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Phytochemical Investigation of the Stem Bark of *Tecomella Undulata* (Sm.) Seem

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Abstract. *Tecomella undulata* (Sm.) Seem. (Bignoniaceae) occurs as a shrub or small tree in southern Asia and Saudi Arabia and its stem bark is used in folklore medicine. Phytochemical investigation of a methanolic extract of the stem bark led to the isolation of ten compounds characterized as *n*-undecanyl octadecanoate (undecanyl stearate, **1**), *n*-eicosanyl cinnamate (**2**), n-hexadecanyl caffeate (**3**), stigmast-5-en-3β-ol-3-O-β-D-arabinopyranosyl-4'4'→2a)-dihydrolapachyl-2', 3'-didecanoate (β-sitosterol arabinosyl dihydrolapachyl diester , **4**), vanillic acid (**5**), 2,7-dimethoxy-3-(6'-hydroxynonan-1'-oxy)-naphtho-1,4-quinone (tecomellanaphtho-quinone A, **6**), 2,7-dimethoxy-3-(12'-hydroxypentadecan-1'-oxy)-naphtho-1,4-quinone (tecomellanaphthoquinone B, **7**), 2-*n*-tetracosanyl - 7,8 - dimethoxy - 3 - (1'',4'' – dimethoxy - 7''- hydroxy-(3 → 2'')-naphthyl) naphthoquinone (tetracosanyl undulatol, **8**), 7,8-dimethoxy -3 (2')-(1',4'-dimethoxy-7'-hydroxyl-(3→2')- naphthyl)-naphthoquinone-7'-O-β-D-glucopyranosyl-(2a→1b)-O-β-D-glucopyranosyl-(2b→1c)-O-β-D-glucopyranosyl-(2c→1d)-O-β-D-glucopyranoside (undulatol teraglucoside, **9**) and 4-hydroxy-3-methoxybenzoate 7-O-β-D-galacturunofuranosyl-(2a→1b)-O-β-D-glucofuranosyl-(2b→1c)-O-β-D-arabinopyranosyl-(2c→1d)-O-β-D-[(arabinopyranosyl)$_8$]--(2k→1L)-O-β-D-arabinopyranoside (vanillic acid dodecaglycoside, **10**). The structures of these phytoconstituents, isolated for the first time from the stem bark, have been established on the basis of spectral data analysis and chemical reactions.

Keywords: *Tecomella undulata,* stem bark, chemical constituents, isolation, structural elucidation.

1 Introduction

Tecomella undulata (Sm.) Seem., syn. *Bignonia glauca* Decne, *B. undulata* Sm. and *Tecoma glauca* DC. (Bignoniaceae), known as rohitaka, rohira and desert teak, **is** found in Thar desert regions of northwest and western India, Saudi Arabia and southern Pakistan up to an elevation of 1200 metres[1]. It is a deciduous, ornamental shrub or a small tree with drooping branches, up to 12 m high. The leaves are linear-oblong, simple, obtuse, entire, margins undulating; flowers large, pale yellow to deep orange, present in corymbose few flowered racemes; fruits slightly curved, linear-oblong, acute and smooth. Its stem bark is analgesic, anthelmintic, anticancer, antifungal, antiseptic, antiviral, astringent, bitter, blood purifier, cholagogue, cardiotonic, choleretic, hepatoprotective, muscle relaxant, pungent, refrigerant and relaxant. It is used to treat abdominal pain, anorexia, ascites, blood disorders, cough, diabetes, eczema, flatulence, gonorrhea, gout, jaundice, hepatitis, leucoderma, liver diseases, obesity, piles, spleen disorders, syphilis, tumors, urinary disorders and worm infestations[2-5]. The root is given with rice water to cure leucorrhea. The seeds are utilized against abscess, hepatitis and taken with pine leaf extract to alleviate piles[2-10]. The heartwood contained radermachol, lapachol, cluytyl ferulate, α- and β-lapachones, steroids and dehydro-α-lapachone[11-15]. The leaves yielded cirsimaritin and cirsili[16,17]. The bark possessed β-sitosterol, iridoid glucosides, alkyl ferulates, rutin, quercetin and luteolin-7-glycoside[18-20]. The roots afforded lapacol, tricontanol-1, β-sitosterol, tectol, veratric acid, 6-O-veratryl catalposide and quinines[21]. The fruit shells and flowers furnished aphanamixin lactone, aphanamixolide and alkaloids[22,23]. This paper describes the isolation and characterization of ten chemical constituents from the stem bark of *T. undulata* collected from Barmer, Rajasthan.

2 Materials and Methods

2.1 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.

2.2 Plant Material

The stem bark of *T. undulata* was collected from Sanwlor region of Barmer, Rajasthan. The drug sample was authenticated by Dr. H.B Singh, Scientist F and Head, Raw Material Herbarium and Museum (RHMD), National Institute of Science Communication and Information Resources (NISCAIR), New Delhi. A voucher specimen was deposited in the Raw Material Herbarium and Museum, NISCAIR, New Delhi with reference number NISCAIR/RHMD/Consult/-2010-11/1464/62.

2.3 Extraction and Isolation

The air-dried powder of the stem bark (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 (196 g, 19.6% yield). Small 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 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 compounds:

2.4 *n*-Undecanyl octadecanoate (1)

Elution of the column with petroleum ether gave colourless crystals of **1**, recrystallized from acetone - methanol (1:1), 346 mg (0.034 % yield), m. p. 70-72 °C, R_f: 0.51 (petroleum ether - chloroform, 9:1), UV λ_{max} (MeOH): 204, 256 nm (log ε 5.3, 1.6); IR υ_{max} (KBr): 2915, 2848, 1721, 1650, 1461, 1383, 1268, 1104, 719 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.03 (2H, t, J = 7.8 Hz, H_2-1'), 2.41 (2H, t, J = 7.2 Hz, H_2-2), 1.67 (2H, m, CH_2), 1.51 (2H, m, CH_2), 1.30 (44H, brs, 22 x CH_2), 0.91 (3H, t, J = 6.3 Hz, Me-18), 0.87 (3H, t, J = 6.6 Hz, Me-11'); +ve FAB MS *m/z* (*rel. int.*): 438 $[M]^+$ ($C_{29}H_{58}O_2$) (1.2), 283 (9.8), 267 (14.2), 171 (11.3); δ 4.03 (2H, brs, H_2-1'), 2.41 (2H, m, H_2-2), 1.67 (2H, m, CH_2), 1.51 (2H, m, CH_2), 1.30 (44H, brs, 22 x CH_2), 0.91 (6H, brs, 2 x CH_3), +ve FAB MS *m/z* (rel. int.): 438 $[M]^+$ ($C_{29}H_{58}O_2$) (1.2), 283 (9.8), 267 (14.2).

2.5 *n*-Eicosanyl cinnamate (2)

Elution of the column with petroleum ether - chloroform (3:1) yielded pale yellow crystals of **2**, recrystallized from acetone - methanol (1:1), 123 mg (0.012 % yield), m. p. 60-62° C, R_f : 0.33 (chloroform), UV λ_{max} (MeOH): 203, 248 nm (log ε 3.1, 1.2), IR υ_{max} (KBr): 2917, 2849, 1727, 1647, 1595, 1462, 1380, 1270, 719 cm^{-1}, ^{1}H NMR ($CDCl_3$): δ 7.09 (1H, d, J = 8.0 Hz, H-2), 6.62 (1H, d, J = 8.0 Hz, H-6), 5.83 (1H, m, H-5), 5.35 (1H, m, H-4), 5.02 (1H, d, *J* = 16.8 Hz, H-7 trans), 4.95 (1H, d, J = 16.8 Hz, H-8), 4.26 (2H, t, J = 7.2 Hz, H_2-1'), 2.33 (2H, m, CH_2), 2.23 (2H, m, CH_2), 2.05 (2H, m, CH_2), 1.66

(2H, m, CH_2), 1.60 (2H, m, CH_2), 1.30 (16H, brs, 8 x CH_2), 1.26 (12H, brs, 6 x CH_2), 0.89 (3H, t, J = 6.4 Hz, Me-21'); ^{13}C NMR ($CDCl_3$): δ 173.07 (C-9), 154.48 (C-2), 139.28 (C-1), 129.76 (C-3), 127.24 (C-4), 125.73 (C-5), 124.04 (C-6), 123.60 (C-7), 115.36 (C-8), 65.01 (C-1'), 34.18 (CH_2), 34.30 (CH_2), 33.85 (CH_2), 31.96 (CH_2), 31.65 (CH_2), 29.73 (4 x CH_2), 29.65 (CH_2), 29.54 (CH_2), 29.50 (CH_2), 29.39 (CH_2), 29.30 (CH_2), 29.19 (CH_2), 29.11 (CH_2), 28.98 (CH_2), 28.03 (CH_2), 24.97 (CH_2), 14.75 (CH_3-21'); +ve FAB MS *m/z* (rel. int.): 442 $[M]^+$ ($C_{30}H_{50}O_2$) (2.3).

2.6 *n*-Hexadecanyl caffeate (3)

Elution of the column with petroleum ether - chloroform (1:1) afforded pale yellow crystals of **3**, recrystallized from acetone - methanol (1:1), 250 mg (0.25 % yield), m. p.: 72-74°C, R_f: 0.13 (petroleum ether - chloroform, 1:1), UV λ_{max} (MeOH): 204, 248 nm (log ε 4.8, 1.7), IR υ_{max} (KBr): 3422, 2916, 2848, 1731, 1595, 1462, 1381, 1287, 1134 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.34 (1H, d, J = 2.5 Hz, H-2), 7.15 (1H, d, J = 8.4 Hz, H-5), 6.86 (1H, dd, J = 8.4, 2.5 Hz, H-6), 5.88 (1H, d, J = 9.6 Hz, H-7), 5.02 (1H, d, J = 9.6 Hz, H-8), 4.31 (2H, t, J = 7.2 Hz, H_2-1'), 2.39 (2H, m, CH_2), 2.11 (2H, m, CH_2), 1.72 (2H, m, CH_2), 1.34 (22H, brs, 11 x CH_2), 0.96 (3H, t, J = 6.4 Hz, Me-16'); +ve FAB MS *m/z* (rel. int.): 404 $[M]^+$ ($C_{25}H_{40}O_4$) (2.3).

2.7 β-Sitosterol arabinosyl dihydrolapachyl diester (4)

Elution of the column with petroleum ether - chloroform (1:1) produced a light brown mass of **4**, further purified by preparative TLC using petroleum ether - chloroform (1:1), 625 mg (0.062 % yield), R_f: 0.45 (petroleum ether - chloroform, 1:1), m. p.: 148-150 °C; UV λ_{max} (MeOH): 204, 241, 253 nm (log ε 5.2, 3.2, 2.8); IR υ_{max} (KBr): 2917, 2849, 1737, 1675, 1595, 1654, 1594, 1461, 1368, 1270, 1195, 1024, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.38 (1H, m, H-6), 4.03 (1H, brm, $w_{1/2}$ = 16.5 Hz, H-3α), 1.01 (3H, brs, Me-19), 0.97 (3H, d, J = 6.8 Hz, Me-21), 0.95 (3H, d, J = 7.6 Hz, Me-26), 0.93 (3H, d, J = 7.4 Hz, Me-27), 0.89 (3H, t, J = 6.2 Hz, Me-29), 0.76 (3H, brs, Me-18), 5.03 (1H, d, J = 8.0 Hz, H-1'), 4.36 (2H, d, J = 7.6 Hz, H-5'), 4.23 (1H, m, H-2'), 4.16 (1H, m, H-3'), 4.07 (1H, m, H-4'), 0.85 (3H, t, J = 7.6 Hz, Me-10''), 0.83 (3H, t, J = 7.2 Hz, Me-10'), 8.18 (1H, dd, J = 2.6, 9.8 Hz, Me-5a), 7.82 (1H, dd, J = 3.0, 8.8 Hz, Me-8a), 7.64 (1H, m, Me- 6a), 7.14 (1H, m, Me-7a), 1.08 (3H, d, J = 6.8 Hz, Me-14a), 1.06 (3H, d, J = 7.4 Hz, Me-15a), 2.85 – 1.16 (66H, m, 29 x CH_2, 8 x CH); ^{13}C NMR ($CDCl_3$): δ 37.27 (C-1), 31.34 (C-2), 71.84 (C-3), 42.34 (C-4), 141.13 (C-5), 121.73 (C-6), 31.94 (C-7), 33.65 (C-8), 50.16 (C-9), 36.17 (C-10), 21.10 (C-11), 39.79 (C-12), 42.29 (C-13), 56.79 (C-14), 24.32 (C-15), 28.23 (C-16), 56.09 (C-17), 12.01 (C-18), 19.81 (C-19), 36.52 (C-20), 19.05 (C-21), 34.07 (C-22), 26.10 (C-23), 45.86 (C-24), 29.72 (C-25), 18.60 (C- 26), 19.17 (C-27), 22.71 (C-28), 11.87 (C-29), 102.86 (C-1'), 68.91 (C-2'), 64.01 (C-3'), 65.59 (C- 4'), 62.13 (C- 5'), 173.16 (C-1'), 33.97 (C-2'), 29.72-29.55 (C- 3'- C-9'), 14.15 (C- 10'), 171.89 (C-1'), 34.22 (C- 2'), 29.72-29.30 (C- 3' - C-9'), 14.12 (C- 10'), 192.18 (C-1a), 162.59 (C- 2a), 132.26 (C-3a), 181.52 (C-4a), 128.09 (C-5a), 110.27 (C-6a), 127.91 (C-7a), 128.09 (C-8a), 130.73 (C-9a), 130.04 (C-10a), 56.07 (C-11a), 32.56 (C-12a), 35.61 (C-13a), 21.36 (C-14a), 22.59 (C-15a); +ve FAB MS *m/z* (rel. int.): 1081 $[M+H]^+$ ($C_{69}H_{109}O_9$) (2.1), 413 (12.3), 227 (9.9), 171 (13.2).

2.8 Vanillic Acid (5)

Elution of the column with chloroform furnished pale yellow crystals of **5**, recrystallized from methanol, 1.23 g (0.12 % yield), R_f: 0.15 (chloroform - methanol, 99:1), m. p. : 208-210 °C, UV λ_{max} (MeOH): 222, 258, 289 nm (log ε 5.2, 4.1, 1.9), IR υ_{max} (KBr): 3452, 2923, 2851, 1676, 1590, 1517, 1466, 1301, 1269, 1024, 916 cm^{-1}, ^{1}H NMR ($CDCl_3$): δ 7.80 (1H, d, J = 8.0 Hz, H-5), 7.62 (1H, d, J = 1.2 Hz, H-2), 6.94 (1H, dd, J = 1.2, 8.0 Hz, H-6), 3.96 (1H, brs, OMe). ^{13}C NMR ($CDCl_3$): δ 124.61(C-1), 112.31 (C-2), 148.68 (C-3), 153.73 (C-4), 110.33 (C-5), 121.73 (C-6), 171.67 (C-7), 56.02 (OMe); +ve FAB MS *m/z* (rel. int.): 168 $[M]^+$ ($C_8H_8O_4$) (1.3).

2.9 Tecomellanaphthoquinone A (6)

Elution of the column with chloroform - methanol (19:1) offered light brown crystals of **6**, recrystallized from acetone - methanol (1:1), 1.88 g (0.19 % yield), R_f: 0.24 (chloroform - methanol, 19:1), m. p. : 51-

52 °C, UV λ_{max} (MeOH): 205, 258, 289 nm (log ε 5.1, 2.2, 1.6), IR υ_{max} (KBr): 3381, 2917, 2849, 1695, 1602, 1514, 1454, 1270, 1022, 835, 765 cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.71 (1H, d, J = 1.6 Hz, H-8), 7.56 (1H, dd, J = 1.6, 8.8 Hz, H-6), 6.82 (1H, d, J = 8.8 Hz, H-5), 3.91 (1H, brm, $w_{1/2}$ = 17.6 Hz, H-6' α), 3.80 (2H, t, J = 7.6 Hz, H_2-1'), 3.37 (3H, brs, OMe), 3.16 (1H, brs, OMe), 2.42 (2H, m, H_2-2'), 2.18 (2H, m, H_2-3'), 1.74 (2H, m, CH_2), 1.51 (2H, m, CH_2), 1.21 (4H, brs, 2 x CH_2), 0.86 (3H, t, J = 6.8 Hz, Me-9'); ^{13}C NMR (DMSO-d_6): δ 172.16 (C-1), 149.82 (C-2), 144.64 (C-3), 167.81 (C-4), 115.58 (C- 5), 115.78 (C-6), 160.97 (C-7), 116.30 (C-8), 130.54 (C-9), 131.98 (C- 10), 66.72 (C-1'), 43.53 (C- 2'), 32.26 (C- 3'), 29.82 (C-4'), 29.46 (C- 5'), 76.56 (C-6'), 29.46 (C- 7'), 24.98 (C- 8'), 14.15 (C-9'), 56.18, 50.07 (2 x OMe); +ve FAB MS *m/z* (rel. int.): 376 $[M]^+$ ($C_{21}H_{28}O_6$) (1.8), 73 (12.6).

2.10 Tecomellanaphthoquinone B (7)

Elution of the column with chloroform - methanol (9:1) yielded brown coloured crystals of **7**, recrystallized from acetone - methanol (1:1), 2.2 g (0.22 % yield), R_f: 0.22 (chloroform - methanol, 9:1), m. p. : 64-65 °C, UV λ_{max} (MeOH): 218, 261, 290 nm (log ε 4.3, 1.6, 1.2), IR υ_{max} (KBr): 3416, 2918, 2849, 1697, 1600, 1515, 1462, 1272, 1089, 873, 765 cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.61 (1H, d, J = 1.8 Hz, H-8), 7.50 (1H, dd, J = 1.8, 10.0 Hz, H-6), 6.84 (1H, d, J = 10.0 Hz, H-5), 3.97 (1H, m, $w_{1/2}$ = 18.1 Hz, H-12α), 3.85 (2H, t, J = 15.6 Hz, H_2-1'), 3.52 (3H, brs, OMe), 3.16 (3H, brs, OMe), 2.71 (4H, brs, H_2-11', H_2-13'), 2.42 (2H, m, CH_2), 2.18 (2H, m, CH_2), 1.52 (2H, m, CH_2), 1.51 (2H, m, CH_2), 1.33 (12H, brs, 6 x CH_2), 0.94 (3H, t, J = 6.1 Hz, Me-15); ^{13}C NMR (DMSO-d_6): δ 171.52 (C-1), 148.57 (C- 2), 152.61 (C-3), 179.85 (C-4), 112.03 (C- 5), 121.07 (C-6), 166.29 (C- 7), 122.75 (C- 8), 139.82 (C-9), 131.73 (C- 10), 62.50 (C-1'), 31.93 (C- 2'), 30.16 (C- 3'), 29.70 (C-4'), 29.70 (C- 5' to C-8'), 29.34 (C-9', C- 10'), 31.91 (C- 11'), 72.93 (C- 12'), 29.76 (C-13'), 24.69 (C- 14'), 14.12 (C- 15'), 55.66, 50.64 (2 x OMe); +ve FAB MS *m/z* (rel. int.): 460 $[M]^+$ ($C_{27}H_{40}O_6$) (1.3), 227 (12.3), 73 (14.6).

2.11 Tetracosanyl undulatol (8)

Elution of the column with chloroform - methanol (9:1) afforded brown coloured mass of **8**, purified by preparative TLC using methanol - chloroform (97:3), 900 mg (0.9 % yield), R_f: 0.26 (chloroform - methanol, 97:3), m. p. : 54-55 °C; UV λ_{max} (MeOH): 206, 258, 287 nm (log ε 5.1, 3.2, 1.5); IR υ_{max} (KBr): 3403, 2923, 2851, 1709, 1597, 1513, 1461, 1269, 1127, 1024, 767 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.82 (1H, d, J = 8.0 Hz, H-6), 7.76 (1H, d, J = 8.0 Hz, H-5), 7.66 (1H, d, J = 2.6 Hz, H-8'), 7.43 (1H, brs, H-3'), 7.02 (1H, dd, J = 8.4, 2.6 Hz, H-6'), 6.93 (1H, d, J = 8.4 Hz, H-5'), 4.03 (3H, brs, OMe), 4.01 (3H, brs, OMe), 4.00 (3H, brs, OMe), 3.99 (3H, brs, OMe), 2.43 (2H, t, J = 7.2 Hz, H_2-1'), 2.35 (2H, m, CH_2), 2.12 (2H, m, CH_2), 1.72 (2H, m, CH_2), 1.70 (2H, m, CH_2), 1.48 (2H, m, CH_2), 1.36 (12H, brs, 6 x CH_2), 1.33 (22H, brs, 11 x CH_2), 0.97 (3H, t, J = 6.4 Hz, Me-24'); ^{13}C NMR ($CDCl_3$): δ 171.24 (C-1), 125.14 (C-2), 124.30 (C-3), 170.86 (C-4), 107.36 (C- 5), 112.31 (C-6), 152.95 (C-7), 153.67 (C-8), 142.82 (C-9), 130.15 (C-10), 34.04 (C-1'), 33.94 (C-2'), 29.71 – 29.24 (C-3' to C-22'), 22.76 (C-23'), 14.15 (C- 24'), 150.03 (C-1'), 124.56 (C-2'), 121.28 (C-3'), 148.67 (C-4'), 110.33 (C-5'), 112.15 (C-6'), 153.89 (C-7'), 114.27 (C-8'), 125.14 (C-9'), 124.56 (C-10'), 60.96, 56.25, 56.08, 56.01 (4 x OMe); +ve FAB MS *m/z* (rel. int.): 756 $[M]^+$ ($C_{48}H_{68}O_7$) (1.6).

2.12 Undulatol tetraglucoside (9)

Elution of the column with chloroform - methanol (9:1) furnished brown coloured mass of **9**, purified by preparative TLC using methanol - chloroform (97:3), 3.7 g (0.037 % yield), R_f: 0.22 (chloroform - methanol, 9:1), m. p. : 51-52 °C; UV λ_{max} (MeOH): 205, 219, 261, 293 nm (log ε 4.1, 3.6, 1.9, 1.7); IR υ_{max} (KBr): 3510, 3414, 3375, 2926, 2845, 1705, 1645, 1515, 1451, 1272, 1225, 1075 cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.56 (1H, d, J = 8.4 Hz, H-6), 7.46 (1H, s, H-2), 6.80 (1H, d, J = 8.4 Hz, H-5), 7.64 (1H, dd, J = 2.0, 8.0 Hz, H-6'), 7.07 (1H, d, J = 8.0 Hz, H-5'), 6.48 (1H, s, H-3'), 6.41 (1H, d, J = 2.0 Hz, H-8'), 5.23 (1H, d, J = 8.8 Hz, H-1a), 4.45 (1H, dd, J = 8.8, 7.2 Hz, H-2a), 3.57 (1H, m, H-3a), 3.71 (1H, m, H-4a), 4.63 (1H, m, H-5a), 3.33 (2H, d, J = 10.8 Hz, H_2-6a), 5.13 (1H, d, J = 8.0 Hz, H-1b), 4.47 (1H, dd, J = 8.0, 10.4 Hz, H-2b), 3.60 (1H, m, H-3b), 3.73 (1H, m, H-4b), 4.64 (1H, m, H-5b), 3.36 (2H, brs. H_2-6b), 4.98 (1H, d, J = 8.0 Hz, H-1c), 4.36 (1H, dd, J = 8.0, 6.6 Hz, H-2c), 3.62 (1H, m, H-3c), 3.94 (1H, m, H-4c), 4.60 (1H, m, H-5c), 3.20 (2H, brs. H_2-6c), 4.94 (1H, d, J = 7.2 Hz, H-1d), 4.13 (1H, dd, J

= 7.2, 6.5 Hz, H-2d), 3.64 (1H, m, H-3d), 3.91 (1H, m, H-4d), 4.51 (1H, m, H-5d), 3.06 (2H, brs. H_2-6d), 3.90 (3H, brs, OMe), 3.71(3H, brs, OMe), 3.39 (3H, brs, OMe), 3.16 (3H, brs, OMe); ^{13}C NMR (DMSO-d_6): δ 167.11 (C-1), 125.46 (C-2), 146.09 (C-3), 165.97 (C-4), 112.20 (C-5), 123.96 (C-6), 160.40 (C-7), 153.69 (C-8), 144.62 (C-9), 130.92 (C-10), 153.61 (C-1'), 141.56 (C- 2'), 121.60 (C- 3'), 148.93 (C-4'), 111.56 (C-5'), 116.27 (C-6'), 148.02 (C- 7'), 113.85 (C- 8'), 146.09 (C-9'), 123.45 (C- 10'), 102.24 (C-1a), 80.38 (C-2a), 76.75 (C-3a), 66.16 (C-4a), 77.89 (C-5a), 63.53 (C-6a), 102.73 (C-1b), 79.72 (C-2b), 73.88 (C-3b), 66.35 (C-4b), 77.59 (C-5b), 61.86 (C-6b), 98.31 (C-1c), 79.39 (C-2c), 73.62 (C-3c), 70.55 (C-4c), 77.29 (C-5c), 61.57 (C-6c), 93.42 (C-1d), 79.06 (C-2d), 72.93 (C-3d), 70.71 (C-4d), 77.07 (C-5d), 61.18 (C-6d), 58.67, 58.96, 56.19, 55.90 (4 x OMe); +ve FAB MS *m/z* (rel. int.): 1069 $[M+H]^+$ ($C_{48}H_{61}O_{27}$) (1.5), 889 (7.1), 649 (10.3), 419 (14.4), 341 (8.5), 179 (22.7), 163 (12.1).

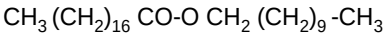
2.13 Vanillic acid tetradecaglucoside (10)

Elution of the column with chloroform-methanol (3:1) gave brown amorphous powder of **10**, recrystallized from methanol, 7.5 g (0.075 % yield), R_f: 0.49 (chloroform - methanol, 3:1), m. p. : 255-257 °C; UV λ_{max} (MeOH): 205, 256, 286 nm (log ε 4.6, 2.1, 1.7); IR υ_{max} (KBr): 3510, 3445, 3350, 3280, 3135, 2935, 2850, 1721, 1696, 1623, 1513, 1418, 1343, 1270, 1074, 760 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 7.57 (1H, dd, J = 9.6, 3.0 Hz, H-6), 6.81 (1H, d, J = 9.6 Hz, H-5), 6.36 (1H, d, J = 3.0 Hz, H-2), 3.16 (3H, brs, OMe), 5.84 (1H, d, J = 7.3 Hz, H-1a), 4.58 (1H, m, H-2a), 4.27 (1H, m, H-3a), 3.27 (1H, s, H_2-5), 5.71 (1H, d, J = 7.2 Hz, H-1b), 4.56 (1H, m, H-2b), 4.25 (1H, d, J = 6.8 Hz, H-3b), 3.08 (2H, s, H_2-5b), 3.12 (2H, brs. H_2-6b), 5.23 (1H, d, J = 7.3 Hz, H-1c), 4.53 (1H, m, H-2c), 3.89 (1H, m, H-3c), 3.60 (1H, m, H-4c), 3.85 (2H, d, J = 6.7 Hz, H_2-5c), 5.20 (1H, d, J = 7.2 Hz, H-1d), 4.52 (1H, m, H-2d), 3.88 (1H, m, H-3d), 3.67 (1H, m, H-4d), 3.82 (2H, d, J = 6.9 Hz, H_2-5d), 5.18 (1H, d, J = 7.1 Hz, H-1e), 4.50 (1H, m, H-2e), 3.66 (1H, m, H-3e), 3.38 (1H, m, H-4e), 3.80 (2H, d, J = 6.9 Hz, H_2-5e), 5.11 (1H, d, J = 7.6 Hz, H-1f), 4.48 (1H, m, H-2f), 3.61 (1H, m, H-3f), 3.36 (1H, m, H-4f), 3.77 (2H, d, J = 6.5 Hz, H_2-5f), 5.09 (1H, d, J = 7.9 Hz, H-1g), 4.46 (1H, m, H-2g), 3.60 (1H, m, H-3g), 3.35 (1H, m, H-4g), 3.80 (2H, d, J = 6.7 Hz, H_2-5g), 5.07 (1H, d, J = 7.7 Hz, H-1h), 4.44 (1H, m, H-2h), 3.59 (1H, m, H-3h), 3.34 (1H, m, H-4h), 3.75 (2H, d, J = 6.5 Hz, H_2-5h), 5.05 (1H, d, J = 7.9 Hz, H-1i), 4.43 (1H, m, H-2i), 3.56 (1H, m, H-3i), 3.32 (1H, m, H-4i), 3.68 (2H, d, J = 6.7 Hz, H_2-5i), 4.96 (1H, d, J = 7.2 Hz, H-1j), 4.41 (1H, m, H-2j), 3.56 (1H, m, H-3j), 3.30 (1H, m, H-4j), 3.65 (2H, d, J = 6.7 Hz, H_2-5j), 4.92 (1H, d, J = 7.4 Hz, H-1k), 4.40 (1H, m, H-2k), 3.52 (1H, m, H-3k), 3.28 (1H, m, H-4k), 3.62 (2H, d, J = 6.3 Hz, H_2-5k), 4.90 (1H, d, J = 7.1 Hz, H-1L), 4.37 (1H, m, H-2L), 3.50 (1H, m, H-3L), 3.26 (1H, m, H-4L), 3.60 (2H, d, J = 6.3 Hz, H_2-5L); ^{13}C NMR (DMSO-d_6): δ 157.99 (C-1), 130.93 (C-2), 163.25 (C-3), 161.54 (C-4), 140.68 (C-5), 116.30 (C-6), 168.99 (C- 7), 50.01 (OMe), 109.84 (C-1a), 79.59 (C- 2a), 73.99 (C- 3a), 82.37 (C-4a), 61.71 (C- 5a), 182.50 (C- 6a), 108.70 (C-1b), 79.21 (C- 2b), 73.87 (C- 3b), 82.21 (C-4b), 61.19 (C-5b), 61.05 (C-6b), 105.64 (C-1c), 77.83 (C- 2c), 73.57 (C-3c), 71.08 (C-4c), 63.34 (C-5c), 103.80 (C-1d), 77.66 (C- 2d), 73.49 (C-3d), 70.80 (C-4d), 63.55 (C-5d), 102.43 (C-1e), 77.54 (C- 2e), 73.25 (C-3e), 70.68 (C-4e), 63.78 (C-5e), 100.36 (C-1f), 77.23 (C- 2f), 73.01 (C-3f), 70.39 (C-4f), 60.90 (C-5f), 100.05 (C-1g), 77.16 (C- 2g), 72.92 (C-3g), 70.23 (C-4g), 64.88 (C-5g), 98..45 (C-1h), 76.84 (C- 2h), 72.84 (C-3h), 69.94 (C-4h), 65.25 (C-5h), 97.35 (C-1i), 76.58 (C- 2i), 72.64 (C-3i), 69.65 (C-4i), 62.83 (C-5i), 94.96 (C-1j), 76.06 (C- 2j), 72.38 (C-3j), 69.41 (C-4j), 63.18 (C-5j), 93.77 (C-1k), 75.47 (C- 2k), 73.87 (C-3k), 68.76 (C-4k), 64.11 (C-5k), 92.68 (C-1L), 75.32 (C- 2L), 73.49 (C-3L), 68.15 (C-4L), 61.71 (C-5L); +ve FAB MS *m/z* (rel. int.): 1827 $[M+H]^+$ ($C_{70}H_{107}O_{55}$) (1.9), 489 (10.1), 327 (8.4), 281 (12.7), 151 (16.1), 149 (21.6).

3 Results and Discussion

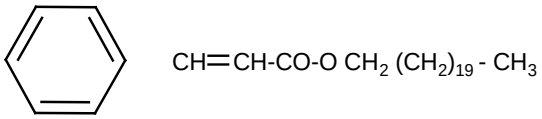
Compound **1**, named undecanyl stearate, showed characteristic IR absorption bands for ester group (1721 cm^{-1}) and a long aliphatic chain (719 cm^{-1}). Its mass spectrum exhibited a molecular ion peak at *m/z* 438 corresponding to a molecular formula of a fatty acid ester, $C_{29}H_{58}O_2$. The ion fragments arising at *m/z* 267 $[CH_3(CH_2)_{16}CO]^+$, 283 $[CH_3(CH_2)_{16}COO]^+$ and 171 $[M - 267]^+$ suggested that stearic acid was esterified with a C_{11} alcohol. The ^{1}H NMR spectrum of **1** displayed two two-proton triplets at δ 4.03 (J = 7.8 Hz, H_2-1') and 2.41 (2H, t, J = 7.2 Hz, H_2-2), assigned to oxymethylene H_2-1'and methylene H_2-2 protons adjacent to the ester carbon, respectively. Three two-proton multiplets at δ 2.41, 1.67 and 1.51

and a broad signal at δ 1.30 (44H) were ascribed to the remaining methylene protons. Two three-proton triplets at δ 0.91 (J = 6.3 Hz, Me-18) and 0.87 (J = 6.6 Hz, Me-11') were attributed to terminal C-18 and C-11' primary methyl protons, respectively. The absence of any signal beyond δ 4.03 suggested saturated nature of the molecule. On the basis of these evidences the structure of **1** has been characterized as *n*-undecanyl octadecanoate.



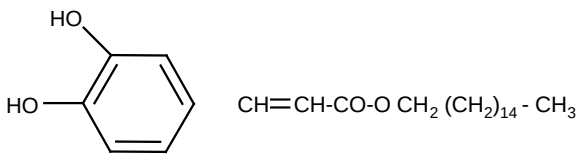
Compound 1. Undecanyl stearate (**1**).

Compound **2**, an eicosanyl ester, showed distinctive IR absorption bands for ester group (1727 cm^{-1}), unsaturation (1647 cm^{-1}), aromatic ring (1595 cm^{-1}) and a long aliphatic chain (719 cm^{-1}). On the basis of FAB mass and ^{13}C NMR spectra, the molecular ion peak of **2** was established at *m/z* 442 consisting to molecular formula of an aromatic ester, $C_{30}H_{50}O_2$. The ^1H NMR spectrum of **2** exhibited two one-proton doublets at δ 7.09 (*J* = 8.0 Hz) and 6.62 (*J* = 8.0 Hz) and two multiplets at δ 5.83 (2H) and 5.35 (1H) assigned to aromatic protons. Two one-proton doublets at δ 5.02 (J = 16.8 Hz) and 4.95 (J = 16.8 Hz) were attributed to *trans*-oriented vinylic H-7 and H-8 protons, respectively. A two-proton triplet at δ 4.26 (J = 7.2 Hz) was due to the oxygenated H_2-1' methylene protons. A three-proton triplet at δ 0.89 (J = 6.4 Hz) was accounted to the terminal C-21' primary methyl protons. The remaining methylene protons appeared from δ 2.33 to 1.26. The ^{13}C NMR spectrum showed signals for ester carbon at δ 173.07 (C-9), aromatic signals between δ 154.48 - 124.04, vinylic carbons at δ 123.60 (C-7) and 115.36 (C-8), oxymethylene carbon at δ 65.01 (C-1'), other methylene carbons from δ 34.18 to 24.97 and a methyl carbon at δ 14.75 (C-21'). On the basis of the foregoing discussion the structure of **2** has been established as *n*-eicosanyl cinnamate.



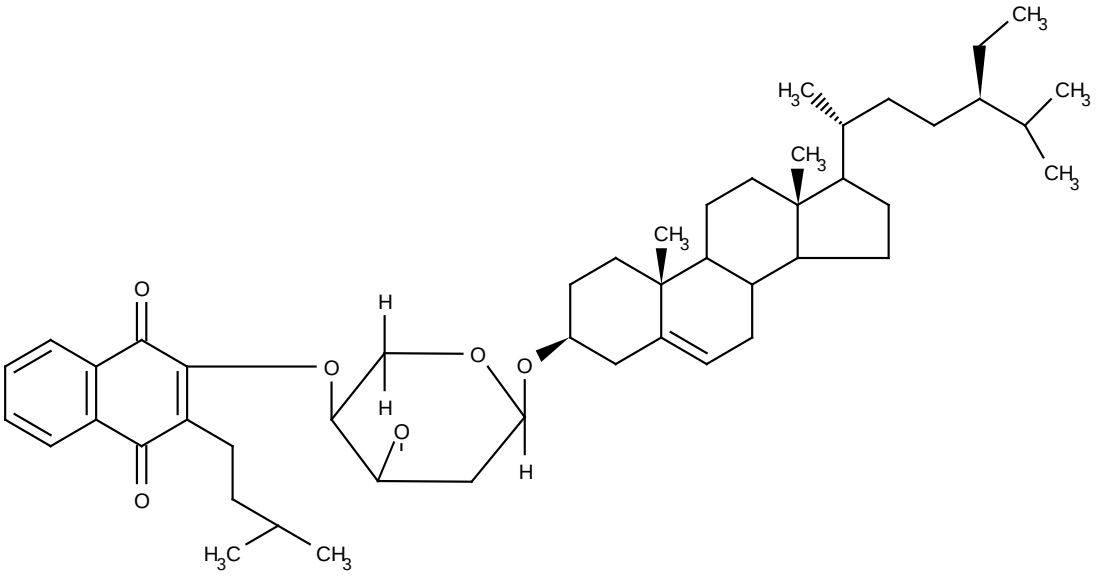
Compound 2. *n*-Eicosanyl cinnamate (**2**).

Compound **3**, an *n*-hexadecanyl ester, gave positive tests for phenols and had characteristic IR absorption bands for hydroxyl groups (3422 cm^{-1}), ester function (1731 cm^{-1}) and aromatic ring (1595 cm^{-1}). Its mass spectrum showed a molecular ion peak at *m/z* 404 consistent to molecular formula $C_{25}H_{40}O_4$. The ^1H NMR spectrum of **3** exhibited two one-proton doublets at δ 7.34 (J = 2.5 Hz) and 7.15 (J = 8.4 Hz) and a one-proton double doublet at δ 6.86 (J = 8.4, 2.5 Hz) assigned to *meta*-coupled H-2, *ortho*-coupled H-5 and *ortho, meta*-coupled H-6 protons, respectively. Two one-proton doublets at δ 5.88 (J = 9.6 Hz) and 5.02 (J = 9.6 Hz) were ascribed to *cis*-oriented vinylic H-7 and H-8 protons, respectively. A two-proton triplet at δ 4.31 (J = 7.2 Hz) was due to oxymethylene H_2-1' protons. The other methylene protons resonated as two-proton multiplets at δ 2.39, 2.11 and 1.72 and a broad signal at δ 1.34 (22H). A three-proton triplet at δ 0.96 (J = 6.4 Hz) was accounted to the terminal C-16' primary methyl protons. On the basis of spectral data analysis, the structure of **3** has been elucidated as *n*-hexadecanyl caffeate.



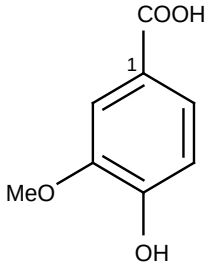
Compound 3. *n*-Hexadecanyl caffeate (**3**).

Compound **4**, named β-sitosterol arabinosyl dihydrolapachyl diester, showed IR absorption bands for ester functions (1737 cm^{-1}), carbonyl group (1675 cm^{-1}), unsaturation (1645 cm^{-1}), aromatic ring (1594, 1024 cm^{-1}) and a long aliphatic chain (720 cm^{-1}). On the basis of FAB mass and ^{13}C NMR spectra, the molecular ion peak of **4** was determined at *m/z* 1081 $[M+H]^+$ consistent with the molecular formula of a steroidal glycosidic ester dihydrolapachol, $C_{69}H_{109}O_9$. The ion peaks arising at *m/z* 413 [O – C_1' fission]$^+$, 227 $[C_{15}H_{19}O_2]^+$ and 171 $[C_{10}H_{19}O_2]^+$ supported the presence of β-sitosterol, lapachol and decanoic acid in the molecule. The ^1H NMR spectrum showed two one-proton double doublets at δ 8.18 (J = 2.6, 9.8 Hz) and 7.82 (J = 3.0, 8.8 Hz) and two one-proton multiplets at δ 7.64 and 7.14 assigned to aromatic *ortho*-, *meta*-coupled H-5a, H-8a, H-6a and H-7a protons, respectively. A one-proton multiplet at δ 5.38, a one-proton doublet at δ 503 (J = 7.3 Hz) and a one-proton broad multiplet at δ 4.03 with half width of 16.5 Hz were attributed correspondingly to vinylic H-6, anomeric H-1' and oxymethine H-3α protons. The other sugar protons resonated between δ 4.07 - 4.36 and shifting of these protons in the deshielded region suggested esterification of sugar carbinols. Two three-proton broad signals δ 0.76 and 1.01 and four three-proton doublets at δ 0.97 (J = 8.4 Hz), 0.95 (J = 7.6 Hz), 0.93 (J = 7.6 Hz) and 0.89 (J = 6.2 Hz) were accounted to tertiary C-18 and C-19, secondary C-21, C-26 and C-27 and primary C-29 methyl protons of the steroid. Two three-proton doublets at δ 1.08 (J = 6.8 Hz) and 1.06 (J = 7.4 Hz) and two three-proton triplets at δ 0.85 (J = 7.6 Hz) and 0.83 (J = 7.2 Hz) were associated with the secondary methyl C-14a and C-15a proton of lapachol unit and primary methyl C-10' and C-10' protons of the fatty acid chains. The other methine and methylene protons appeared from δ 2.85 to 1.16. The ^{13}C NMR spectrum of **4** showed signals for carbonyl carbons at δ 192.18 (C-1a) and 181.52 (C-4a), ester carbons at δ 173.16 (C-1' and 171.89 (C-1'), aromatic and vinylic carbons between δ 162.59 - 110.27, anomeric carbon at δ 102.86 (C-1'), other sugar carbons from δ 68.91 to 62.13 and methyl carbons between δ 22.59 - 11.87. The ^1H and ^{13}C NMR spectral data of the steroidal nucleus were compared with the reported spectral values of steroids[24-26]. On the basis of the foregoing account, the structure of **4** has been formulated as stigmast-5-en-3β-ol-3β-D-arabinopyranosyl-4'(4'→2a)-dihydrolapachyl-2',3'didecanoate. This is a new steroidal arabinosyl diester.



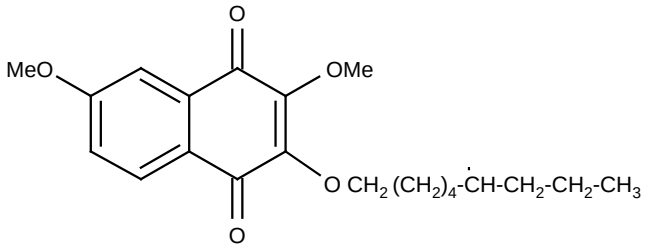
Compound 4. β-Sitosterol arabinosyl dihydrolapachyl diester (**4**).

Compound **5**, was the known phytoconstituents identified as vanillic acid.



Compound 5. Vanillic acid (**5**).

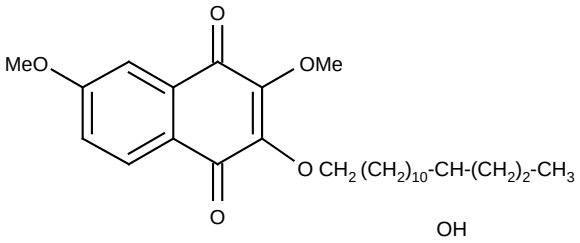
Compound **6**, named tecomellanaphthoquinone A, displayed distinctive IR absorption bands for hydroxyl group (3381 cm^{-1}), carbonyl functions (1695cm^{-1}), aromatic ring (1602, 1514, 1022 cm^{-1}) and aliphatic chain (765 cm^{-1}). On the basis of FAB mass and ^{13}C NMR spectral data, the molecular ion peak of the **6** was determined at *m/z* 376 consistent with the molecular formula of a naphthoquinone derivative, $C_{21}H_{28}O_6$. An important ion peak arising at *m/z* 73 [$C_{5'}$ - $C_{6'}$ fission, $CH(OH)CH_2CH_2CH_3]^+$ suggested that the hydroxyl function was located in the aliphatic side chain at C-6'. The ^1H NMR spectrum of **6** exhibited two one-proton doublets at δ 7.71 (J = 1.6 Hz) and 6.82 (J = 8.8 Hz) assigned to *meta*-coupled H-8 and *ortho*-coupled H-5, a one-proton double doublet at δ 7.56 (J = 1.6, 8.8 Hz) ascribed to *ortho*-, *meta*-coupled H-6, a one-proton broad multiplet at δ 3.91 with half width of 17.6 Hz attributed to α-oriented carbinol H-6' proton, a two-proton triplet at δ 3.80 (J = 7.6 Hz) associated with oxymethylene H_2-1' protons and two three-proton broad signals at δ 3.37 and 3.16 due to methoxy protons. A three-proton triplet at δ 0.86 (J = 6.8 Hz) was accounted to C-9' primary methyl protons. The remaining methylene protons resonated as multiplets between δ 2.42-1.51 and as a four-proton broad singlet at δ 1.21. The ^{13}C NMR spectrum of **6** displayed signals for carbonyl carbons at δ 172.16 (C-1) and 167.81 (C-4), aromatic carbons between δ 160.97-115.78, hydroxymethine carbon at δ 76.56 (C-6'), oxymethylene carbon at δ 66.72 (C-1'), methoxy carbons at δ 56.18 and 50.07 and methyl carbon at δ 14.15 (C-9'). Based on these evidences, the structure of **6** has been formulated as 2,7-dimethoxy-3-(6' β -hydroxynonan-1'-oxy)-naphtho-1,4-quinone. This is a new naphthoquinone derivative.



Compound 6. Tecomellanaphthoquinone A (**6**).

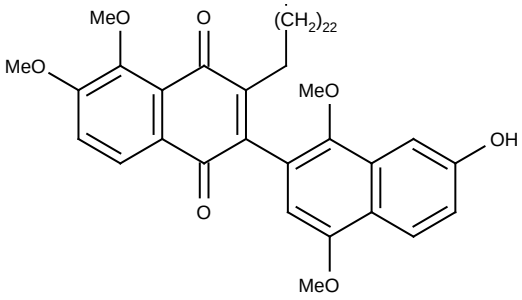
Compound **7**, designated as tecomellanaphthoquinone B, exhibited characteristic IR absorption bands for hydroxyl group (3416 cm^{-1}), carbonyl functions (1697 cm^{-1}), aromatic ring (1600, 1515, 1089 cm^{-1}) and aliphatic chain (785 cm^{-1}). On the basis of FAB mass and ^{13}C NMR spectral data, the molecular ion peak of **7** was determined at *m/z* 460 corresponding to the molecular formula of a naphthoquinone derivative, $C_{27}H_{40}O_6$. The ion peaks arising at *m/z* 227 [O – $C_{1'}$ fission, $(CH_2)_{11}CH(OH)(CH_2)_2CH_3]^+$ and 73 [$C_{11'}$ - $C_{12'}$ fission, $CH(OH)CH_2\ CH_2\ CH_3]^+$ indicated that a pentadecanyl carbon chain with the hydroxyl group at C-12' was attached to the naphthoquinone moiety. The ^1H NMR spectrum of **7** showed two one-proton doublets at δ 7.61 (J = 1.8 Hz) assignable to *meta*-coupled H-8 and at δ 6.84 (J = 10.04 Hz) ascribable to *ortho*-coupled H-5 and a *meta*-, *ortho*- coupled H-6 at δ 7.50 (J = 1.8, 10.0 Hz). A one-proton broad multiplet at δ 3.97 with half-width of 18.1 Hz was accounted to hydroxymethine H-12α proton. A two-proton triplet at δ 3.83 (J = 15.6 Hz) was attributed to oxymethylene H_2-1' protons. Two three-proton broad singlets at δ 3.52 and 3.16 were due to methoxy protons. A three-proton triplet at δ 0.94 (J = 6.1 Hz) was associated with C-15' terminal primary methyl protons. The remaining methylene protons appeared from δ 2.71 to 1.33. The ^{13}C NMR

spectrum of **7** displayed signals for carbonyl carbons at δ 171.52 (C-1) and 179.85 (C-4), aromatic carbons between δ 166.29-112.03, methoxy carbons at δ 55.66 and 50.64, hydroxymethine carbon at δ 72.93 (C-12'), oxymethylene carbon at δ 62.50 (C-1'), methylene carbons from δ 31.93 to 24.69 and methyl carbon at δ 14.12 (C-15'). On the basis of the foregoing account, the structure of **7** has been elucidated as 2,7-dimethoxy-3-(12'β-hydroxypentadecan-1'- oxy)-naphtho-1,4-quinone. This is a new naphthoquinone derivative.



Compound 7. Tecomellanaphthoquinone B (**7**).

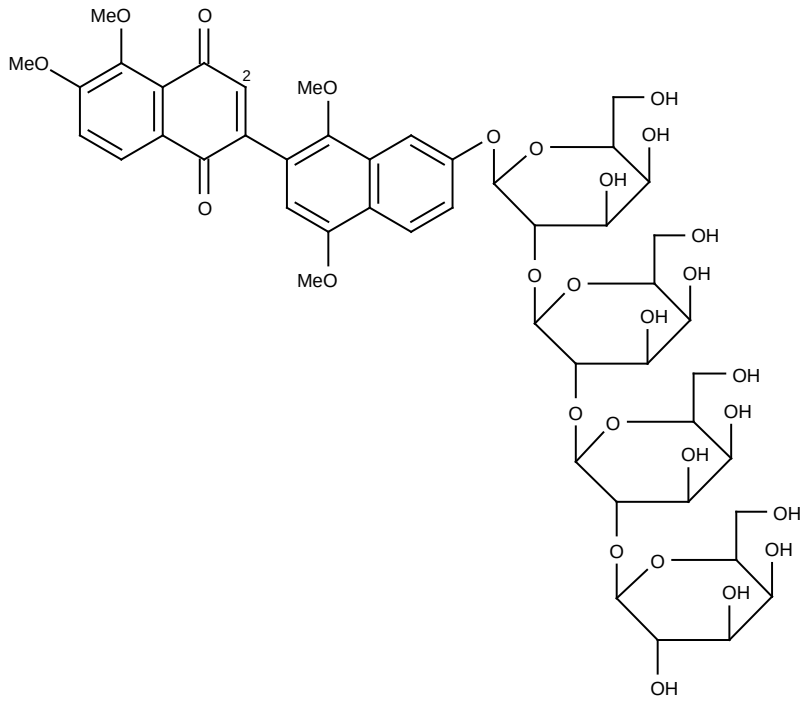
Compound **8**, designated as tetracosanyl undulatol, exhibited characteristic IR absorption bands for hydroxyl group (3403 cm^{-1}), carbonyl groups (1709 cm^{-1}), aromatic ring (1597, 1513, 1024 cm^{-1}) and long aliphatic chain (767 cm^{-1}). On the basis of FAB mass and ^{13}C NMR spectra, the molecular ion peak of **8** was determined at *m/z* 756 consistent to the molecular formula of a tectol - type component, $C_{48}H_{68}O_7$. The ^1H NMR spectrum of **8** showed four one-proton doublets at δ 7.82 (J = 8.0 Hz), 7.76 (J = 8.0 Hz), 6.93 (J = 8.4 Hz) and 7.66 (J = 2.6 Hz) assigned correspondingly to *ortho*-coupled H-6, H-5 and H-5' and *meta*-coupled H-8' protons. A one-proton broad singlet at δ 7.43 and a one-proton double doublet at δ 7.02 (J = 8.4, 2.6 Hz),were ascribed to *para*-coupled H-3' and o*rtho*-, *meta*-coupled H-6' protons, respectively. Four three-proton broad singlets at δ 4.03, 4.01, 4.00 and 3.99 were associated with the methoxy protons. A two-proton triplet at δ 2.43 (J = 7.2 Hz) was attributed to methylene H_2-1' protons linked with the naphthalene ring. The other methylene protons appeared from δ 2.35 to 1.33. A three-proton triplet at δ 0.97 (J = 6.4 Hz) was accounted to C-24' primary methyl protons. The ^{13}C NMR spectrum of **8** exhibited important signals for carbonyl carbons at δ 171.24 (C-1) and 170.86 (C-4), aromatic carbons between δ 153.89-107.36, methoxy carbons from δ 60.96 to 56.01, methylene carbons in range of δ 34.04-22.76 and methyl carbon at δ 14.15 (C-24'). On the basis of spectral data analysis, the structure of **8** has been established as 2-*n*-tetracosanyl - 7,8 - dimethoxy - 3 - (1'',4' dimethoxy - 7' hydroxy (3 → 2')- naphthyl) naphthoquinone. This is a new tectol-type constituent isolated from the herbal drug.



Compound 8. Tetracosanyl undulatol (**8**).

Compound **9**, named undulatol teraglucoside, responded to chemical tests for glycosides positively and had IR absorption bands for hydroxyl groups (3510, 3414, 3375 cm^{-1}), carbonyl functions (1705 cm^{-1}) and aromatic ring (1645, 1515, 1075 cm^{-1}). On the basis of FAB mass and ^{13}C NMR spectra, the molecular ion peak of **9** was determined at *m/z* 1069 $[M+H]^+$ corresponding to a molecular formula of

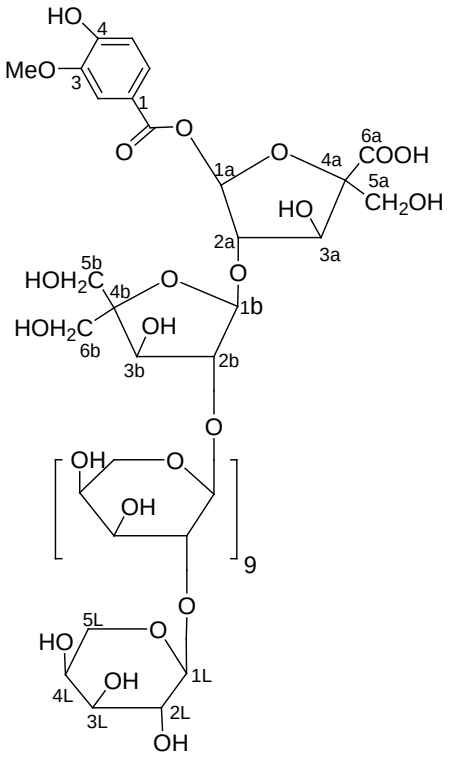
tectol-type tetraglucoside, $C_{48}H_{61}O_{27}$. The ion peaks arising at *m/z* 163 [O – C_{1d} fission, $C_6H_{11}O_5]^+$, 179 [C_{2c} – O fission, $C_6H_{11}O_6]^+$, 341 [C_{2b} – O fission, $C_{12}H_{21}O_{11}]^+$, 649 [O – C_{1a} fission, $C_{24}H_{41}O_{20}]^+$, 889 [M – 179]$^+$ and 419 [M – $C_{24}H_{41}O_{20}]^+$ suggested linkage of a tetraglycoside chain to tectol. The ^{1}H NMR spectrum of **9** showed four one-proton doublets at δ 6.80 (J = 8.4 Hz), 7.56 (J = 8.4 Hz), 7.07 (J = 8.0 Hz) and 6.41 (J = 2.0 Hz) and a one-proton double doublet at δ 7.64 (J = 2.0, 8.0 Hz), assigned correspondingly to *ortho*-coupled H-5, H-6 and H-5', *meta*-coupled H-8' and *ortho-, meta*-coupled H-6' protons. Two one-proton singlets at δ 7.46 and 6.48 were due to H-2 and H-3' protons, respectively. The methoxy protons resonated as three-proton singlets at δ 3.90, 3.71, 3.39 and 3.16. Four one-proton doublets at δ 5.23 (J = 8.8 Hz), 5.13 (J = 8.0 Hz), 4.98 (J = 8.0 Hz)and 4.94 (J = 7.2 Hz) were ascribed to anomeric H-1a, H-1b, H-1c and H-1d protons, respectively. The other sugar protons appeared from δ 4.63 to 3.06. The appearance of the H-2 sugar protons in the deshielded region as double doublets at δ 4.45 (*J* = 8.8, 7.2 Hz), 4.47 (*J* = 8.0, 10.4 Hz), 4.36 (*J* = 8.8, 6.6 Hz) suggested (2→1) linkages of the sugar units. The ^{13}C NMR spectrum of **9** showed signals for carbonyl carbons at δ 167.11 (C-1) and 165.97 (C-4), aromatic signals from δ 160.40 to 111.27, anomeric carbons at δ 102.24 (C-1a), 102.73 (C-1b), 98.31 (C-1c) and 93.42 (C-1d), other sugar carbons from δ 80.38 to 61.18 and methoxy carbon in the range of 58.96-55.90. The shifting of the C-2 carbons of the sugar units in the deshielded region at δ 80.38 (C-2a), 79.72 (C-2b) and 79.39 (C-2c) supported (2→1) linkages of the sugar units. Based on these evidences, the structure of **9** has been formulated as 7,8-dimethoxy -3 (2')-(1',4'dimethoxy-7'hydroxyl-(3→2')- naphthyl)- naphthoquinone-7' -O- β - D -glucopyranosyl-(2a→1b)-O-β-D-glucopyranosyl-(2b→1c)-O-β-D-glucopyranosyl-(2c→1d)- O-β -D- glucopyranoside. This is a new tectol type tetraglucoside.



Compound 9. Undulatol teraglucoside (**9**).

Compound **10**, named vanillic acid dodecaglycoside, gave positive tests for glycosides and had UV absorption maxima at 256 and 286 nm indicating the presence of aromatic ring. Its IR spectrum of 10 exhibited characteristic absorption bands for hydroxyl groups (3510, 3445, 3350, 3280, 3135 cm^{-1}), ester function (1721 cm^{-1}), carboxylic group (1696 cm^{-1}) and aromatic ring (1623, 1513, 1074 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, the molecular ion peak of **10** was determined at *m/z* 1827 [M+H]$^+$ consistent to the molecular formula of an aromatic acid polysaccharide, $C_{70}H_{107}O_{55}$. The ion peaks arising at *m/z* 151 $[C_6H_3(OH)(OMe)CO]^+$, 327 $[C_6H_3(OH)(OMe)CO\text{-}C_6H_8O_6$; $C_{14}H_{15}O_9]^+$ and 489 $[C_6H_3(OH)(OMe)CO\text{-}C_6H_8O_6\text{-}C_6H_{10}O_5$; $C_{20}H_{25}O_{14}]^+$ suggested attachment of vanillic acid with

glucuronosyl glucoside unit. The ion fragments generated at *m/z* 149 $[C_5H_9O_5]^+$ and 281 $[C_5H_9O_5\text{-}C_5H_8O_9; C_{10}H_{17}O_9]^+$ indicated the existence of the pentose sugar moieties at one of the terminal of the vanillyl polysaccharide. The ^{1}H NMR spectrum of **10** showed a one-proton double doublet at δ 7.57 (J = 9.6, 3.0 Hz) assigned to *ortho*-coupled aromatic H-6 proton. Two one-proton doublets at δ 6.36 (J = 3.0 Hz) and 6.81 (J = 9.6 Hz) were ascribed to *meta*-coupled H-2 and ortho-coupled H-5 protons, respectively. A three-proton broad signal at δ 3.16 was attributed to methoxy protons. The β-oriented anomeric proton signals appeared as one-proton doublets from δ 5.84 to 4.90 with coupling interactions between 7.9 – 7.1 Hz. The other sugar protons resonated in the range of δ 4.58-3.08. The ^{13}C NMR spectrum of **10** displayed signals for carboxylic carbon at δ 182.50 (C-6a), ester carbon at δ 168.99 (C-7), aromatic carbons between δ 163.25-116.30, anomeric carbons in the range of δ 109.84-92.68 and other sugar carbons from δ 82.37 to 60.09. The presence of anomeric carbons C-1a at 109.84 and C-1b at 108.70, C-2a and C-2b at δ 79.59 and 79.21, C-4a at δ 82.37 and C-4b at δ 82.21 indicated furanic forms of first two rings. The presence of H-2a to H-2k proton signals of the sugar units in the deshielded region from δ 4.58 to 4.42 and C-2 sugar carbon signals from δ 79.59 to 75.47 suggested (1→2) linkages of the sugar units. Acid hydrolysis of **10** yielded yellow crystals of vanillic acid, m. p. 210-212° C, R_f: 0.98 (ethyl acetate : formic acid : acetic acid : water. 100 : 11 : 11 : 26 v/v), galacturonic acid, R_f : 0.15 (*n*-butanol-acetic acid-water , 4:1:5 v/v), D-glucose , R_f : 0.18 (*n*-butanol-acetic acid-water, 4:1:5 v/v) and D-arabinose, R_f: 0.54 (*n*-butanol-ethanol-water, 4:1:2.2, v/v). On the basis of spectral data analysis and chemical tests, the structure of **10** has been established as 4**-**hydroxy-3-methoxybenzoate 7-O**-**β-D-galacturunofuranosyl-(2a→1b)-O-β-D-glucofuranosyl-(2b→1c)-O-β-D-arabinopyranosyl-(2c→1d)-O-β-D-arabino-pyranosyl-(2d→1e)-O-β-D-arabinopyranosyl-(2e→1f)-O-β-D-arabinopyranosyl-2f→1g)-O-β-D-arabinopyranosyl-(2g→1h)-O-β-D-arabinopyranosyl-(2h→1i)-O-β-D-arabinopyranosyl-(2i→1j)-O-β-D-arabinopyranosyl-(2j→1k)-O-β-D-arabinopyranosyl-(2k→1L)-O-β-D-arabinopyranoside. This is a new vanillic acid polysaccharide.



Compound 10. Vanillic acid dodecaglycoside (**10**).

4 Conclusions

Phytochemical investigation of a methanolic extract of the stem bark of *Tecomella undulata* led to the isolation of aliphatic and aromatic esters, β-sitosterol arabinosyl diester, naphthoquinones and vanillic acid dodecaglycoside. This work has enhanced understanding about the phytoconstituents of the plant. These secondary metabolites can be used as analytical markers for quality control of the stem bark of this plant.

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