{13}C NMR spectrum supported the saturated nature of the molecule. Acid hydrolysis of **1** yielded a fatty acid which gave effervescences with sodium bicarbonate solution. Thus, on the basis of spectral data analysis and chemical reaction, the compound **1** elucidated as *n*-octanyl decasanoate.

The ethyl acetate eluents of the column afforded colourless crystalline mass of **2**. It did not decolourized with bromine water and also not reacted with the normal acetylating and oxidizing reagents indicating saturated nature of the molecule and devoid of any functional group. IR spectrum did not show presence of any characteristic band in the functional group region. The ^{1}H NMR spectrum of **2** showed the broad signals for methylene protons at δ 1.50 (2H) and 1.25 (56H) and a six protons broad signals at δ 0.84 ascribed to terminal C-1 and C-31 primary methyl protons. Its ^{13}C NMR spectrum signals for methylene carbons between δ 33.30-24.14 and methyl carbons at 13.46 and 13.01. The mass spectrum showed a molecular ion peaks at m/z 436 corresponding to the saturated aliphatic hydrocarbon ($C_{31}H_{64}$). On the basis of the foregoing discussion the structure of compound **2** has been identified as *n*-eintriacontane.

The chloroform eluents of the column furnished colourless mass of compound **3**. It gave positive Liebermann Burchard test indicating steroidal nucleus. IR spectrum showed characteristics absorption bands for hydroxyl group at δ 3434 cm^{-1} and unsaturation at δ 1637 cm^{-1}. Its mass spectrum displayed a molecular ions peak at m/z 412 assigned to a sterol. ^{1}H NMR spectrum of compound **3** showed one-proton broad signal at δ 5.32 assigned to vinylic H-6. Two one-proton multiplets at δ 5.26 and 5.09 were attributed to vinylic H-22 and H-23, respectively. A one-proton broad multiplets at δ 4.06 with half width of 18.5 Hz was ascribed to α-oriented H-3 carbinol proton. Two three-proton broad at δ 1.25 and 0.68 were accounted to C-19 and C-18 teritary methyl signals. Three doublet at δ 0.96 (J = 6.0 Hz), 0.86 (J = 6.1 Hz), 0.84 (J = 6.3 Hz), all integrated for three protons, were associated with secondary C-21, C-26 and C-27 and primary C-29 methyl protons, respectively. The presence of all the methyl signals between δ 1.25-0.68 indicated their attachments to saturated carbon. ^{13}C NMR spectrum showed the presence C_{29} atoms. The methyl carbons resonated at δ 13.40 (C-18),

19.97 (C-19), 18.76 (C-21), 21.65 (C-26), 22.52 (C-27) and δ 11.55 (C-29). The vinylic carbons resonated at δ 137.46 (C-5), 119.92 (C-6), 128.73 (C-22) and 127.42 (C-23). On the basis of foregoing discussion of structure **3** has been determined as stigmast-5,22-diene-3β-ol.

The methanolic eluents of the column furnished a colourless amorphous mass of compound **4**. It gave effervescences with sodium bicarbonate solution indicating carboxylic nature of the molecule. IR spectrum showed characteristics absorption bands for carboxylic groups (3391, 1669 cm^{-1}) and long aliphatic chain (825, 719 cm^{-1}). The mass spectrum showed a molecular ions peak at m/z 508 corresponding a long chain aliphatic fatty acid ($C_{34}H_{68}O_2$). It indicated one double equivalent which was adjusted in the carboxylic groups. ^{1}H NMR spectrum of **4** showed two one-proton doublets at δ 2.25 (J = 6.6 Hz) and δ 2.19 (J = 6.6 Hz) assigned to methylene protons adjacent to the carboxylic groups, two multiplets at δ 1.99 and δ 1.49, both integrated for two proton each and a broad signal at 1.23 (58H) were ascribed to the methylene protons. A three-proton triplet at δ 0.82 (J = 5.4 Hz) was attributed to the terminal C-34 primary methyl proton. ^{13}C NMR spectrum of compound **4** showed signals for carboxylic carbon at δ 180.11, methylene carbons between δ 31.13-22.33 and C-34 methyl carbon at δ 14.37. The absence of any signal beyond δ 2.25 in the ^{1}H NMR spectrum and between δ 180.11-31.13 in the ^{13}C NMR spectrum indicated the saturated nature of molecule. On the basis of the foregoing evidences the structure of the compound **4** has been identified as *n*-tetratriacontanoic acid.

The methanol eluents of the column gave a colourless crystalline mass of compound **5**. It did not decolourized bromine water and also failed to give yellow colour with tetranitromethane indicating saturated nature of the molecule. The IR spectrum showed characteristics absorption bands for alcoholic group (3397 cm^{-1}) and long alihatic chain (825, 725 cm^{-1}). The mass spectrum showed a molecular ions peak at m/z 452 corresponding to a saturated aliphatic alcohol ($C_{31}H_{64}O$). A prominent ion peak generated at m/z 323 due to fission of C7-C8 linkage indicated the existence of the hydroxyl group at C-8. ^{1}H NMR spectrum of **5** displayed a one-proton broad multiplets at δ 3.15 with half-width of δ 16.5 Hz assigned to α-oriented C-8 carbinol proton. Two broad signals at δ 1.47 (4H) and δ 1.23 (52H) were accumulated to the methylene protons. A six-proton broad signal at δ 0.85 was associted with C-1 and C-31 terminal methyl protons. ^{13}C NMR spectrum showed signal for carbinol carbon at δ 77.89 (C-8), methylene carbons between δ 33.95-22.71 and methyl carbon at 13.95 Hz. The absence of any signal beyond δ 3.15 in the ^{1}H NMR spectrum and 77.89 Hz in the ^{13}C NMR spectrum supported the saturated nature of the molecule. On the basis of the spectral data analysis and chemical reactions the structure of compound **5** has been characterized as *n*-eintriacontan-8β-ol. This is a new aliphatic alcohol isolated from natural source for the first time.

ACKNOWLEDGEMENT

The authors are thankful to the Head, SAIF, CDRI, Lucknow for scanning the various spectra.

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(*Received*: 6 September 2007; *Accepted*: 2 May 2008) AJC-6562