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Aliphatic Constituents from the Leaves of *Dillenia indica* L., *Halothamus bottae* Jaub. and *Xylosma longifolium* Clos

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Abstract The leaves of *Dillenia indica* L. (Dilleniaceae), are used to treat cold, cough, diarrhoea, fever, swellings and wounds. *Halothamnus bottae* Jaub. et Spach (Amaranthaceae) is useful to relieve women diseases and to strengthen the hair. *Xylosma longifolium* Clos **(**Flacourtiaceae) is beneficial to cure dysentery, insomnia, anxiety, acne, piles, ringworm, scabies, stomachache, liver diseases and physical injuries. Our study was planned to isolate chemical constituents of the methanolic extracts of the leaves of *D. indica*, *H. bottae* and *X. longifolium* and to characterize their structures using spectral data analysis.

The air-dried plant materials were exhaustively extracted with methanol in a Soxhlet apparatus. The concentrated methanol extracts were adsorbed on silica gel (60-120 mesh) for preparation of slurries. The dried slurries were chromatographed over silica gel columns individually. The columns were eluted with petroleum ether, chloroform and methanol, successively, in order of increasing polarity to isolate the chemical constituents. Phytochemical investigation of the leaves of *D. indica* afforded *n*-nonyl oleate (**1**), *n*-heptacosan-9-one (**2**), *n*-nonatriacontan-20-one (**3**) and stigmasteryl palmitate (**4**). The leaves of *H. bottae* furnished *n*-hexacosane (**5**), 1-triacosanol (**6),** 1-triacontanol (**7**), 1-henetriacontanol **(8**), stigmasterol (**9**) and 1-tritriacontanol (**10**). The leaves of *X. longifolium* on subjection to silica gel column chromatography led to isolate *n*-hentriacontane (**11**) and β-sitosterol (**12**).

Keywords *Dillenia indica*, *Halothamnus bottae***,** *Xylosma longifolium*, leaves, phytoconstituents, isolation, characterization

Introduction

Dillenia indica L., syn. *D. elongata* Miq., *D. speciosa* Thunb., *D. speciosa* Thunberg (Dilleniaceae), known as outenga, elephant apple, chulta, Indian catmon and hondapara tree, is found in China, India, Sri Lanka and other south-eastern Asian countries. It is an evergreen medium-sized tree, up to 15 m tall; leaves oblong-lanceolate, acuminate, serrated, glabrous above, silky beneath with a corrugated surface and impressed veins; flowers solitary, large, white, with numerous yellow stamens; fruits large, greenish yellow, round, edible, pulp fibrous; seeds many. A leaf or stem bark paste is applied to cure swellings and wounds. The leaves, bark and fruits are used as an astringent, laxative and to treat cold, cough, diarrhoea and fever. The fruit is taken as a cardiotonic, expectorant and galactagogue, to relieve abdominal disorders, hydrocele, debility and to wash the hair.

Fruits mucilage is applied to kill lice and to heal burns and dandruff. The bark is utilized to cure boils and as a mouthwash to treat thrush [1-3]. The leaves contained dillenetin, betulinic acid, alkyl ketones, phytosterols and quercetin [4-6]. The flowers and fruits possessed tannins, malic acid, arabinogalactan, glucose, betulin, betulinic acid and flavonoids [7,8]. The stem, bark and wood yielded flavonoids, betulin, betulinic acid, betulinaldehyde, lupeol, β-sitosterol, myricetin, hydroxylactone, dihydroisorhamnetin, dillentin and glucosides [9,10].

Halothamnus bottae Jaub. et Spach, syn. *Caroxylon bottae* (Jaub. et Spach) Moq., *Salsola bottae* (Jaub. et Spach) Boiss. (Amaranthaceae), commonly known as hamḍ al-arnab, tiḥyan, hamdeh, kizzot, asal and tanēt, is found in Saudi Arab, Oman, UAE, Yemen, Turkey, Azerbaizan, Afganistan, Turkistan, China and Pakistan [11]. It is a standing, much branched, 30-50 cm high herb with bluish-green, thorny branches, triangular leaves; flowers solitary in axils and winged fruits. In Oman, the dried parts of *H. bottae* are taken as a snuff. The plant is grown as a fodder for animals, used to strengthen hair, to treat women diseases and for sheep to cure anthrax, scabies and wounds. The roots of *H. somalensis* are given against parasitic worm diseases in animals or humans [12,13]. Quercetin 3-O-glucoside, apigenin 8C-glucoside, quercetin 3′,4′-dimethyl ether, flavones, allantoic acid, allantoin, oleanolic acid, β-sitosterol, its 3-O-glucoside and lupeol were isolated from the whole plant of *H. auriculus* [14].

Xylosma longifolium Clos, syn. *X. fascicuflorum* S. S. Lai **(**Flacourtiaceae), known as batti, diệp tạc mộc and Mộc hương lá dài, is distributed in the sub-Himalayan zone from west Pakistan to the eastern Himalaya in India and in China. It is a medium sized trees having scented wood; acute, glabrous, elliptic, oblong to lanceolate, serrate, petioled leaves; flowers in short branched racemes; fruit globose, small, black; seeds oblong to obovoid. The plant is used for intoxication and to treat dysentery, insomnia and anxiety. The leaves and stem bark are utilized to cure acne, piles, ringworm, scabies and stomachache [15-17]. In Vietnam, the plant is recommended to relieve liver diseases and physical injuries [18]. The stem bark contained xylongosides A and B, 8-hydroxy-6-methoxy-pentylisocoumarin, 2-(6-benzoyl-β-D-glucopyranosyloxy)-7-(l,2,6-trihydroxy 5-oxocyclohex-3-enoyl)-5-hydroxy-benzyl alcohol, friedelin, epifriedelanol, atraric acid and methyl orsellinate [19]. The leaves afforded β-sitosterol, β-amyrin, friedelin, olean-12-en-3α-ol-28-oic acid 3α-D-glucopyranoside, kaempferol, quercetin, kaempferol-3-rhamnoside, quercetin-3-rhamnoside, rutin, catechin, and kaempferol-3-β-xylopyranoside-4′-α-rhamnoside [20-22]. Keeping in view the high reputation and application of *Dillenia indica*, *Halothamnus bottae* and *Xylosma longifolium* in the indigenous medicinal systems, it has been aimed to carry out isolation and characterization of chemical constituents from the leaves of these plants.

Material and Methods

General Procedures

Melting points were determined on a Perfit melting point apparatus and are uncorrected. UV spectra were determined on Shimadzu-120 double beam spectrophotometer with methanol as a solvent. IR spectra were recorded in KBr pellet on a Shimadzu FTIR-8400 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were scanned on a Bruker DRX (300 MHz) instrument using TMS as an internal standard and coupling constants (J values) are expressed in Hertz (Hz). Mass spectra were recorded by affecting electron impact ionization at 70 eV on a Jeol SX-102 mass spectrometer equipped with direct inlet prob system. The *m/*z values of the more intense peaks are mentioned and the figures in bracket attached to each *m/*z values indicated relative intensities with respect to the base peaks. Column chromatography was performed on silica gel (60-120 mesh; Qualigen, Mumbai, India). TLC was run on silica gel G 60 F_{254} precoated TLC plates (Merck, Mumbai, India). Spots were visualised by exposing to iodine vapours and UV radiations (254 and 366 nm) and spraying with ceric sulphate solution.

Plant Materials

The leaves of *D. indica*, *H. bottae* and *X. longifolium* were collected from Delhi, Dehradun (Uttarakhand, India) and Jazan (Saudi Arabia), respectively, and authenticated by Prof. M. P. Sharma, Taxonomist, Department of Botany, Jamia Hamdard, New Delhi. Their voucher specimens are preserved in the herbarium of the Department of Pharmacognosy and Phytochemistry, Jamia Hamdard, New Delhi.

Extraction and Isolation

One kilogramme (1 kg) each of the leaves of of *D. indica*, *H. bottae* and *X. longifolium* were coarsely powdered and extracted separately and exhaustively with methanol in a Soxhlet apparatus. The extracts were concentrated under reduced pressure to get dark brown masses, 123.4 g, 132.6 g and 116.2 g, respectively. The dried residue (100 g each) was dissolved in minimum amount of methanol and adsorbed on silica gel column grade (60-120 mesh) separately to obtain slurries. Each slurry was air-dried and chromatographed over silica gel columns loaded in petroleum ether (b. p. 60 - 80°C) individually. Each column was eluted with petroleum ether, petroleum ether - chloroform (9:1, 3:1, 1:1, 1:3, *v/v*) and chloroform. Various fractions were collected separately and matched by TLC to check homogeneity. Similar fractions having the same R_f values were combined and crystallized with solvents. The isolated compounds were recrystallized to get pure compounds.

Isolation of Phytoconstituents from the Leaves of *Dillenia indica*

***n*-Nonyl oleate (1)**

Elution of the column with petroleum ether gave a pale yellow semisolid mass of **1**, yield 208 mg, IR γ_{max} (KBr) : 2924, 2853, 1736, 1646, 1457, 1374, 1171, 1093, 980, 726 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.38 (1H, m, H-9), 5.33 (1H, m, H-10), 4.54 (2H, t, J = 7.8 Hz, H_2 -1′), 2.81 (2H, t, J = 5.3 Hz, H_2 -2), 2.32 (2H, m, H_2 -8), 2.06 (2H, m, H_2 -11), 1.71 (2H, m, CH_2), 1.62 (2H, m, CH_2), 1.34 (4H, m, 2 x CH_2), 1.28 (28H, brs, 14 × CH_2), 0.87 (3H, t, J = 6.3 Hz, Me-18), 0.83 (3H, t, J = 6.5 Hz, Me-9′); ^{13}C NMR ($CDCl_3$): δ 171.24 (C-1), 128.26 (C-9), 117.51 (C-10), 64.25 (C-1′), 33.62 (C-2), 31.33 (CH_2), 29.14 (21 x CH_2), 28.95 (CH_2), 27.66 (CH_2), 25.17 (CH_2), 22.67 (CH_2), 14.16 (Me - 18), 13.91 (Me - 9′); ESI MS *m/*z (rel.int.): 408 $[M]^+$ ($C_{27}H_{520}O_2$) (3.8), 281 (8.5), 265 (14.8).

***n*-Heptacosan-9-one (2)**

Elution of the column with petroleum ether – chloroform (1:1) furnished colorless powder of **2**, 186 mg, m. p. 86 - 88 °C, UV λmax (MeOH): 212 nm; IR γ_{max} (KBr): 2917, 2849, 1706, 1635, 1467, 1374, 1305, 1118, 1046, 726 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.35 (2H, m, H_2-8), 2.02 (2 H, t, J = 7.2 Hz, H_2-10), 1.67 (2 H, m, CH_2), 1.56 (2 H, m, CH_2), 1.32 (2 H, m, CH_2), 1.27 (38 H, br s, 19 x CH_2), 0.88 (3 H, t, J = 6.5 Hz, Me-1), 0.82 (3 H, t, J = 6.3 Hz, Me-27); ^{13}C NMR ($CDCl_3$): δ 193.78 (C-9), 31.94 (CH_2), 29.75 (21 x CH_2), 29.33 (CH_2), 22.72 (CH_2), 14.29 (Me-1), 14.10 (Me-27); ESI MS *m/*z (rel. int.): 394 $[M]^+$ ($C_{27}H_{54}O$) (33.6), 281 (8.8), 253 (6.9), 113 (12.5).

***n*-Nonatriacontan-20-one (3)**

Elution of the column with chloroform afforded colorless amorphous powder of **3**, 225 mg, m. p. 91 - 92 °C, UV λmax (MeOH): 213 nm; IR *γ*max (KBr): 2928, 2851, 1707, 1633, 1454, 1289, 1249, 943, 723 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.37 (4H, t, J = 7.6 Hz, H_2-19, H_2-21), 2.07 (4H, m, 2 x CH_2), 1.65 (2H, m, CH_2), 1.55 (2H, m, CH_2), 1.34 (4 H, m, 2 × CH_2), 1.28 (56 H, brs, 28 × CH_2), 0.89 (3H, t, J = 6.3 Hz, Me-1), 0.85 (3H, J = 6.2 Hz, Me-39); ^{13}C NMR ($CDCl_3$): δ 195.73 (C-7), δ 31.92 - 22.67 (36 x CH_2), 13.22 (C-1), 12.91 (C-39); ESI MS *m/*z: 562 $[M]^+$ ($C_{39}H_{78}O$) (2.5), 295 (48.7), 267 (18.1).

Stigmasteryl palmitate (**4**)

Further elution of the column with chloroform yielded colourless amorphous powder of **3**, recrystallized from chloroform, 237 mg, R_f : 0.42 (chloroform); m. p. 125-127 ^{o} C; UV λmax (MeOH): 207, 232 (log ε 4.2, 3.1); IR νmax (KBr): 2927, 2857, 1733, 1640, 1461, 1375, 1251, 1118, 1049, 963, 727 cm^{-1} ; ^1H NMR ($CDCl_3$): δ 5.35 (1H, m, H-6), 5.22 (1H, m, H-22), 5.11 (1H, m, H-23), 4.01 (1H, brm, $w_{1/2}$ = 16.5 Hz, H-3α), 1.04 (3H, brs, Me-19), 0.94 (3H, d, J = 6.3 Hz, Me-21), 0.89 (3H, d, J = 6.4 Hz, Me-26), 0.86 (3H, d, J = 6.1 Hz, Me27), 0.82 (3H, t, J = 6.1 Hz, Me-16′), 0.79 (3H, t, J = 6.3 Hz, Me-29), 0.68 (3H, brs, Me-18), 2.48 (2H, t, J = 7.2 Hz, H_2 -2′), 2.27 to 2.03 (4H, m, H_2 - 3′, H_2 -4′), 1.25 (22H, brs, 11 × CH_2); ^{13}C NMR ($CDCl_3$): δ 37.24 (C-1), 31.53 (C-2), 69.76 (C-3), 42.23 (C-4), 141.06 (C-5), 121.18 (C-6), 31.81 (C-7), 33.85 (C-8), 51.10 (C-9), 36.44 (C-10), 21.16 (C-11), 39.12 (C-12), 42.11 (C-13), 56.78 (C-14), 24.19 (C-15), 28.12 (C-15), 28.12 (C-16), 55.95 (C-17), 11.89 (C-18), 20.96 (C-19), 36.01 (C-20), 18.69 (C-21), 138.20 (C-22), 129.14 (C-23), 45.73 (C-24), 29.08 (C-25), 19.31 (C-26), 19.71 (C-27), 22.54 (C-28), 11.76 (C-29), 175.88 (C-1′), 50.07 (C-2′), 34.11 (C-3′), 29.54 (C-4′ to C-9′), 29.35 (C-10′), 29.20 (C-11′), 28.76 (C-12′), 26.02 (C-13′), 25.26 (C-14′), 22.97 (C-15′), 12.13 (C-16′); ESI MS *m/*z (rel. int.): 650 $[M]^+$ ($C_{45}H_{78}O_2$) (2.1), 411 (30.2), 397 (100), 395 (52.1), 381 (12.1), 255 (13.6), 239 (30.6).

Isolation of Phytoconstituents from the Leaves of *Halothamnus bottae*

***n*-Hexacosane (5)**

Elution of the column with petroleum ether afforded colourless amorphous powder of **5**, m. p. 55 - 58 °C; UV λ_{max} (MeOH): 207 nm (log ε 3.2). IR γ_{max} (KBr): 2957, 2845, 1469, 1375, 1255, 1115, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.54 (2H, m, CH_2), 1.32 (2H, m, CH_2), 1.29 (2H, m, CH_2), 1.27 (8H, m, 4 x CH_2), 1.25 (32H, brs, 16 x CH_2), 1.20 (2H, m, CH_2), 0.88 (3H, t, J = 6.4 Hz, Me-1), 0.84 (3H, t, J = 6.5 Hz, Me-26); ^{13}C NMR ($CDCl_3$): δ 31.94 (CH_2), 29.97 (15 x CH_2), 29.72 (CH_2), 29.68 (CH_2), 29.51 (CH_2), 29.47 (CH_2), 29.43 (CH_2), 29.37 (CH_2), 25.75 (CH_2), 22.71 (CH_2), 14.13 (Me-1, Me-26); ESI MS *m/z* (rel. int.): 366 $[M]^+$ ($C_{26}H_{54}$) (100).

1-Tricosanol (6)

Further elution of the column with petroleum ether produced colourless amorphous powder of **6**, yield 46 mg, m. p. 62 - 63 °C; IR γ_{max} (KBr): 3411, 2919, 2850, 1467, 1060, 724 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.65 (2H, t, J = 6.8 Hz, H_2-1), 1.58 (2H, m, H_2-2), 1.54 (2H, m, CH_2), 1.33 (2H, m, CH_2), 1.30 (4H, br s, 2 x CH_2), 1.25 (32H, br s, 16 × CH_2), 0.88 (3H, t, J = 6.5 Hz, Me-23); ^{13}C NMR ($CDCl_3$): δ 63.12 (C-1), 32.82 (C-2), 31.94 CH_2), 29.71 (13 × CH_2), 29.68 (CH_2), 29.63 (CH_2), 29.45 (CH_2), 29.37 (CH_2), 25.75 (CH_2), 22.70 (CH_2), 14.13 (Me-30); FAB MS (+ve ion) *m/*z (rel. int.): 340 $[M]^+$ ($C_{23}H_{48}O$) (27.8).

1-Triacontanol (7)

Elution of the column with petroleum ether - chloroform (1 : 1) yielded colourless amorphous powder of **7**, yield 69 mg, m. p. 85 - 86 °C; IR (KBr) γ_{max}: 3395, 2918, 2850, 1458, 1261, 1059, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.64 (2H, t, J = 6.5 Hz, H_2-1), 1.56 (2H, m, H_2-2), 1.53 (2H, m, CH_2), 1.32 (2H, m, CH_2), 1.30 (2H, m, CH_2), 1.27 (8H, br s, 4 × CH_2), 1.25 (40H, br s, 20 × CH_2), 0.88 (3H, t, J = 6.4 Hz, Me-30); ^{13}C NMR ($CDCl_3$): δ 63.16 (C-1), 32.77 (C-2), 31.89 (CH_2), 29.74 (21 × CH_2), 29.56 (CH_2), 29.41 (CH_2), 29.33 (CH_2), 25.71 (CH_2), 22.69 (CH_2), 14.16 (Me-30); FAB MS (+ve ion) *m/z* (rel. int.): 438 $[M]^+$ ($C_{30}H_{62}O$) (100).

1-Henetriacontanol (8)

Further elution of the column with petroleum ether - chloroform (1 :1) gave colourless amorphous powder of **8**, yield 48 mg, m. p. 86 - 87 °C; IR (KBr) γ_{max}: 3423, 2917, 2852, 1467, 1261, 1163, 1062, 724 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.66 (2H, t, J = 6.8 Hz, H_2-1), 1.63 (2H, m, H_2-2), 1.58 (2H, m, CH_2), 1.35 (2H, m, CH_2), 1.31 (4H, m, 2 x CH_2), 1.29 (4H, br s, 2 × CH_2), 1.25 (44H, br s, 22 × CH_2), 0.88 (3H, t, J = 6.5 Hz, Me-31); ^{13}C NMR ($CDCl_3$): δ 63.13 (C-1), 32.82 (C-2), 31.94 (CH_2), 29.71 (19 × CH_2), 29.68 (CH_2), 29.63 (CH_2), 29.58 (CH_2), 9.52 (CH_2), 29.45 (CH_2), 29.35 (CH_2), 25.75 (CH_2), 22.70 (CH_2), 14.13 (Me-31); FAB MS (+ve ion) *m/z* (rel. int.): 452 $[M]^+$ ($C_{31}H_{64}O$) (32.4).

Stigmasterol (9)

Elution of the column with chloroform yielded a colourless amorphous powder of **9**, yield 187 mg; m. p. 166-168 °C; R_f 0.43 (petroleum ether - chloroform - methanol , 7:1:2, *v/v/v*); UV λ_{max} (MeOH): 211 nm (log ε 5.8); IR γ_{max} (KBr): 3425, 2920, 2852, 1641, 1463, 1373, 1225, 1173, 801 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.28 (1H, m, H-6), 5.08 (1H, m, H-22), 4.95 (1H, m, H-23), 3.45 (1H, brm, $w_{1/2}$ = 16.5 Hz, H-3α), 2.23 to 1.01 (25 H, m, 9 x CH_2. 7 x CH), 1.13 (3H, brs, Me-19), 0.97 (3H, d, J = 6.3 Hz, Me-21), 0.84 (3H, d, J = 6.6 Hz, Me-26), 0.75 (3H, d, J = 6.0 Hz, Me-27), 0.73 (3H, d, J = 6.6 Hz, Me-29), 0.62 (3H, brs, Me-18); ^{13}C NMR ($CDCl_3$): δ 36.52 (C-1), 31.90 (C-2), 71.81 (C-3), 41.90 (C-4), 140.75 (C-5), 121.72 (C-6), 31.66 (C-7), 33.94 (C-8), 51.24 (C-9), 37.26 (C-10), 21.07 (C-11), 39.76 (C-12), 42.30 (C-13), 56.87 (C-14), 24.17 (C-15), 28.67 (C-16), 55.96 (C-17), 11.99 (C-18), 19.41 (C-19), 36.68 (C-20), 18.79 (C-21), 138.33 (C-22), 129.27 (C-23), 45.83(C-24), 27.28 (C-25), 19.83 (C-26), 18.99 (C-27), 23.11 (C-28), 11.87 (C-29); EIMS *m/*z (rel. int.): 412 $[M]^+$ ($C_{29}H_{48}O$) (76.2), 396 (51.2), 394 (41.3), 381 (21.2), 271 (38.2), 255 (66.6), 240 (27.2), 213 (36.5).

1-Tritriacontanol (**10**)

Further elution of the column with chloroform furnished colourless crystals of **10**, yield 71 mg, m. p. 88 - 89 °C; IR γ_{max} (KBr): 3401, 2919, 2849, 1473, 1258, 1161, 1059, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.63 (2H, t, J = 6.9 Hz, H_2-1), 1.59 (2H, m, H_2-2), 1.54 (2H, m, CH_2), 1.33 (2H, m, CH_2), 1.31 (4H, m, 2 x CH_2), 1.29 (4H, br s, 2 × CH_2), 1.25

(48H, br s, 24 × CH_2), 0.88 (3H, t, J = 6.5 Hz, Me-33); ^{13}C NMR ($CDCl_3$): δ 63.11 (C-1), 32.83 (C-2), 31.95 (CH_2), 29.70 (2 × CH_2), 29.63 (18 x CH_2), 29.58 (CH_2), 29.55 (CH_2), 29.51 (CH_2), 29.48 (CH_2), 29.45 (CH_2), 29.41 (CH_2), 29.38 (CH_2), 25.75 (CH_2), 22.71 (CH_2), 14.15 (Me-33); ESI MS *m/*z (rel. int.): 480 $[M]^+$ ($C_{33}H_{68}O$) (8.3).

Isolation of Phytoconstituents from the Leaves of *Xylosma longifolium*

***n*-Hentriacontane (11)**

Elution of the column with petroleum ether – chloroform (1:1) furnished a colourless crystals of **11**, recrystallized from acetone - methanol (1:1), 1.88 mg, m. p. 68 - 71 °C; UV λ_{max} (MeOH): 206 nm (log ε 2.6); IR υ_{max} (KBr): 2931, 2852, 1453, 1372, 1169, 1078, 1017, 795 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.25 (2H, m, CH_2), 1.88 (2H, m, CH_2), 1.53 (2H, m, CH_2), 1.42 (2H, m, CH_2), 1.37 (2H, m, CH_2), 1.28 (2H, m, CH_2), 1.25 (46H, brs, 23 x CH_2), 0.91 (3H, t, J = 6.9 Hz, Me-1), 0.82 (3H, t, J = 6.3 Hz, Me-31); ^{13}C NMR ($CDCl_3$): δ 31.89 (CH_2), 29.71 (CH_2), 29.68 (12 x CH_2), 29.63 (14 x CH_2), 29.32 (CH_2), 29.37 (CH_2), 24.38 (CH_2), 22.679 (CH_2), 14.16 (Me-35), 14.13 (Me-1); ESI MS *m/*z (rel. int.): 436 $[M]^+$ ($C_{31}H_{64}$) (12.8).

β-Sitosterol (12)

Elution of the column with petroleum ether - chloroform (1:3) yielded colourless amorphous powder of **12**, R_f 0.35 (chloroform – methanol, 9: 1); m. p. 137-138 ^{o}C; UV λ_{max} (MeOH): 211 nm (log ε 2.9); IR γ_{max} (KBr): 3401, 2918, 2849, 1654, 1377, 1261, 1172, 1082 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.34 (1H, m, H- 6), 3.54 (1H, brs, $w_{½}$ = 18.5 Hz, H-3), 1.01 (3H, brs, Me-19), 0.94 (3H, d, J = 6.2 Hz, Me-21), 0.87 (3H, d, J = 6.5 Hz, Me-27), 0.84 (3H, J = 6.3 Hz, Me-26), 0.82 (3H, t, J = 6.1 Hz, Me-29), 0.67 (3H, brs, Me-18), 2.28 - 1.05 (29H, 11 x CH_2, 7 x CH); ^{13}C NMR ($CDCl_3$): δ 37.28 (C- 1), 31.93 (C- 2), 71.81 (C- 3), 42.34 (C- 4), 140.78 (C- 5), 121.68 (C- 6), 29.33 (C- 7), 34.23 (C- 8), 50.21 (C- 9), 36.14 (C- 10), 22.66 (C- 11), 38.89 (C- 12), 39.81 (C- 13), 56.80 (C- 14), 27.21 (C- 15), 28.22 (C- 16), 56.11 (C- 17), 11.85 (C- 18), 19.33 (C- 19), 36.73 (C- 20), 19.03 (C- 21), 33.98 (C- 22), 26.18 (C- 23), 45.90 (C- 24), 29.68 (C- 25), 21.07 (C- 26), 19.78 (C- 27), 24.94 (C- 28), 11.97 (C- 29); EIMS *m/*z (rel.int.): 414 $[M]^+$ ($C_{29}H_{50}O$) (22.3), 398 (100), 383 (13.5).

Results and Discussion

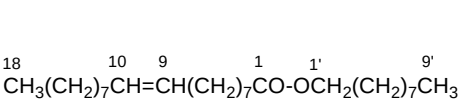
Compound **1** was a fatty ester identified as *n*-nonyl oleate [23].

Compound **2** showed IR absorption bands for carbonyl group (1706 cm^{-1}) and long aliphatic chain (726 cm^{-1}). Its mass spectrum displayed a molecular ion peak at *m/*z 394 corresponding to a molecular formula of an aliphatic ketone, $C_{27}H_{54}O$. The ion peaks generating at *m/*z 281 [$C_9 - C_{10}$ fission, CH_3 $(CH_2)_{19}CO]^+$, 113 [M – 281, CH_3-$(CH_2)_7]^+$ and 253 [$C_9 - C_{10}$ fission, CH_3 $(CH_2)_{17}]^+$ suggested the presence of the carbonyl function at C_9 carbon. The ^{1}H NMR spectrum of **2** exhibited five two-proton signals as a triplet at δ 2.02 (J = 7.2 Hz, H_2-10), as multiplets at δ 2.35, 1.67, 1.56, 1.32 and 1.27 and as a broad singlet at δ 1.27 (38H) assigned to methylene protons. Two three-proton triplets at δ 0.88 (J = 6.5 Hz) and 0.82 (J = 6.3 Hz) were accounted to terminal C-1 and C-27 primary methyl protons, respectively. The ^{13}C NMR spectrum of **2** showed signals for the carbonyl carbon at δ 193.78 (C-9), methylene carbons between δ 31.94 - 22.72 and methyl carbons at δ 14.29 (C-1) and 14.10 (C-27). The absence of any signal beyond δ 2.35 in the ^{1}H NMR spectrum and between δ 193.78 - 31.94 in the ^{13}C NMR spectrum ruled out the unsaturated nature of the molecule. On the basis of foregoing spectral data analysis, the structure of **2** has been elucidated as *n*-heptacosan-9-one, a new aliphatic ketone (Fig. 1).

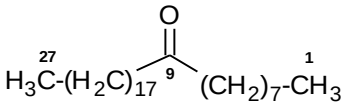
Compound **3**, $[M]^+$ at *m/*z 562 ($C_{39}H_{78}O$), exhibited IR absorption bands for carbonyl group (1707 cm^{-1}) and long aliphatic chain (723 cm^{-1}). The ion peaks produced at *m/*z 295 [$C_{20} - C_{19}$ fission, CH_3 $(CH_2)_{18}CO]^+$ and 267 [M - 295, CH_3 $(CH_2)_{18}]^+$ suggested the existence of the carbonyl function at C_{20} carbon. The ^{1}H NMR spectrum of **3** displayed a four - proton triplet at δ 2.37 (J = 7.6 Hz) assigned to methylene H_2-19 and H_2-21 protons adjacent to the carbonyl function, four multiplets at δ 2.07 (4H), 1.65 (2H), 1.55 (2H) and 1.34 (4H) and a broad singlet at δ 1.28 (56) associated with the remaining methylene proton and two three - proton triplets at δ 0.89 (J = 6.3 Hz) and 0.85 (J = 6.2 Hz) accounted to terminal C-1 and C-39 primary methyl protons, respectively. The ^{13}C NMR spectrum of **3** showed signals for the carbonyl carbon at δ 195.73 (C - 7), methylene carbons between δ 31.92 - 22.67 and methyl carbons at δ 13.22 (C-1) and 12.91 (C-40). The absence of any signal beyond δ 2.33 in the ^{1}H NMR spectrum and

between δ 195.73 - 31.92 in the ^{13}C NMR spectrum supported saturated nature of the molecule. On the basis of foregoing spectral data analysis, the structure of **3** has been elucidated as *n*-nonatriacontan-20-one, a new aliphatic ketone (Fig. 1).

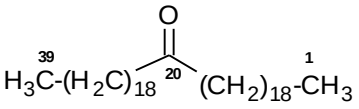
Compound **4** was a known steroidal ester characterized as sigmasteryl palmitate [24,25].



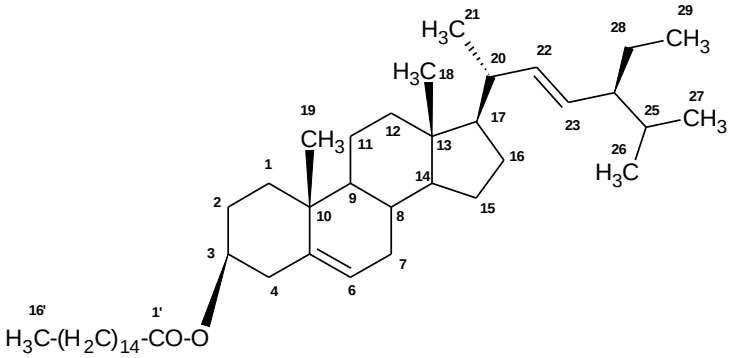
n-Nonyl oleate **(1)**



n-Heptacosan-9-one (**2**)



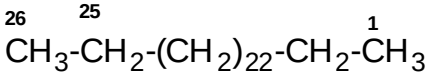
n-Nonatriacontan-20-one (**3**)



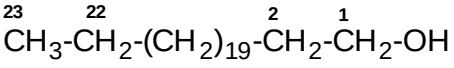
Stigmasteryl palmitate (**4**)

*Figure 1: Structural formulae of the compounds **1** - **4** isolated from the leaves of Dillenia indica*

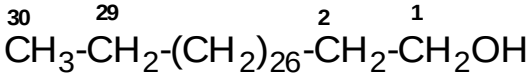
Compounds **5, 6**, **7, 8** and **10** were the long chain aliphatic alcohols identified as 1-tritriacontanol [26,27], 1-tricosanol [28,29], 1-triacontanol [30,31], 1-henetriacontanol [32,33] and 1-tritriacontanol [34,35], respectively. Compounds **9** was a known phytosterol and its structure was elucidated as stigmasterol [36 - 38] (Fig. 2).



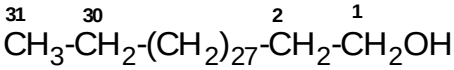
n-Hexacosane (**5**)



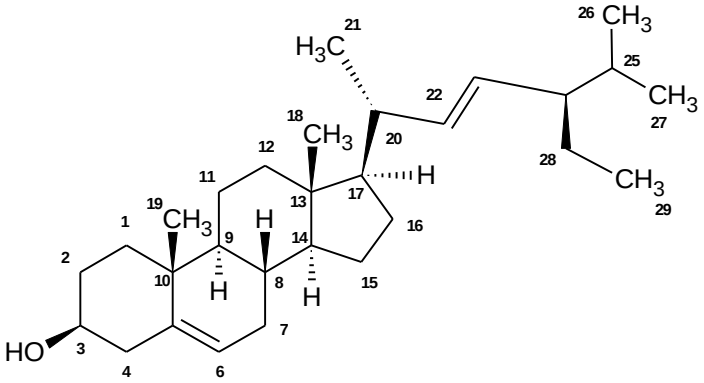
1- Triacosanol (**6)**



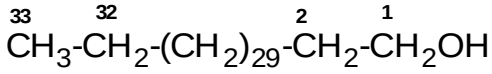
1- Triacontanol (**7**)



1-Henetriacontanol **(8**)



Stigmasterol (**9**)

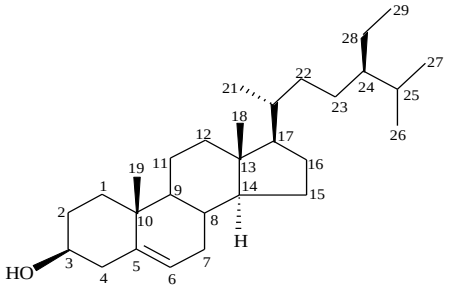


1-Tritriacontanol (**10**)

*Figure 2: Structural formulae of the compounds **5 - 10** isolated from the leaves of Halothamnus bottae.*

Compound **11** was an aliphatic constituent identified as *n*-hentriacontane [39, 40]. The structure of **12**, $[M]^+$ at *m/*z 414 ($C_{29}H_{50}O$), was elucidated as β-sitosterol [41, 42] ((Fig. 3).

n-Hentriacontane (**11**)



β-Sitosterol **(12)**

*Figure 3: Structural formulae of the compounds **11** and **12** isolated from the leaves of Xylosma longifolium*

Conclusion

The leaves of *Dillenia indica* contained an acyl ester *n*-nonyl oleate, two aliphatic ketones *n*-heptacosan-9-one and *n*-nonatriacontan-20-one and stigmasteryl palmitate. The leaves of *Halothamnus bottae* afforded an alkane, viz. *n*-hexacosane, four aliphatic alcohols and stigmasterol. The leaves of *Xylosma longifolium* yielded *n*-hentriacontane and β-sitosterol. This work has enhanced understanding about the phytoconstituents of the undertaken plants. These secondary metabolites can be used as analytical markers for quality control of the aforementioned herbal drugs.

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