Chemical constituents from the Aerial parts of *Rumex hastatus* D. Don

Shahnaz Sultana[1], Mohammed Ali[2,*], Showkat Rasool Mir[3]

[1]College of Pharmacy, Jazan University, Jazan, Saudi Arabia, [2,3]Phytochemistry Research Laboratory, School of Pharmaceutical Education & Research, Jamia Hamdard, New Delhi

***Corresponding Author:**
Email: maliphyto@gmail.com

Abstract

Rumex hastatus D. Don (Polygonaceae) occurs in Afghanistan, Pakistan, India, Bhutan and western China as a small perennial shrub and is used as an alternative, astringent, carminative, diuretic, laxative, tonic and to treat bloody dysentery, bilious complaints, blood pressure, cough, diarrhoea, dysentery, fevers, jaundice, headache, lung bleeding, piles, neoplasm, rheumatism, skin diseases, wounds and throat pain. Phytochemical investigation of a methanolic extract of the leaves led to isolate seven new chemical constituents characterized as 3′,4′-dihydroxybenzyl oleate (**2**), β-sitosterol 3-benzyl ether 3′-capriate (**4**), β-sitosterol 3-benzyl ether 3′-oleate (**5**), β-sitosterol 3-(3′,4′-dihydroxybenzyl) ether 3′-linoleate (**6**), β-sitosterol-3β-benzyl 3′-oxy-3′-O-β-D-galactopyranosyl-(6a→1b)-O-β-D-galactopyranosyl-(6b→1c)-O-β-D-galactopyranosyl-(6c→1d)-O-β-D-galactopyranosyl-2d-capriate (β-sitosterol 3-(3′-hydroxybenzyl) 3′-O-β-D-tetragalactoside 2d-capriate, **7**), 1-undecanoxy-3-phenol-3-O-β-D-xylopyranosyl-(2a→1b)- O-β-D-xylopyranosyl-(2b→1c)- O-β-D-xylopyranosyl-(2c→1d)- O-β-D-xylopyranosyl-(2d→1e)- O-β-D-xylopyranoside (*n*-undecanoxyphenol 3-O-β-D-pentaxyloside, **8**) and α-L-glucopyranosyl-(2a→1b)-O-α-L-glucopyranosyl-(2b→1c)-O-α-L-glucopyranosyl-(2c→1d)-O-α-L-gluco- pyranosyl -(2d→1e)-O- α-L -glucopyranosyl-(6e→1f)-O- α-L –glucopyranoside (α-L-hexaglucoside, **9**) together with the known compounds tridecyl oleate (**1**) and β-sitosteryl linoleate (**3**). The structures of all the isolated phytoconstituents have been established on the basis of spectral data analysis and chemical reactions.

Keywords: *Rumex hastatus*, Aerial parts, Chemical constituents, Isolation, Structures elucidation.

Introduction

Rumex hastatus D. Don, syn. *R. dissectus* H. Lév. (Polygonaceae), known as churka, arrow leaf dock, yellow sock and curled sock, occurs in Afghanistan, Pakistan, India, Bhutan and western China up to elevations of 2600 meters.(1) It is a small perennial shrub up to 60 cm tall with erect and branched stem, herbaceous above and woody below; leaves simple, pale green, hastate; flowers small, numerous, pinkish in terminal paniculate clusters; fruits pinkish and one-seeded nutlets. The plant juice is alterative, astringent, carminative, diuretic, laxative, tonic and used to treat bloody dysentery, bilious complaints, blood pressure, cough, diarrhoea, dysentery, fevers, headache, lung bleeding, piles, neoplasm, rheumatism, skin diseases, wounds and Aids.(2-7) The fresh tuber is chewed to relieve the throat pain. A decoction of the fresh roots of *R. hastatus* and fresh bark of *Quercus incana* mixed with ground wheat flour and clarified butter is given to cure asthma, cough and fever.(8-11) The young leaves are taken in chutneys and as spinach to improve taste, and as a flavouring agent. In Bageshwar valley of Uttarakhand, the root extract is used as an antiseptic and to alleviate jaundice.(12) The plant is also used as a fodder for cattle, goats and sheep.(13)

The plant contained nepalin, nepodin, rumicin, phenolic compounds, hastatusides A and B, resveratrol, rumexoside, torachrysone-8-yl β-D-glucopyranoside, rutin, and orientaloside.(13-17) The roots yielded naphthalene acylglucosides, rumexneposides A and B and other compounds.(18) Previously, *R. hastatus* has been evaluated for anticholinesterase, antioxidant, anti-tumor, anti-angiogenic, anthelmintic, anti-viral,(19) anti-bacterial, antifungal,(20) anti-diarrheal,(21) hepatoprotective,(16) antioxidant,(22) cytotoxic and phytotoxic potentials.(11,23-29) Based on the ethnomedicinal uses and bioactivities *R. hastatus*, the current study was designed to find out phytoconstituents of this plant responsible for therapeutic uses.

Materials and Method

General procedures: Melting points were determined on a Perfit melting point apparatus (Ambala, Haryana, India). UV spectra were measured on Shimadzu UV-1601 spectrophotometer in methanol. IR spectra were recorded on KBr discs, using a Jashco FTIR-410 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained using Bruker Advance DRX 400 and 100 spectrospin instruments (Karlsruhe, Germany), respectively, using TMS as an internal standard. FAB mass spectra were recorded on a Jeol D-300 spectrometer. Column chromatography was performed on silica gel 60-120 mesh (Merck, Mumbai, India) and silica gel G coated TLC plates (Merck, Mumbai, India) were used for thin-layer chromatography. Spots were visualized by exposing to iodine vapors and UV radiation and spraying with ceric sulfate solution.

Plant material: The aerial parts of *Rumex hastatus* were collected from Almora, Uttarakhand, India and authenticated by Dr. Tariq Husain, Scientist, National Botanical Research Institute. Lucknow, India. A

voucher specimen has been preserved for further verification (ref no. 97817).

Extraction and isolation: The air-dried plant powder (1.0 kg) was extracted with methanol exhaustively in a Soxhlet apparatus. The methanolic extract was concentrated under reduced pressure to obtain a reddish brown viscous mass (125.2 g, 12.5 % yield). A portion of the extract was analyzed chemically to determine the presence of different chemical constituents. It was dissolved in small amount of methanol and adsorbed on silica gel (60-120 mesh) for column chromatography for preparation of a slurry. The slurry was dried in air and subjected to chromatography over a silica gel column packed in petroleum ether. The column was eluted successively with petroleum ether, mixture of petroleum ether and chloroform (9:1, 3:1, 1:1, 1:3), chloroform and the mixture of chloroform and methanol (99:1, 97:3, 95:5, 92:8, 9:1, 3:1, 1:1, 1:3). Various fractions were collected separately and matched by TLC to check homogeneity. Similar fractions having the same R_f values were combined and crystallized. The isolated compounds were purified to get the following phytoconstituents:

Tridecyl oleate (1): Elution of the column with petroleum ether furnished viscous yellow liquid **1**, yield 185 mg, R_f 0.76 (chloroform – methanol, 1 :1), IR γ_{max} (KBr) :2973, 2845, 1721, 1644, 1438, 1387, 1043, 879, 721 cm^{-1}; ^1H NMR ($CDCl_3$):δ 5.34 (1H, m, H-9), 5.25 (1H, m, H-10), 4.04 (2H, t, J = 7.8 Hz, H_2 -1′), 2.20 (2H, t, J = 7.2 Hz, H_2 -2), 1.96 (2H, m, H_2 -8), 1.73 (2H, m, H_2 -11), 1.68 (2H, m, CH_2), 1.49 (2H, m, CH_2), 1.44 (2H, m, CH_2), 1.31 (2H, m, CH_2), 1.28 (4H, brs, 2 × CH_2), 1.21 (32H, brs, 16 x CH_2), 0.83 (3H, t, J = 6.8 Hz, Me-18), 0.79 (3H, t, J = 6.5 Hz, Me-13′); ^{13}C NMR ($CDCl_3$):δ 173.11 (C-1), 128.23 (C-9), 117.49 (C-10), 66.26 (C-1′), 33.66 (C-2), 31.30 (CH_2), 29.04 (21 x CH_2), 28.98 (CH_2), 27.69 (CH_2), 25.10 (CH_2), 22.31 (CH_2), 13.86 (Me - 18), 12.87 (Me - 13′); TOF MS *m/z* (rel.int.):464 $(M)^+$ ($C_{31}H_{60}O_2$) (4.8), 265 (25.2).

3′,4′-Dihydroxybenzyl oleate (**2**): Elution of the column with petroleum ether - chloroform (9:1) yielded pale yellow amorphous mass of **2**, yield 157 mg, R_f 0.32 (ethyl acetate – chloroform – methanol, 2 :2 :1); m. p. 108 – 109 °C, UV λ_{max} (MeOH) 211, 282 nm (log ε 2.6, 3.8); IR γ_{max} (KBr):3385, 2927, 2858, 1721, 1637, 1526, 1455, 1382, 1249, 1105, 1027, 826, 726 cm^{-1}; ^1H NMR (DMSO-d_6):δ 7.67 (1H, dd, J = 8.4, 2.6 Hz, H-6′), 7.64 (1H, d, J = 2.6 Hz, H-2′), 6.74 (1H, d, J = 8.4 Hz, H-5′), 5.35 (1H, m, H-9), 5.29 (1H, m, H-10), 4.12 (2H, s, H_2 -7′), 2.27 (2H, t, J =7.6 Hz, CH_2-2), 2.06 (2H, m, CH_2-8), 1.97 (2H, m, CH_2-11), 1.56 (2H, brs, CH_2), 1.48 (2H, m, CH_2), 1.32 (2H, m, CH_2), 1.22 (16H, brs, 8 × CH_2), 0.84 (3H, t, J =7.1 Hz, Me-18); ^{13}C NMR ($CDCl_3$):δ 142.37 (C-1′), 133.67 (C-2′), 153.12 (C-3′), 148.23 (C-4′), 128.29 (C-5′), 116.03 (C-6′), 66.23 (C-7′), 173.23 (C-1), 129.56 (C-9), 129.31 (C-10), 32.38 - 22.54 (14 x CH_2), 13.42 (C-18); TOF MS *m/z* (rel. int.):404 $(M)^+$ ($C_{25}H_{40}O_4$) (10.1), 265 (9.8), 139 (56.2).

β-Sitosteryl linoleate (3): Elution of the column with petroleum ether - chloroform (1 :1) afforded colourless amorphous powder of **3**, yield 208 mg; R_f 0.63 (petroleum ether - chloroform, 1 :3), m. p. :117-118 °C; UV λ_{max} (MeOH):211 nm (log ε 2.9); IR γ_{max} (KBr):2928, 2855, 1722, 1634, 1456, 1377, 1167, 1042, 725 cm^{-1}; ^1H NMR ($CDCl_3$):δ 5.28 (1H, d, J = 5.3 Hz, H- 6), 5.23 (2H, m, H- 9′, H-10′), 5.03 (2H, m, H- 12′, H-13′), 4.04 (1H, brm, w ½ = 18.2 Hz, H- 3α), 2.71 (2H, m, H_2-11′), 2.25 (2H, m, H_2- 4), 2.21 (2H, t, J = 7.2 Hz, H_2-2′), 1.03 (3H, brs, M- 19), 0.95 (3H, d, J= 6.8 Hz, Me- 21), 0.87 (3H, d, J= 6.3 Hz, Me- 26), 0.82 (3H, J= 6.5 Hz, Me- 27), 0.81 (3H, t, J = 6.1 Hz, Me- 29), 0.79 (3H, t, J = 6.4 Hz, Me- 18′), 0.67 (3H, brs, Me-18), 1.98 – 1.35 (33H, 13 x CH_2, 7 x CH), 1.23 (16H, brs, 8 x CH_2); ^{13}C NMR ($CDCl_3$):δ 38.79 (C- 1), 32.15 (C- 2), 70.12 (C- 3), 42.04 (C- 4), 140.85 (C- 5), 120.29 (C- 6), 33.32 (C- 7), 31.23 (C- 8), 50.77 (C- 9), 36.87 (C- 10), 22.56 (C- 11), 39.78 (C- 12), 41.71 (C- 13), 56.18 (C-14), 23.77 (C- 15), 29.15 (C- 16), 55.42 (C- 17), 11.58 (C- 18), 19.38 (C- 19), 35.97 (C- 20), 18.36 (C- 21), 33.62 (C- 22), 26.62 (C- 23), 45.17 (C- 24), 27.75 (C-25), 18.94 (C- 26), 18.68 (C- 27), 24.49 (C- 28), 11.49 (C- 29), 174.57 (C-1′), 49.58 (C-2′), 29.05 (C-3′), 28.71 (C-4′), 28.81 (C-5′), 28.95 (C-6′), 28.66 (C-7′), 28.62 (C-8′), 131.25 (C-9′), 129.49 (C-10′), 59.36 (C-11′), 127.49 (C-12′), 123.79 (C-13′), 28.52 (C-14′), 28.59 (C-15′), 25.10 (C-16′), 22.05 (C-17′), 13.36 (C-18′); +ve ion TOF MS *m/z* (rel.int.): 676 $(M)^+$ ($C_{47}H_{80}O_2$) (2.1), 413 (11.5), 279 (3.8), 263 (4.6).

β-Sitosterol 3-benzyl ether 3′-capriate (4): Elution of the column with chloroform produced brown amorphous powder of **4**, yield 217 mg; R_f 0.7 (chloroform – ethyl acetate (1 :1), m. p. 148 – 150 °C; UV λ_{max} (MeOH):284 nm (log ε 2.1); IR γ_{max} (KBr):2938, 2843, 1721, 1656, 1525, 1452, 1387, 1276, 1086, 1044, 880 cm^{-1}; ^1H NMR ($CDCl_3$):δ 7.39 (1H, d, J = 2.0 Hz, H-2′), 7.31 (1H, m, H-6′), 6.76 (1H, m, H-4′), 6.73 (1H, m, H-5′), 5.33 (1H, m, H- 6), 3.74 (2H, s, H_2- 7′), 3.47 (1H, brm, w ½ = 18.3 Hz, H- 3α), 2.17 (2H, t, J = 7.6 Hz, H_2-2″), 1.01 (3H, brs, M- 19), 0.91 (3H, d, J= 6.5 Hz, Me- 21), 0.88 (3H, d, J= 6.5 Hz, Me- 26), 0.85 (3H, J= 6.2 Hz, Me- 27), 0.81 (3H, t, J = 6.2 Hz, Me- 29), 0.79 (3H, t, J = 6.5 Hz, Me- 10″), 0.65 (3H, brs, Me-18), 2.51 – 1.33 (29H, 11 x CH_2, 7 x CH), 1.22 (4H, brs, 2 x CH_2), 1.20 (10H, brs, 5 x CH_2); ^{13}C NMR ($CDCl_3$):δ 38.68 (C- 1), 32.69 (C- 2), 72.43 (C- 3), 41.74 (C- 4), 144.75 (C- 5), 120.73 (C- 6), 31.32 (C- 7), 32.96 (C- 8), 49.86 (C- 9), 36.43 (C- 10), 22.15 (C- 11), 39.87 (C- 12), 40.48 (C- 13), 55.37 (C- 14), 24.42 (C-15), 28.54 (C- 16), 54.15 (C- 17), 11.54 (C- 18), 19.41 (C- 19), 36.17 (C- 20), 18.32 (C- 21), 35.72 (C- 22), 26.61 (C- 23), 45.16 (C- 24), 25.12 (C- 25), 20.51 (C-26), 18.62 (C- 27), 23.06 (C- 28), 11.47 (C- 29), 137.35 (C-1′), 124.47 (C-2′), 167.86 (C-3′), 129.32 (C-4′), 108.97 (C-5′), 115.56 (C-6′), 63.17 (C-7′), 174.65 (C-

1″), 33.68 (C-2″), 31.28 (C-3″), 29.07 (C-4″, C-5″), 29.04 (C-6″), 28.90 (C-7″), 28.74 (C-8″), 22.48 (C-9″), 13.71 (C-10″); +ve ion TOF MS *m/z* (rel.int.):674 $(M)^+$ ($C_{46}H_{74}O_3$) (1.8), 413 (11.2), 171 (76.3), 155 (14.6).

β-Sitosterol 3-benzyl ether 3′-oleate (5): Further elution of the column with chloroform gave a yellow amorphous powder of **5**, yield 174 mg; R_f 0.83 (benzene – ethyl acetate – acetic acid, 8 :1.5 :0.5)); m. p. 143 -145 ^oC; UV λ_{max} (MeOH):286 nm (log ε 3.2); IR γ_{max} (KBr):2927, 2854, 1723, 1636, 1514, 1456, 1378, 1271, 1109, 1043, 835, 725 cm^{-1}; ^1H NMR ($CDCl_3$):δ 8.35 (1H, d, J = 2.5 Hz, H-2′), 7.35 (1H, dd, J = 2.5, 8.8 Hz, H-4′), 7.19 (1H, m, H-6′), 6.74 (1H, m, H-5′), 5.30 (1H, m, H- 6), 5.28 (1H, m, H- 9″), 5.24 (1H, m, H- 10″), 3.80 (2H, s, H_2- 7′), 3.39 (1H, brm, $w_{½}$= 18.1 Hz, H- 3α), 2.19 (2H, t, J = 7.5 Hz, H_2-2″), 1.02 (3H, brs, M- 19), 0.94 (3H, d, J= 6.6 Hz, Me- 21), 0.87 (3H, d, J= 6.3 Hz, Me- 26), 0.84 (3H, J = 6.5 Hz, Me- 27), 0.82 (3H, t, J = 6.2 Hz, Me- 29), 0.78 (3H, t, J = 6.5 Hz, Me- 18″), 0.67 (3H, brs, Me-18), 2.51 – 1.33 (33H, 13 x CH_2, 7 x CH), 1.24 (6H, brs, 3 x CH_2), 1.22 (16H, brs, 8 x CH_2); ^{13}C NMR ($CDCl_3$):δ 38.90 (C- 1), 33.32 (C- 2), 72.74 (C- 3), 41.76 (C- 4), 140.25 (C- 5), 120.37 (C- 6), 31.35 (C- 7), 31.86 (C- 8), 49.84 (C- 9), 36.38 (C- 10), 21.99 (C- 11), 39.17 (C- 12), 41.88 (C- 13), 55.87 (C- 14), 24.46 (C- 15), 28.74 (C- 16), 55.35 (C- 17), 11.65 (C- 18), 19.98 (C- 19), 35.47 (C- 20), 18.43 (C- 21), 33.67 (C- 22), 26.63 (C- 23), 45.14 (C- 24), 26.61 (C- 25), 19.53 (C- 26), 18.72 (C- 27), 22.16 (C- 28), 11.49 (C- 29), 142.23 (C-1′), 127.48 (C-2′), 164.95 (C-3′), 124.39 (C-4′), 115.60 (C-5′), 114.98 (C-6′), 63.09 (C-7′), 174.61 (C-1″),129.51 (C-9″), 129.26 (C-10″), 32.38 – 22.52 (14 x CH_2) 13.81 (C-18″); +ve ion TOF MS *m/z* (rel.int.):784 $(M)^+$ ($C_{54}H_{88}O_3$) (1.3), 413 (31.4), 265 (9.1).

β-Sitosterol 3-(3′,4′-dihydroxybenzyl) ether 3′-linoleate (6): Elution of the column with chloroform – methanol (49 :1) offered yellow amorphous powder of **6**, yield 168 mg; R_f 0.83 (benzene – ethyl acetate – acetic acid, 8 :1.5 :0.5); m. p. 149 – 152 ^oC; UV λ_{max} (MeOH):286 nm (log ε 3.2); IR γ_{max} (KBr):3421, 2925, 2857, 1721, 1631, 1524, 1457, 1375, 1261, 1145, 1041, 726 cm^{-1}; ^1H NMR ($CDCl_3$):δ 7.81 (1H, d, J = 2.5 Hz, H-2′), 7.61 (1H, d, J = 8.5 Hz, H-5′), 7.21 (1H, m, H-6′), 5.33 (1H, m, H- 6), 5.08 (2H, m, H- 9″, H-10″), 5.03 (2H, m, H- 12″, H-13″), 3.82 (2H, s, H_2- 7′), 3.36 (1H, brm, $w_{½}$ = 18.2 Hz, H- 3α), 2.18 (2H, t, J = 7.2 Hz, H_2-2″), 1.01 (3H, brs, M- 19), 0.95 (3H, d, J= 6.3 Hz, Me- 21), 0.86 (3H, d, J= 6.7 Hz, Me- 26), 0.83 (3H, J = 6.2 Hz, Me- 27), 0.81 (3H, t, J = 5.8 Hz, Me- 29), 0.79 (3H, t, J = 6.5 Hz, Me- 18″), 0.67 (3H, brs, Me-18), 2.31 – 1.19 (35H, 14 x CH_2, 7 x CH), 1.23 (6H, brs, 3 x CH_2), 1.19 (12H, brs, 6 x CH_2); ^{13}C NMR ($CDCl_3$):δ 38.77 (C- 1), 32.13 (C- 2), 70.21 (C- 3), 41.72 (C- 4), 140.79 (C- 5), 120.41 (C- 6), 33.32 (C- 7), 31.36 (C- 8), 49.54 (C- 9), 36.83 (C- 10), 21.94 (C- 11), 39.97 (C- 12), 41.95 (C- 13), 56.14 (C- 14), 23.76 (C- 15), 31.14 (C- 16), 55.39 (C- 17), 11.56 (C- 18), 19.48 (C- 19), 35.97 (C- 20), 18.34 (C- 21), 35.51 (C- 22), 26.63 (C- 23), 45.64 (C- 24), 30.91 (C- 25), 18.95 (C- 26), 18.67 (C- 27), 22.24 (C- 28), 11.42 (C- 29), 144.06 (C-1′), 133.28 (C-2′), 164.27 (C-3′), 157.41 (C-4′), 129.53 (C-5′), 127.40 (C-6′), 62.31 (C-7′), 174.89 (C-1″), 31.33 (C-2″), 29.09 (C-3″), 29.07 (C-4″), 29.66 (C-5″), 28.93 (C-6″), 28.67 C-7″), 28.62 (C-8″), 129.46 (C-9″), 129.36 (C-10″), 59.63 (C-11″), 129.17 (C-12″), 127.44 (C-13″), 27.70 (C-14″), 25.44 (C-15″), 25.09 (C-16″), 22.51 (C-17″), 13.73 (C-18″); +ve ion TOF MS *m/z* (rel.int.):798 $(M)^+$ ($C_{54}H_{86}O_4$) (1.6), 413 (9.8), 263 (19.3).

β-Sitosterol 3-(3′-hydroxybenzyl) 3′-O-β-D-tetragalactoside 2d-capriate (7): Elution of the column with chloroform – methanol (7 :3) yielded brown amorphous powder of **7**, yield 152 mg; R_f 0.61 (chloroform – methanol. 1 :1); m. p. 212 – 215 ^oC; UV λ_{max} (MeOH):273 nm (log ε 3.5); IR γ_{max} (KBr):3415, 3375, 3260, 2926, 2855, 1721, 1631, 1521, 1454, 1375, 1236, 1039, 725 cm^{-1}; ^1H NMR ($CDCl_3$):δ 8.36 (1H, d, J = 2.6 Hz, H-2′), 7.19 (1H, m, H-4′), 7.08 (1H, m, H-5′), 6.91 (1H, m, H-6′), 5.31 (1H, m, H- 6), 3.85 (2H, s, H_2- 7′), 3.71 (1H, brm, $w_{1/2}$ = 18.2 Hz, H-3α), 1.02 (3H, brs, M- 19), 0.92 (3H, d, J= 6.5 Hz, Me- 21), 0.86 (3H, d, J= 6.6 Hz, Me- 26), 0.84 (3H, d, J = 6.6 Hz, Me- 27), 0.81 (3H, t, J = 6.5 Hz, Me- 29), 0.66 (3H, brs, Me-18), 5.16 (1H, d, J = 7.2 Hz, H-1a), 4.90 (1H, d, J = 7.5 Hz, H-1b), 4.71 (1H, d, J = 7.3 Hz, H-1c), 4.62 (1H, d, J = 7.4 Hz, H-1d), 4.03 (1H, m, H-2d), 3.95 (1H, m, H-5a), 3.91 (1H, m, H-5b,), 3.78 (1H, m, H-5c), 3.75 (1H, m, H-5d), 3.69 (1H, m, H-2a), 3.67 (1H, m, H-2b), 3.65 (1H, m, H-2c), 3.64 (2H, m, H-3a, H-3b), 3.61 (1H, m, H-3c), 3.59 (1H, m, H-3d), 3.56 (2H, m, H-4a, H-4b), 3.53 (2H, m, H-4c, H-4d), 3.32 (2H, d, J = 10.4 Hz, H_2-6a), 3.29 (2H, d, J = 6.8 Hz, H_2-6b), 3.26 (2H, d, J = 6.2 Hz, H_2-4c), 3.09 (2H, d, J = 7.1 Hz, H_2-4d), 2.15 (2H, t, J = 7.2 Hz, H_2-2″), 2.31 – 1.19 (31H, m, 12 x CH_2, 7 x CH), 1.20 (12H, brs, 6 x CH_2) 0.79 (3H, t, J = 6.5 Hz, Me- 18″); ^{13}C NMR ($CDCl_3$):δ 37.68 (C- 1), 32.93 (C- 2), 71.69 (C- 3), 41.37 (C- 4), 139.27 (C- 5), 120.81 (C- 6), 33.46 (C- 7), 32.83 (C- 8), 49.81 (C- 9), 36.43 (C- 10), 21.23 (C- 11), 39.70 (C- 12), 42.16 (C- 13), 55.45 (C- 14), 23.76 (C- 15), 31.28 (C- 16), 55.12 (C- 17), 11.68 (C- 18), 19.59 (C- 19), 35.62 (C- 20), 18.47 (C- 21), 35.50 (C- 22), 26.39 (C- 23), 45.11 (C- 24), 27.41 (C- 25), 20.52 (C- 26), 18.79 (C- 27), 22.14 (C- 28), 11.72 (C- 29), 148.50 (C-1′), 138.50 (C-2′), 156.12 (C-3′), 145.21 (C-4′), 137.15 (C-5′), 124.72 (C-6′), 63.65 (C-7′), 108.12 (C-1a), 73.03 (C-2a). 72.14 (C-3a), 70.14 (C-4a), 76.55 (C-5a), 64.23 (C-6a), 103.83 (C-1b), 72.77 (C-2b), 71.20 (C-3b), 69.86 (C-4b), 75.83 (C-5b), 64.19 (C-6b), 101.84 (C-1c), 72.30 (C-2c), 70.58 (C-3c), 69.55 (C-4c), 75.06 (C-5c), 63.60 (C-6c), 97.93 (C-1d), 81.73 (C-2d), 70.39 (C-3d), 67.75 (C-4d), 74.66 (C-5d), 61.25 (C-6d), 173.15 (C-1″), 30.12 (C-2″), 29.01 (C-3″, C-4″, C-5″), 28.92 (C-6″), 28.70 C-7″), 28.59 (C-8″), 22.96 (C-9″), 13.85 (C-10″); +ve ion

TOF MS *m/z* (rel.int.):1322 $(M)^+$ ($C_{70}H_{114}O_{23}$) (1.5), 413 (12.8), 334 (21.9), 317 (4.6), 171 (32.6).

***n*-Undecanoxyphenol 3-O-β-D-pentaxyloside (8):** Elution of column with chloroform - methanol (3:1) afforded brown coloured mass of **8**, yield 341 mg, R_f :0.51 (chloroform – methanol, 1 :1), m. p. 238 - 240 ºC, UV λ_{max} (methanol):278 nm (log ε 3.1); IR γ_{max} (KBr):3425, 3391, 3265, 2928, 2837, 1635, 1522, 1447, 1384, 1283, 1104, 1065, 771 cm^{-1}; ^1H NMR (DMSO-d_6):δ 8.37 (1H, d, J = 2.8 Hz, H-2), 7.53 (1H, m, H-4), 7.18 (1H, m, H-5), 6.93 (1H, m, H-6), 4.32 (1H, d, J = 7.6 Hz, H-1a), 4.22 (1H, d, J = 7.2 Hz, H-1b), 4.14 (1H, d, J = 7.8 Hz, H-1c), 4.07 (1H, d, J = 7.7 Hz, H-1d), 4.04 (1H, d, J = 7.6 Hz, H-1e), 3.99 (2H, m, H-2a, H-2b), 3.96 (2H, m, H-2c, H-2d), 3.89 (1H, m, H-2e), 3.79 (2H, m, H-3a, H-3b), 3.76 (2H, m, H-3c, H-3d), 3.72 (1H, m, H-3e), 3.65 (1H, m, H-4a), 3.63 (1H, m, H-4b), 3.61 (1H, m, H-4c), 3.57 (1H, m, H-4d), 3.52 (1H, m, H-4e), 3.40 (2H, d, J = 5.2 Hz, H_2-5a), 3.35 (2H, d, J = 6.0 Hz, H_2-5b), 3.31 (2H, d, J = 7.2 Hz, H_2-5c), 3.27 (2H, d, J = 6.4 Hz, H_2-5d), 3.22 (2H, J = 6.4 Hz, H_2-5e), 3.70 (2H, t, J = 6.6 Hz, H_2-1′), 1.65 (2H, m, H_2-2′), 1.54 (2H, m, H_2-3′), 1.32 (2H, m, H_2-4′), 1.25 (12H, brs, 6 x CH_2), 0.83 (3H, t, J = 6.4 Hz, Me-11′); ^{13}C NMR (DMSO-d_6):δ 154.23 (C-1), 146.71 (C-2), 152.16 (C-3), 124.48 (C-4), 120.16 (C-5), 144.35 (C-6), 64.21 (C-1′), 31.36 (C-2′), 29.07 (C-3′, C-4′, C-5′), 28.93 (C-6′), 26.75 (C-7′), 25.67 (C-8′), 25.24 (C-9′), 22.67 (C-10′), 14.16 (C-11′), 103.80 (C-1a), 81.23 (C-2a), 76.11 (C-3a), 72.77 (C-4a), 62.51 (C-5a), 101.82 (C-1b), 80.86 (C-2b), 75.43 (C-3b), 72.28 (C-4b), 61.55 (C-5b), 97.81 (C-1c), 7.21 (C-2c), 74.56 (C-3c), 68.41 (C-4c), 61.37 (C-5c), 96.15 (C-1d), 77.48 (C-2d), 73.89 (C-3d), 68.16 (C-4d), 64.13 (C-5d), 92.16 (C-1e), 72.77 (C-2e), 73.21 (C-3e), 67.33 (C-4e), 60.57 (C-5e); +ve FAB MS *m/z* (rel. int.):924 $(M)^+$ ($C_{42}H_{68}O_{22}$) (2.3), 155 (14.6).

α-L-Hexaglucoside (9): Elution of the column with chloroform - methanol (4 :1) furnished yellow crystals of **9**, yield 215 mg, R_f:0.60 (chloroform – methanol, 1 :1), m. p. 227 -230 °C; IR γ_{max} (KBr):3425, 3396, 3267, 2928, 2842, 1616, 1446, 1381, 1266, 1065 cm^{-1}; ^1H NMR (DMSO d_6):δ 5.19 (1H, d, J = 3.5 Hz, H-1a), 4.93 (1H, d, J = 3.6 Hz, H-1b), 4.90 (1H, d, J = 3.5 Hz, H-1c), 4.36 (2H, br m, $w_{1/2}$ = 3.9 Hz, H-1d, H-1e), 4.34 (1H, d, J = 3.8 Hz, H-1f), 4.19 (1H, m, H-2a), 4.12 (1H, m, H-2b), 4.04 (1H, m, H-2c), 3.99 (1H, m, H-2d), 3.94 (1H, m, H-2e), 3.89 (1H, m, H-2f), 3.83 (2H, m, H-5a, H-5b), 3.78 (2H, m, H-5c, H-5d), 3.75 (1H, m, H-5e), 3.72 (1H, m, H-5f), 3.67 (1H, m, H-3a), 3.64 (1H, m, H-3b), 3.62 (2H, m, H-3c, H-3d), 3.60 (1H, m, H-3e), 3.58 (1H, m, H-3f), 3.55 (1H, m, H-4a), 3.52 (1H, m, H-4b), 3.48 (2H, m, H-4c, H-4d), 3.45 (1H, m, H-4e), 3.43 (1H, m, H-4f), 3.39 (2H, d, J = 8.8 Hz, H_2-6e), 3.16 (2H, d, J = 11.6 Hz, H_2-6a), 3.12 (2H, d, J = 8.4 Hz, H_2-6b), 3.09 (2H, d, J = 12.9 Hz, H_2-6c), 3.05 (2H, d, J = 9.6 Hz, H_2-6d), 3.03 (2H, d, J = 7.6 Hz, H_2-6f); ^{13}C NMR (DMSO d-$_6$):δ 104.13 (C-1a), 82.75 (C-2a), 72.66 (C-3a), 70.41 (C-4a), 77.11 (C-5a), 62.70 (C-6a), 103.88 (C-1b), 81.89 (C-2b), 72.35 (C-3b), 70.15 (C-4b), 76.55 (C-5b), 62.60 (C-6b), 101.87 (C-1c), 81.71 (C-2c), 72.21 (C-3c), 69.83 (C-4c), 75.74 (C-5c), 61.16 (C-6c), 98.01 (C-1d), 80.91 (C-2d), 71.76 (C-3d), 69.12 (C-4d), 75.10 (C-5d), 61.10 (C-6d), 96.74 (C-1e), 73.01 (C-2e), 71.70 (C-3e), 67.67 (C-4e), 74.69 (C-5e), 64.18 (C-6e), 92.11 (C-1f), 72.76 (C-2f), 71.66 (C-3f), 70.15 (C-4f), 74.67 (C-5e), 61.06 (C-6e); TOF MS *m/z* (rel.int.):990 $(M)^+$ ($C_{36}H_{62}O_{31}$) (2.1), 504 (5.7), 342 (11.7), 179 (36.4).

Results and Discussion

Compound **1** was a fatty ester identified as tridecyl oleate.[30]

Compound **2** had UV absorption maximum at 282 nm for aromatic compounds, showed IR absorption bands for hydroxyl groups (3385 cm^{-1}), ester function (1721 cm^{-1}), aromaticity (1637, 1526, 1027 cm^{-1}) and long aliphatic chain (726 cm^{-1}) and gave positive tests for phenols. Its mass spectrum showed a molecular ion peak at *m/z* 404 consistent with the molecular formula of a benzyl ester, $C_{25}H_{40}O_4$. The ion peaks arising at *m/z* 139 ($C_{1'}$ - O fission, $C_6H_3(OH)_2$-$CH_2O)^+$ and 265 (M – 139, $CO(CH_2)_7CH{=}CH(CH_2)_7CH_3)^+$ indicated that oleic acid was esterified with dihydroxybenzyl alcohol. The ^1H NMR spectra of **2** exhibited two one - proton doublets at δ 7.64 (J = 2.6 Hz) and 6.74 (J = 8.4 Hz) and a one-proton double doublet at δ 7.67 (J = 8.4, 2.6 Hz) assigned to aromatic *meta*-coupled H-2′, *ortho*-coupled H-5′ and *meta*-, *ortho*-coupled H-6′ protons, respectively, two one – proton multiplets at δ 5.35 and 5.29 accounted correspondingly to vinylic protons H-9 and H-10 protons, a two – proton singlet at δ 4.12 due to oxymethylene H_2-7′, methylene protons from δ 2.27 to 1.22 and a three – proton triplet at δ 0.84 (J = 7.1 Hz) ascribed to primary C-18 methyl protons. The ^{13}C NMR spectrum of **2** displayed signals for aromatic and vinylic carbons between δ 153.12 – 116.03, ester carbon at δ 173.23 (C-1), oxymethylene carbon at δ 66.23 (C-7′) and methyl carbon at δ 13.42 (C-18). On the basis of these evidences, the structure of **2** has been characterized as 3′,4′-dihydroxybenzyl oleate, a new aromatic ester (Fig. 1).

Compound **3** is a known sterol ester identified as β-sitosteryl linoleate.[31,32]

Compound **4** showed IR absorption bands for ester group (1721 cm^{-1}), unsaturation (1656 cm^{-1}) and aromatic ring (1525, 1044 cm^{-1}). On the basis of mass and ^{13}C NMR spectra the molecular ion peak of **4** was determined at *m/z* 674 consistent with a molecular formula of a stearyl benzyl ester, $C_{46}H_{74}O_3$. The ion peaks arising at *m/z* 413 ($C_{7'}$ - O fission, $C_{29}H_{49}O)^+$, 155 ($C_{1''}$ - O fission, $CO(CH_2)_8CH_3)^+$ and 171 ($C_{3'}$ - O fission, $OCO(CH_2)_8CH_3)^+$ indicated that β-sitosterol and capric acid were present in the molecule. The ^1H NMR spectrum of **4** exhibited a one - proton doublet at δ 7.39 (J = 2.0 Hz) and four one - proton multiplets at δ 7.31, 6.76, 6.73 and 5.33 assigned to aromatic *meta*-

coupled H-2′ and other aromatic and vinylic protons. A one -proton broad multiplet at δ 3.47 with half width of 18.3 Hz and a two-proton singlet at δ 3.74 were attributed to oxymethine H-3α proton and oxymethylene H_2-7′ protons, respectively. Two broad singlets at δ 1.01 and 0.65, three doublets at δ 0.91 (*J* = 6.5 Hz), 0.88 (*J* = 6.5 Hz) and 0.85 (*J* = 6.2 Hz) and two triplets at δ 0.81 (*J* = 6.2 Hz) and 0.79 (*J* = 6.2 Hz), all integrating for three protons each, were attributed to tertiary C-19 and C-18, secondary C-21, 26 and 27 and primary C-29 and C-18″ methyl protons, respectively, all attached to saturated carbons. The other methylene and methine protons resonated in the range of 2.51 - 1.33. The ^{13}C NMR spectrum of **4** displayed signals for ester carbon at δ 174.65 (C-1″), aromatic and vinylic carbons from δ 167.86 - 115.56 and methyl carbons between δ 20.51 to 11.47. The ^{1}H and ^{13}C NMR spectral data of the steroidal unit of **4** were compared with the reported data of similar steroids.[33,34] These evidences led to establish the structure of **4** as β-sitosterol 3-benzyl ether 3′-capriate, a new steroidal ester (Fig. 1).

Compound **5,** $(M)^+$ at *m/z* 784 ($C_{54}H_{88}O_3$), displayed IR absorption bands for ester group (1723 cm^{-1}), unsaturation (1636 cm^{-1}), aromatic ring (1514, 1043 cm^{-1}) and long aliphatic chain (725 cm^{-1}). The ion peaks arising at *m/z* 413 ($C_{7'}$ - O fission, $C_{29}H_{49}O)^+$ and 265 ($C_{2''}$ - O fission, $CO(CH_2)_7CH{=}CH{-}(CH_2)_7CH_3)^+$ indicated that β-sitosterol and a oleate unit were present in the molecule. The ^{1}H NMR spectrum of **5** exhibited a one - proton doublet at δ 8.35 (J = 2.5 Hz), a one - proton double doublet at δ 7.35 (J = 2.5, 8.8 Hz) and five one - proton multiplets between δ 7.19 - 5.24 assigned to aromatic and vinylic protons. A one-proton broad multiplet at δ 3.39 with half width of 18.1 Hz and a two-proton singlet at δ 3.80 were attributed to oxymethine H-3α and oxymethylene H_2-7′ protons, respectively. The methyl protons resonated as three – proton singlets at δ 1.02 (Me-19) and 0.67 (Me-18), as doublets at δ 0.94 (J = 6.6 Hz, Me-21), 0.87 (J = 6.3 Hz, Me-26) and 0.84 (J = 6.5 Hz, Me-27) and as triplets at δ 0.82 (J = 6.2 Hz, Me-29) and 0.78 (J = 6.5 Hz, Me-18″). The other methylene and methine protons resonated in the range of δ 2.51 - 1.22. The ^{13}C NMR spectrum of **5** displayed signals for an ester carbon at δ 174.61 (C-1″), aromatic and vinylic carbons from δ 164.95 - 114.98 and methyl carbons between δ 19.98 to 11.49.[33,34] These spectral data analysis led to elucidate the structure of **5** as β-sitosterol 3-benzyl ether 3′-oleate, a new steroidal ester (Fig. 1).

Compound **6,** $(M)^+$ at *m/z* 798 ($C_{54}H_{86}O_4$), showed IR absorption bands similar to compound **5** in addition to a hydroxyl band at 3421 cm^{-1}. The ion peaks arising at *m/z* 413 ($C_{7'}$ - O fission, $C_{29}H_{49}O)^+$ and 263 ($C_{2''}$ - O fission, $CO(CH_2)_7(CH{=}CH{-}CH_2)_2(CH_2)_3CH_3)^+$ indicated that β-sitosterol and linoleate group were present in the molecule. The ^{1}H NMR spectrum of **6** exhibited two one-proton doublets at δ 7.81 (J = 2.5 Hz) and 7.61 (J = 8.5 Hz, H-5′), a one-proton double doublet at δ 7.35 (J = 2.5, 8.8 Hz) and four one-proton multiplets between δ 7.21 - 5.03 assigned to aromatic and vinylic protons. A one-proton broad multiplet at δ 3.36 with half width of 18.2 Hz and a two-proton singlet at δ 3.82 were attributed to oxymethine H-3α and oxymethylene H_2-7′ protons, respectively. The methyl protons resonated as three – proton singlets at δ 1.01 (Me-19) and 0.67 (Me-18), as doublets at δ 0.95 (J = 6.3 Hz, Me-21), 0.86 (J = 6.7 Hz, Me-26) and 0.83 (J = 6.2 Hz, Me-27) and as triplets at δ 0.81 (J = 5.8 Hz, Me-29) and 0.79 (J = 6.5 Hz, Me- 18″). The other methylene and methine protons appeared in the range of δ 2.31 - 1.19. The ^{13}C NMR spectrum of **6** displayed signals for ester carbon at δ 174.89 (C-1″), aromatic and vinylic carbons between δ 164.27 - 127.40 and methyl carbons from δ 19.48 to 11.42.[33,34] On the basis of this discussion the structure of **6** was characterized as β-sitosterol 3-(3′,4′-dihydroxybenzyl) ether 3′-linoleate, a new steroidal ester (Fig. 1).

Compound **7,** named β-sitosterol 3-(3′-hydroxybenzyl) 3′-O-β-D-tetragalactoside 2d-capriate, gave positive tests for glycosides and showed IR absorption bands for hydroxyl groups (3415, 3375, 3260 cm^{-1}), ester function (1721 cm^{-1}), unsaturation (1631 cm^{-1}) and a long aliphatic chain (725 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, the molecular ion peak of **7** was determined at *m/z* 1322 corresponding to a molecular formula of a steroidal benzyl tetraglycosidic ester, $C_{70}H_{114}O_{23}$. The ion fragments arising at *m/z* 171 (C_{2d} – O fission, $CH_3(CH_2)_8COO)^+$, 413 ($C_{7'}$ - O fission, $C_{29}H_{49}O)^+$, 317 (C_{1d} – O fission, $C_6H_{10}O_5$-CO-$(CH_2)_8CH_3)^+$ indicated that the presence of β-sitosterol in the glycoside and capric acid was linked with the glycosidal chain. The ^{1}H NMR spectrum of **7** showed a one - proton doublet at δ 8.36 (J = 2.6 Hz) and four one - proton multiplets at δ 7.19, 7.08, 6.91 and 5.31 assigned to aromatic and vinylic proton. A two-proton singlet at δ 3.85 and a one-proton broad multiplet at δ 3.71 ($w_{1/2}$ = 18.2 Hz) were attributed to oxymethylene H_2- 7′ and oxymethine H-3α protons, respectively. Four one - proton doublets at δ 5.16 (J = 7.2 Hz), 4.90 (J = 7.5 Hz), 4.71 (J = 7.3 Hz) and 4.62 (J = 7.4 Hz) were ascribed to anomeric H-1a, H-1b, H-1c and H-1d, respectively. The remaining sugar protons resonated as multiplets between δ 4.03 – 3.53 and as two-proton doublets at δ 3.32 (J = 10.4 Hz), 3.29 (J = 6.8 Hz), 3.26 (J = 6.2 Hz) and 3.09 (J = 7.1 Hz) due to oxymethylene H_2-6a to H_2-6d protons. Two three - proton singlets at δ 1.02 and 0.66, three doublets at δ 0.92 (J = 6.5 Hz), 0.86 (J = 6.6 Hz) and 0.84 (J = 6.6 Hz) and two triplets at δ 0.81 (J = 6.5 Hz) 0.79 (J = 6.5 Hz) and were accounted to tertiary C-19 and C-18, secondary C-21, C-26 and C-27 and primary C-29 and C-10′ methyl protons, respectively. The remaining methine and methylene protons appeared from δ 2.31 to 1.20. The ^{13}C NMR spectrum of **7** showed important signals for aromatic and vinylic carbons between δ

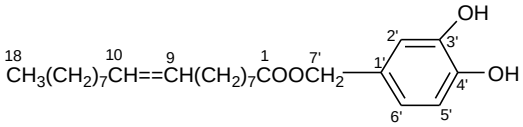
156.12 - 120.8, oxymethine carbon at δ 71.69 (C-3), oxymethylene carbon at δ 63.65 (C-7′), anomeric carbons at δ 108.12 (C-1a), 103.83 (C-1b), 101.84 (C-1c) and 97.93 (C-1d), other sugar carbons from δ 81.73 to 61.25, ester carbon at δ 173.15 (C-1″) and the methyl carbons between δ 19.59 – 11.68. The ^{1}H NMR and ^{13}C NMR spectral data of the steroidal nucleus were compared with other stigmastene-type molecules.[33,34] The presence of H-2d in the ^{1}H NMR spectrum in the deshielded region at δ 4.03 and C-2d carbon signal in the ^{13}C NMR spectrum at δ 81.73 suggested the attachment of capryl unit at C-2d carbon. The existence of oxymethylene proton signals in the downfield region at δ 3.32 (H_2-6a), 3.29 (H_2-6b) and 3.26 (H_2-4c) and their respective carbon signals at δ 64.23 (C-6a), 64.19 (C-6b) and 63.60 (C-6c) indicated (6 → 1) linkages of the sugar units. Acid hydrolysis of **6** yielded β-sitosterol (m. p. 137-138 °C; R_f 0.35 (chloroform:methanol:9:1), β-D-galactose, R_f 0.16 (n-butanol-acetic acid-water, 4:1:5 v/v) and capric acid (m. p, 31 - 32° C). On the basis of spectral data analysis and chemical reactions, the structure of **7** has been formulated as β-sitosterol-3β-benzyl 3′-oxy-3′-O-β-D-galactopyranosyl-(6a→1b)-O-β- D-galactopyranosyl-(6b→1c)-O-β-D-galactopyranosyl-(6c→1d)-O-β- D-galactopyranosyl-2d-capriate, a new steroidal tetragalactoside (Fig. 1).

Compound **8**, named *n*-undecanoxyphenol 3-O-β-D-pentaxyloside, **(**M)$^+$ at *m/z* 924 ($C_{42}H_{68}O_{22}$), gave positive tests of glycosides and exhibited IR absorption bands for hydroxyl groups (3425, 3391, 3265 cm^{-1}), aromatic ring (1635, 1522, 1065 cm^{-1}) and aliphatic chain (771 cm^{-1}). An ion peak generating at *m/z* 155 $(C_{11}H_{23})^+$ suggested the existence of an undecanyl unit linked to the aromatic ring. The ^{1}H NMR spectrum of **8** demonstrated the presence of a one – proton doublet at δ 8.37 (J = 2.8 Hz) and three one – proton multiplets δ 7.53, 7.18 and 6.93 assigned to aromatic H-2, H-4, H-5 and H-6 protons, respectively, five one – proton doublets at δ 4.32 (J = 7.6 Hz), 4.22 (J = 7.2 Hz), 4.14 (J = 7.8 Hz), 4.07 (J = 7.7 Hz) and 4.04 (J = 7.6 Hz) ascribed correspondingly to anomeric H-1a to H-1e protons, other sugar protons in the range of δ 3.99 – 3.22, a two – proton triplet at δ 3.70 (J = 6.6 Hz) accounted to oxymethylene H_2-1′, other methylene protons between δ 1.65 – 1.25 and a three – proton triplet at δ 0.83 (J = 6.4 Hz) associated with the primary C-11′ methyl protons. The ^{13}C NMR spectrum of **8** displayed signals for aromatic carbon from δ 154.23 to 120.16, oxymethylene carbon at δ 64.21 (C-1′), anomeric carbons at δ 103.80 (C-1a), 101.82 (C-1b), 97.81 (C-1c), 96.15 (C-1d) and 92.16 (C-1e), other sugar carbons between δ 81.23 – 60.57, methylene carbons in the range of δ 31.36 - 22.67 and terminal methyl carbon at 14.16 (Me-11'). The presence of ^{1}H NMR signals of H-1a and H-1b in the deshielded region at δ 3.99 and H-2c and H-2d at δ 3.96 and their respective carbon signals at δ 81.23 (C-2a), 80.86 (C-2b), 78.21 (C-2c) and 77.48 (C-2d) suggested the attachment of the sugar units through (2→1) linkages. Acid hydrolysis of **8** yielded D-xylose, R_f 0.63 (*n*-butanol- acetic acid – water, 2:1:1). On the basis of spectral data analysis and chemical reactions, the structure of **8** had been formulated as 1-undecanoxy-3-phenol-3-O-β-D-xylopyranosyl-(2a→1b)- O-β-D-xylopyranosyl-(2b→1c)- O-β-D-xylopyranosyl-(2c→1d)- O-β-D-xylopyranosyl-(2d→1e)- O-β-D-xylopyranoside, a new phenolic pentaxyloside (Fig. 1).

Compound **9,** named α-L-hexaglucoside**,** (M)$^+$ at *m/z* 990 ($C_{36}H_{62}O_{31}$), gave positive tests for glycosides and showed IR absorption bands for hydroxyl groups (3425, 3396, 3267 cm^{-1}). The ion peaks produced at *m/z* 179 $(C_6H_{11}O_6)^+$, 342 $(C_6H_{11}O_6$- $C_6H_{11}O_5)^+$, 504 $(C_6H_{11}O_6$- $C_6H_{10}O_5$-$C_6H_{10}O_5)^+$ indicated that the sugar unit was consisted of hexose units. The ^{1}H NMR spectrum of compound **9** exhibited six one – proton doublets for anomeric proton signals as one-proton doublets at δ δ 5.19 (J = 3.5 Hz), 4.93 (J = 3.6 Hz), 4.90 (J = 3.5 Hz) and 4.34 (J = 3.8 Hz) and as a two – proton multiplet at δ 4.36 with half-width of 3.9 Hz assigned to α-oriented anomeric H-1a, H-1b, H-1c and H-1f and to H-1d and H-1e protons, respectively. The other sugar protons resonated as multiplets between δ 4.19 - 3.43 due to oxymethine and as two proton doublets at δ 3.39 (J = 8.8 Hz), 3.16 (J = 11.6 Hz), 3.12 (J = 8.4 Hz), 3.09 (J = 12.9 Hz), 3.05 (J = 9.6 Hz) and 3.03 (J = 7.6 Hz) associated with the oxymethylene H_2-6e, H_2-6a, H_2-6b, H_2-6c, H_2-6d and H_2-6f protons, respectively. The ^{13}C NMR spectrum of compound **9** displayed signals for anomeric carbons from δ 104.13 to 92.11 and other sugar carbons between 82.75 - 61.06. The presence of the sugar protons from H-2a to H-2d in the deshielded region from δ 4.19 to 3.99 in the ^{1}H NMR spectrum and carbon signals C-2 to C-2d between δ 82.75 – 80.91 in the ^{13}C NMR spectrum suggested (2→1) linkages of the first four sugar units. The existence of the oxymethylene H_2-6e protons in the downfield region as a two-proton doublet at δ 3.39 (J = 8.8 Hz) in the ^{1}H NMR spectrum and C-6e carbon signal at δ 64.18 indicated (6e→1f) linkage of the last two sugar units. Acid hydrolysis of **9** yielded L-glucose, m. p. 153 – 156 °C. On the basis of the foregoing discussion the structure of **9** has been established as α-L-glucopyranosyl-(2a→1b)-O-α-L-glucopyranosyl-(2b→1c)-O-α-L-glucopyranosyl-(2c→1d)-O-α-L-gluco- pyranosyl-(2d→1e)-O- α-L -glucopyranosyl-(6e→1f)-O- α-L-glucopyranoside, a new α-L-hexaglucoside derivative (Fig. 1).

^{18} ^{10} ^{9} ^{1} $^{1'}$ $^{13'}$
$CH_3(CH_2)_7CH{=}{=}CH(CH_2)_7COOCH_2(CH_2)_{11}CH_3$

1



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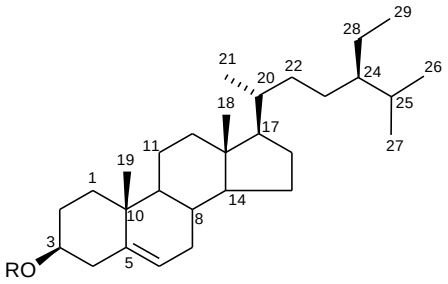
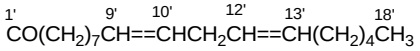
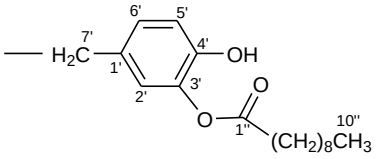
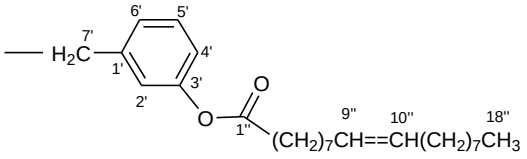
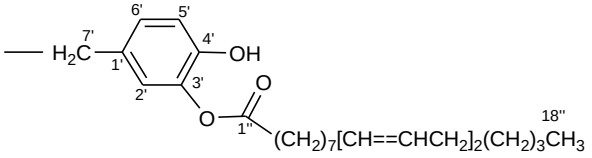
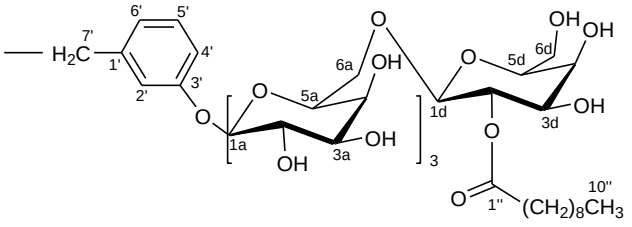
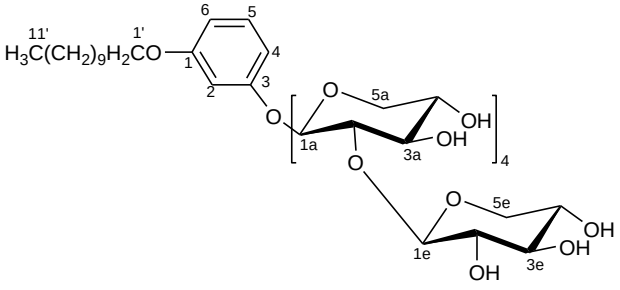
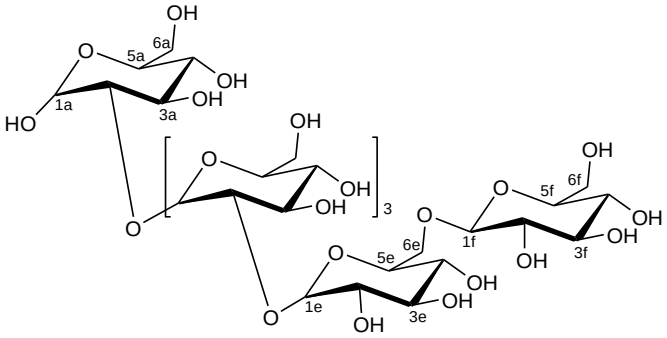


Compound	**R**
3.	
4.	
5.	
6.	
7.	



8



9

Fig. 1: Structural formulae of the compounds 1 – 9

Conclusion

Phytochemical investigation of a methanolic extract of the aerial parts of *R. hastatus* led to isolate one each fatty, aromatic steroidal esters, β-sitosterol benzyl ether esters, β-sitosterol benzyl tetragalactoside, alkyl phenoloxy pentaxyloside and α-L-hexaglucoside. This work has enhanced understanding about the phytoconstituents of the plant. These compounds may be used as chromatographic markers for standardization of the plant leaves.

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Conflicts of interests

We declare that we have no conflict of interest.

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