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Chemical Constituents from the Whole Plant of *Eryngium caeruleum* and Leaves of *Leea indica*

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Abstract *Eryngium caeruleum* M. Bieb. (family Apiaceae) is a perennial, up to 1 m tall plant. It is used as an antiseptic, anti-inflammatory, appetizer, diuretic, lenitive and to treat piles. *Leea indica* (Burm.f.) Merr. (family Vitaceae) is an evergreen, large shrub. Its leaves are digestive, used for birth control and to cure body pains, bone fracture, cardiac diseases, cuts, diabetes, diarrhoea, dizziness, dysentery, eczema, fever, headache, intestinal worms, leprosy, leucorrhoea, muscle spasm, obstetric diseases, piles, skin diseases, ulcers, vertigo, warts and wounds. Our study was planned to isolate chemical constituents from the methanolic extracts of these plants and to characterize their structures on the basis spectral data analysis. Phytochemical investigation of the whole plant of *Eryngium caeruleum* led to isolate a fatty acid ester identified as triacontyl palmitate (triacontylhexadecanoate, myricyl palmitate, **1**). The leaves of *Leea indica* afforded three fatty acid esters characterized as hexadecyl (Z)-octadec-9-enoate (palmityl oleate, **2**), 6′β-hydroxyundecanyl *n*-decanoate (**4**) and 7′β-hydroxydodecanyl *n*-decanoate (**5**), a new mixed, glyceride glyceryl-1-linoleio-2-dotriacontanyl -3-linoleniate (**3**) and a known higher aliphatic alcohol, viz., 1-triacontanol (**6**).

Keywords *Eryngium caeruleum* whole plant, *Leea indica* leaves, phytoconstituents, isolation, characterization

Introduction

Eryngium caeruleum M. Bieb., syn. *E. caucasicum* Trautv., *E. pskemense* Pavlov (family Apiaceae), known as Pahari gaajar, dudhali and saleli-misri, is found in the western Himalayas, Kashmir, Turkey, Caucasus, Iran, Kyrgyzstan, Tajikistan, Turkmenistan, Afghanistan, northern Pakistan and northwest India. It is a perennial, up to 1 m tall plant. The roots are used as an aphrodisiac, diaphoretic, diuretic, expectorant, haematinic, nervine and stimulant and to relieve paralysis. *E. caeruleum* leaves are used as a flavouring vegetable. The plant is taken to enforce generative power and as an appetizer, diuretic and lenitive [1-3]. The plant ash is antiseptic and anti-inflammatory, administered orally to treat piles [4, 5]. The plant aerial parts contained essential oils composed of cyclobutane, dicyclo-octene, *n*-hexadecanoic acid, linoleic acid, limonene and *cis*-α-bisabolene [6]; limonene, δ-3-carene, β-sesquiphellandrene, α-pinene and δ-2-carene [7]; 3-hexyne, β-sesquiphellandrene, limonene, 5-methyl-2-pyrimidone, 6-acetoxy-2,3-dihydro-1H-pyrrolizin, *trans*-β-farnesene and 4-(1,5-dimethyl hex-4-enyl) cyclohex-2-enone [8]. The leaves produced D-mannitol and essential oils consisting of 4 (5)-acetyl-1*H*-imidazole, thymol and β-

sesquiphellandrene. [8]. The plant afforded flavonol glycosides identified as kaempferol 3-O-[6-O-E-p-coumaroyl]-β-D-glucopyranoside and kaempferol 3-O-(2′′,6′′-di-O-E-p-coumaroyl)-β-D-glucopyranoside [9]. Threonine was the dominant essential amino acids in all parts of *E. caeruleum* [10]. The underground parts yielded saponins [4].

Leea indica (Burm.f.) Merr. (Vitaceae), known as Hastipalash, Chhatri and bandicoot berry, is distributed in Australia, Indochina, Indomalaya, Pacific Islands and throughout India. It is an evergreen, large shrub or small tree, up to 5 m tall; leaves 2 or 3-pinnate, spiral, alternate, glabrous, leaflets oblong or elliptic-lanceolate, apex caudate-acuminate, serrate-dentate, young leaves bright-red; flowers greenish-white; berries depressed, globose, purple black; seeds 4-6, red-glandular. The plant is used to treat asthma, body ache, bone fracture, burns, dental caries, diarrhoea, dysentery, fever, headache, malaria, piles, muscle spasm, rheumatism, ringworm, skin diseases, gastric ulcer, warts and wounds [11-16]. The leaves are digestive, ingested for birth control and to cure body pains, bone fracture, cardiac diseases, cuts, diabetes, diarrhoea, dizziness, dysentery, eczema, fever, headache, intestinal worms, leprosy, leucorrhoea, muscle spasm, obstetric diseases, piles, skin diseases, ulcers, vertigo, warts and wounds [11-16]. The shoots are taken to relieve body pains, cough, cystitis, fevers, insomnia, sores and strangury [11-16]. The roots are regarded as antispasmodic, diaphoretic, febrifuge, refrigerant, sudorific and to comfort boils, cardiac diseases, colic, diabetes, diarrhoea, dizziness, dysentery, eczema, fever, gastric ulcers, headache, interspinal cancer, leprosy, leucorrhoea, muscular pain, piles, skin complaints with rashes and allergic reactions, soreness, stomach ache, uterine cancer, to induce perspiration and to relieve thirst [11-16].

The leaves of *L. indica* contained a carotene lycopersene, C-18, C-21, C-23, C-24, C-26, C-28, C-35 (17-ene), C-43 and C-44 hydrocarbons, phthalic acid, palmitic acid, 1-eicosanol, solanesol, farnesol, phthalic acid esters, gallic acid, lupeol, β-sitosterol and ursolic acid [17], gallic acid, methyl gallate, (−)-epigallocatechin-3-*O*-gallate, myricetin-3-*O*-rhamnoside, quercetin-3-*O*-rhamnoside, and 4′,6′-dihydroxy-4-methoxydihydrochalcone 2′-*O*-β-D-glucopyranoside [18]. The plant yielded triterpenoid glycosides viz., mollic acid arabinoside and mollic acid xyloside, quercetin and gallic acid [19, 20]. An essential oil of the flowers was composed of esters of phthalic acid, di-isobutylphthalate, di-*n*-butyl phthalate, *n*-butylisobutyl phthalate and butylisohexyl phthalate [21].

The presence of herbal chemical constituents vary due to many factors such as geographic regions, soils, seasonal changes, plant species and application of fertilizers. Keeping in views the various therapeutic values and variation aspects of chemical constituents of the plants and development of ecofriendly, biodegradable and safer herbal preparations, it has been aimed to establish chemical structures of phytoconstituents isolated from the whole plant of *Eryngium caeruleum* and leaves of *Leea indica*.

Materials and Methods

The protocols of all methodologies (procedures, experimental designs and spectral data analysis) were adopted from the earlier published work [22-24].

General Procedures

Melting points were measured using one end open capillary tubes on a thermoelectrically heated melting point apparatus (Perfit, India) without correction. UV spectra were determined with Lambda Bio 20 spectrophotometer (Perkin Elmer, Schwerzenbach, Switzerland) in methanol. The IR spectra were obtained by using KBr pellets with Jasco FT/IR-5000 Spectrometer (FTS 135, Hong Kong). The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker DRX Spectrometer (Rheinstetten, 2 Germany) using $CDCl_3$ and DMSO-d_6 as solvents. TMS (Fluka analytical, Sigma-Aldrich, Netherland) was taken as an internal standard and the 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 (Waters Corp., UK) instrument 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 peak. Column chromatography was performed on silica gel (Qualigens, Mumbai, India) with 60-120 mesh particle size. The purity of the isolated compounds was checked on precoated

TLC plates with silica gel 60 F_{254} (0.25 mm, Merck, Mumbai, India). The spots were visualized by exposure to iodine vapours and under UV radiations at 254 and 366 nm and spraying with ceric sulphate solution.

Collection and Authentication of Plant Materials

The whole plant of *Eryngium caeruleum* and leaves of *Leea indica* were collected from Dehradun, Uttarakhand. The plant materials were identified and authenticated by Prof. M. P. Sharma, Taxonomist, Department of Botany, Jamia Hamdard, New Delhi. Voucher specimens of the plant materials were preserved in the herbarium of the Department of Pharmacognosy and Phytochemistry, Jamia Hamdard, New Delhi.

Extraction and Isolation

The whole plant of *E. caeruleum* and leaves of *L. indica* (1 kg each) were dried in air, 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, 193.21 g and 171.61 g, respectively. Each 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*), chloroform and chloroform - methanol (99:1, 49:1 *v/v*). 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 a Phytoconstituent from the Whole Plant of *Eryngium caeruleum*

Myricyl palmitate (1)

Elution of the column with petroleum ether – chloroform (1 : 1) produced a colourless amorphous powder of **1**, yield 113 mg, recrystallized from chloroform-methanol (1:1), m. p. 66 - 67 °C; R_f 0.56 (benzene -chloroform, 3 : 1); IR υ_{max} (KBr) : 2923, 2851, 1723, 1621, 1491, 1456, 1379, 1219, 1078, 968, 772 cm^{-1};^{1}H NMR ($CDCl_3$): δ 4.24 (2H, t, J = 6.5 Hz, H_2 -1′), 2.32 (2H, t, J = 7.2 Hz, H_2 -2), 2.16 (2H, m, H_2-3), 2.16 (2H, m, H_2-4), 1.55 (4H, m, H_2-2′, H_2-3′), 1.31 (12H, brs, 6 x CH_2), 1.27 (58H, brs, 29 x CH_2), 1.24 (6H, m, H_2-15, H_2-29′, H_2-28′), 0.92 (3H, t, J = 7.2 Hz, Me-16), 0.86 (3H, t, J = 6.8 Hz, Me-30′); ^{13}C NMR ($CDCl_3$): δ 172.67 (C-1), 60.94 (C-1′), 35.41 (C-2), 29.81 (38 x CH_2), 27.69 (C-14), 25.24 (C-15), 22.62 (C-29′), 18.69 (Me - 16), 14.33 (Me -30′); ESI MS *m/z* (rel.int.): 676 $[M]^+$ ($C_{46}H_{92}O_2$) (10.6).

Isolation of Phytoconstituents from the Leaves of *Leea indica*

Palmityl oleate (2)

Elution of the column with petroleum ether – chloroform (1:1) afforded a pale yellow semisolid mass of **2**, yield 127 mg, R_f 0.71 (benzene-chloroform-methanol, 5:4:1); IR υ_{max} (KBr): 2925, 2853, 1724, 1635, 1445, 1381, 1262, 1216, 1079, 967, 761 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.91 (1H, m, H-9), 5.73 (1H, m, H-10), 4.19 (2H, t, J = 7.5 Hz, H_2 -1′), 2.32 (2H, t, J = 7.2 Hz, H_2 -2), 2.20 (2H, m, H_2 -8), 2.09 (2H, m, H_2 -11), 1.64 (2H, m, H_2-3), 1.56 (2H, m, H_2-7), 1.31 (6H, m, H_2-4, H_2-5, H_2 -12), 1.29 (8H, brs, 4 x CH_2), 1.25 (32H, brs, 16 x CH_2), 0.89 (3H, t, J = 6.5 Hz, Me-18), 0.86 (3H, t, J = 6.8 Hz, Me-16′); ^{13}C NMR ($CDCl_3$): δ 170.18 (C-1), 34.87 (C-2), 30.19 (C-3), 29.70 (C-4), 29.68 (C-5), 29.63 (C-6), 25.07 (C-7), 34.52 (C-8), 124.47 (C-9), 121.26 (C-10), 31.93 (C-11), 29.51 (C-12), 29.48 (C-13), 29.35 (C-14), 29.30 (C-15), 29.37 (C-16), 22.70 (C-17), 14.13 (C-18), 63.41 (C-1′), 31.44 (C-2′), 28.26 C-3′), 29.37 C-4′), 29.70 C-5′), 29.70 C-6′), 29.65 C-7′), 29.58 C-8′), 29.37 C-9′), 29.33 C-10′), 29.26 C-11′), 29.22 C-12′), 28.06 C-13′), 27.18 (C-14′), 23.28 (C-15′), 14.55 (C-16′);ESI MS *m/*z (rel.int.): 506 $[M]^+$ ($C_{34}H_{66}O_2$) (46.7), 281 (3.1).

Glyceryl-1-linoleio-2-dotriacontanyl -3-linoleniate (3)

Elution of the column with petroleum ether – chloroform (1:3) furnished a yellow semisolid mass of **3**, yield 201 g, purified by preparative TLC using petroleum ether - chloroform (1:1), UV λ_{max} (MeOH): 217 nm (log ε 2.9); IR

υ_{max}(KBr): 2924, 2851, 1737, 1734, 1731, 1635, 1445, 1381, 1261, 1158, 1081, 1020, 967, 803, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.14 (2H, m, H-9′, H-9‴), 5.09 (2H, m, H-10′, H-10‴), 5.06 (2H, m, H-12′, H-12‴), 5.03 (2H, m, H-13′, H-13‴), 5.01 (2H, m, H-15‴, H-16‴), 4.17 (2H, m, H_2-1), 4.31 (1H, m, H-2), 4.05 (2H, m, H_2-3), 2.67 (2H, m, H_2-11′), 2.51 (2H, m, H_2-11‴), 2.49 (2H, m, H_2-14‴), 2.33 (2H, m, H_2-2′), 2.30 (2H, m, H_2-2″), 2.27 (2H, m, H_2-2‴), 2.13 (4H, m, H_2-8′, H_2-8″), 2.06 (4H, m, H_2-14′, H_2-17‴), 1.83 (2H, m, H_2-3′), 1.72 (2H, m, H_2-3″), 1.63 (4H, m, H_2-3‴, H_2-4‴), 1.56 (4H, m, H_2-4′, H_2-15′), 1.39 (2H, m, H_2-5′), 1.33 (6H, brs, 3 x CH_2), 1.28 (8H, brs, 4 x CH_2), 1.25 (50H, brs, 25 x CH_2), 0.93 (3H, t, J = 6.5 Hz, Me-18′), 0.87 (3H, t, J = 6.3 Hz, Me-18‴), 0.84 (3H, t, J = 6.4 Hz, Me-32″);^{13}C NMR ($CDCl_3$): δ 68.17 (C-1), 70.33 (C-2), 65.58 (C-3), 173.21 (C-1′), 34.88 (C-2′), 124.48 (C-9′), 147.67 (C-10′), 44.16 (C-11′), 147.69 (C-12′), 123.99 (C-13′), 22.71 (C-17′), 168.93 (C-1″), 34.54 (C-2″), 29.68 (C-25″), 29.37 (C-26″), 29.10 (C-27″), 28.94 (C-28″), 23.76 (C-29″), 23.01 (C-30″), 19.20 (C-31″), 168.85 (C-1‴), 34.54 (C-2‴), 123.99 (C-9‴), 138.55 (C-10‴), 41.22 (C-11‴), 138.46 (C-12‴), 130.90 (C-13‴), 38.74 (C-14‴), 128.83 (C-15‴), 119.10 (C-16‴),29.72 (C-17‴), 31.95 (5 x CH_2), 31.46 (6 x CH_2), 30.59 (16 x CH_2), 30.37 (5 x CH_2), 30.21 (5 x CH_2),14.15 (Me-18′), 10.99 (Me-18″), 14.08 (Me-18‴) ; ESI MS *m/z* (rel. int.):1076 $[M]^+$ ($C_{71}H_{128}O_6$) (22.3), 463 (9.5), 279 (3.1), 277 (12.3).

6′β-Hydroxyundecanylcapriate (4)

Elution of the column with chloroform gave a colourless semisolid mass of **4**, yield 103 mg, R_f 0.70 (*n*-butanol – acetic acid- water, 5: 4: 1); IR υ_{max} (KBr): 3437, 2958, 2852, 1723, 1635, 1415, 1381, 1278, 1216, 1081, 967, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.24 (2H, t, J = 6.7 Hz, H_2 -1′), 3.93 (1H, m, $w_{1/2}$= 15.3 Hz, H -6′α), 2.97 (2H, t, J = 6.4 Hz, H_2 -2), 2.20 (2H, m, H_2 -3), 2.06 (2H, m, H_2 -7′), 1.79 (2H, m, H_2-5′), 1.57 (2H, m, H_2-4), 1.36 (4H, m, H_2-2′, H_2-3′), 1.32 (4H, m, H_2-4′, H_2-8′), 1.25 (14H, brs, 7 x CH_2), 0.91 (3H, t, J = 6.3 Hz, Me-10), 0.85 (3H, t, J = 6.8 Hz, Me-11′); ^{13}C NMR ($CDCl_3$): δ 169.25 (C-1), 34.32 (C-2), 28.70 (C-3), 31.28 (C-4), 30.98 (C-5), 29.68 (C-6), 29.55 (C-7), 29.03 (C-8), 22.07 (C-9), 13.73 (C-10), 63.81 (C-1′), 34.29 (C-2′), 29.03 (C-3′), 29.03 (C-4′), 24.83 (C-5′), 73.28 (C-6′), 29.05 (C-7′), 29.68 (C-8′), 28.65 (C-9′), 21.34 (C-10′), 14.68 (C-11′); ESI MS *m/*z (rel.int.): 342 $[M]^+$ ($C_{21}H_{42}O_3$) (100), 171 (47.1), 101 (3.5).

7′β-Hydroxydodecanylcapriate (5)

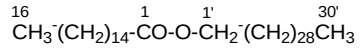
Further elution of the column with chloroform produced a colourless semisolid mass of **5**, yield 90 mg, R_f 0.49 (benzene – chloroform, 3:2); IR υ_{max}(KBr): 3405, 2951, 2849, 1725, 1634, 1408, 1259, 1076, 961, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.30 (2H, t, J = 7.6 Hz, H_2 -1′), 3.76 (1H, m, $w_{1/2}$= 18.9 Hz, H -7′α), 2.80 (2H, t, J = 7.1 Hz, H_2 -2), 2.13 (2H, m, H_2 -3), 1.77 (2H, m, H_2 -8′), 1.57 (2H, m, H_2-6′), 1.43 (4H, m, H_2-2′, H_2-3′), 1.35 (4H, m, H_2-4′, H_2-9′), 1.31 (8H, brs, 4 x CH_2), 1.28 (10H, brs, 5 x CH_2), 0.95 (3H, t, J = 6.3 Hz, Me-10), 0.87 (3H, t, J = 6.5 Hz, Me-12′); ^{13}C NMR ($CDCl_3$): δ 170.16 (C-1), 53.40 (C-2), 35.18 (C-3), 31.23 (C-4), 29.92 (C-5), 29.92 (C-6), 29.57 (C-7), 24.26 (C-8), 22.71 (C-9), 13.12 (C-10), 63.55 (C-1′), 35.12 (C-2′), 29.92 (C-3′), 29.81 (C-4′), 29.68 (C-5′), 29.57 (C-6′), 70.08 (C-7′), 31.47 (C-8′), 26.48 (C-9′), 24.31 (C-10′), 22.68 (C-11′), 18.41 (C-12′); ESI MS *m/*z (rel.int.): 356 $[M]^+$ ($C_{22}H_{44}O_3$) (10.3), 171 (34.2), 101 (4.8).

1-Triacontanol (6)

Further elution of the column with chloroform yielded a colourless amorphous powder of **6**, yield 125 mg, m. p. 86 - 87 °C; IR υ_{max} (KBr): 3436, 2921, 2833, 1410, 1384, 1219, 1018, 873, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.34 (2H, t, J = 6.7 Hz, H_2-1), 2.53 (2H, m, H_2-2), 2.10 (2H, m, H_2-3), 1.55 (2H, m, H_2-4), 1.30 (2H, m, H_2-5), 1.25 (48H, br s, 24 × CH_2), 0.86 (3H, t, J = 6.5 Hz, Me-30); ^{13}C NMR ($CDCl_3$): δ 63.11 (C-1), 32.81 (C-2), 31.92 (C-2), 29.71 (21 × CH_2), 29.53 (C-25), 29.41 (C-26), 29.35 (C-27), 25.74 (C-28), 22.72 (C-29), 14.19 (Me-30); ESI MS *m/z* (rel. int.): 438 $[M]^+$ ($C_{30}H_{62}O$) (12.2).

Results and Discussion

Compound **1** and **2** were the known fatty acid ester identified as triacontyl palmitate (triacontylhexadecanoate, myricyl palmitate) (Fig. 1)[25-27] and hexadecyl (Z)-octadec-9-enoate (palmityl oleate) (Fig. 2) [28], respectively.



Myricyl palmitate **(1)**

*Figure 1: Chemical constituent **1** isolated from the whole plant of Eryngium caeruleum M. Bieb.*

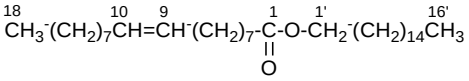
Compound **3** showed IR absorption bands for ester functions (1737, 1734, 1731 cm^{-1}), unsaturation (1635 cm^{-1}) and long aliphatic chain (759 cm^{-1}). Its mass spectrum showed a molecular ion peak at *m/z* 1076 consistent with the molecular formula of a mixed glyceride, $C_{71}H_{128}O_6$. The ion peaks generating at *m/z* 463 [O - $C_{1''}$ fission, CO-$(CH_2)_{30}$-$CH_3]^+$ indicated the attachment of dotriacontanoic acid (lacceroic acid) to the glycerol unit. The ion fragments arising at *m/z* 279 [C_1 - O fission, OCO-$(CH_2)_7$-$(CH{=}CH\text{-}CH_2)_2$-$(CH_2)_3$-$CH_3]^+$ and 277 [C_3 - O fission, OCO-$(CH_2)_7$-$(CH{=}CH\text{-}CH_2)_3$-$CH_3]^+$ suggested the linkages of linoleic and linolenic acids to the glycerol unit. The ^{1}H NMR spectrum of **3** displayed five two–proton deshielded multiplets at δ 5.14, 5.09, 5.06, 5.03 and 5.01 assigned to vinylic protons, two two-proton multiplets at δ 4.17 and 4.05 ascribed to oxymethylene H_2-1 and H_2-3 protons, respectively, a one-proton multiplet at δ 4.31 attributed to oxymethine H-2 proton, methylene protons between δ 2.67 – 1.25, and three triplets at δ 0.93 (J = 6.5 Hz), 0.87 (J = 6.3 Hz) and 0.84 (J = 6.4 Hz) integrating for three protons each associated correspondingly with primary C-18′, C-18‴ and C-32″ methyl protons. The ^{13}C NMR spectrum of **3** displayed signals for ester carbons at δ 173.21 (C-1'), 168.93 (C-1″) and 168.85 (C-1‴), vinylic carbons between δ 147.69 – 119.10, oxymethylene carbons at δ 68.17 (C-1) and 65.58 (C-3), oxymethine carbon at δ 70.33 (C-2), methylene carbons in the range of δ 44.16 – 23.01 and methyl carbons at δ 14.15 (Me-18′), 10.99 (Me-18″) and 14.08 (Me-18‴). On the basis of these evidences, the structure of **3** has been elucidated as glyceryl-1-linoleio-2-dotriacontanyl -3-linoleniate, a new mixed glyceride (Fig. 2).

Compound **4**, designated as 6′β-hydroxyundecanylcapriate, displayed distinctive IR absorption bands for a hydroxyl group (3437 cm^{-1}), ester function (1723 cm^{-1}) and long aliphatic chain (759 cm^{-1}). Its mass spectrum showed a molecular ion peak at *m/z* 342 consistent with a molecular formula of a fatty acid ester, $C_{21}H_{42}O_3$. The formation of the ion peaks at *m/*z 171 [$C_{1'}$ - O fission, CH_3-$(CH_2)_8$-$COO]^+$ and 101 [$C_{6'}$ - $C_{7'}$ fission, CH(OH)-$(CH_2)_4$-CH_3, C_6H_{13}-$O]^+$ indicated that capric acid was esterified with undecanol containing a hydroxyl group at C-6′ carbon. The ^{1}H NMR spectrum of **4** exhibited two two-proton triplets at δ 4.24 (J = 8.3 Hz) and 2.97 (J = 6.4 Hz) assigned to oxymethylene H_2-1′ and methylene H_2-2 protons nearby to the ester function, respectively. A one-proton multiplet at δ 3.93 with half-width of $w_{1/2}$= 15.3 Hz was ascribed to α-orientation carbinol H-6′ proton. The remaining methylene protons appeared as multiplets between δ 2.20 - 1.32 and as a broad singlet 1.25 (14H). Two three-proton triplets at δ 0.91 (J = 6.3 Hz) and 0.85 (J = 6.8 Hz) were due to C-10 and C-11′ primary methyl protons, respectively. The ^{13}C NMR spectrum of **4** showed signals for the ester carbon at δ 169.25 (C-1), oxymethylene carbon at δ 63.81 (C-1′), carbinol carbon at δ 73.28 (C-6′), methylene carbons between δ 34.32 – 21.34 and methyl carbons at δ 13.73 (C-10) and 14.68 (C-11′). The absence of any ^{1}H NMR signal beyond δ 4.24 and carbon signals between δ 169.25 –73.28 supported the saturated nature of the molecule. On the basis of these spectral data analysis, the structure of **4** was elucidated as 6′β-hydroxyundecanyl*n*-decanoate, a new fatty acid ester (Fig. 2).

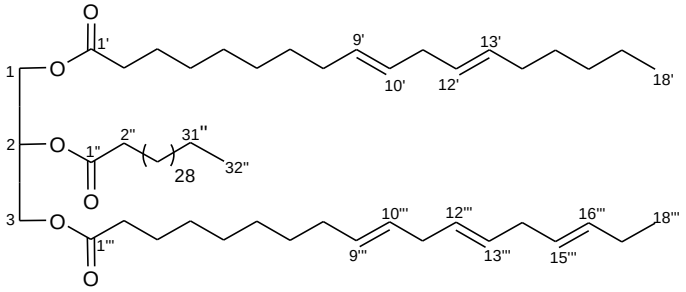
Compound **5**, named 7′β-hydroxydodecanylcapriate, showed characteristic IR absorption bands for a hydroxyl group (3405 cm^{-1}), ester function (1725 cm^{-1}) and long aliphatic chain (721 cm^{-1}). The molecular ion peak of **5** was determined at *m/z* 356 in its mass spectrum corresponding to a molecular formula of a fatty acid ester, $C_{22}H_{44}O_3$. The formation of the ion fragments at *m/*z 171 [$C_{1'}$ - O fission, CH_3-$(CH_2)_8$-$COO\ ]^+$ and 101 [$C_{6'}$ - $C_{7'}$ fission, CH(OH)-$(CH_2)_4$-CH_3, C_6H_{13}-$O]^+$ suggested that capric acid was esterified with dodecanol containing the hydroxyl group at C-7′ carbon. The ^{1}H NMR spectrum of **5** displayed two two-proton triplets at δ 4.30 (J = 7.6 Hz) and 2.80 (J = 7.1 Hz) assigned to oxymethylene H_2-1′ and methylene H_2 -2 protons adjacent to the ester function, respectively. A one-proton multiplet at δ 3.76 with half-width of $w_{1/2}$= 18.9 Hz was attributed to α-orientation carbinol H -7′ proton. The remaining methylene protons appeared as multiplets from δ 2.13 to 1.35 and as broad

singlets at δ 1.31 (8H) and 1.28 (10H). Two three-proton triplets at δ 0.95 (J = 6.3 Hz) and 0.87 (J = 6.5 Hz) were associated correspondingly with C-10 and C-12′ primary methyl protons. The ^{13}C NMR spectrum of **5** showed signals for the ester carbon at δ 170.16 (C-1), oxymethylene carbon at δ 63.55 (C-1′), carbinol carbon at δ 70.08 (C-7′), methylene carbons between δ 53.40 – 22.68 and methyl carbons at δ 13.12 (C-10) and 18.41 (C-11′). The absence of any ^{1}H NMR signal beyond δ 4.30 and carbon signals between δ 170.16 –70.08 supported the saturated nature of the molecule. On the basis of these spectral data analysis, the structure of **5** was elucidated as 7′β-hydroxydodecanyl *n*-decanoate, a new fatty acid ester (Fig. 2).

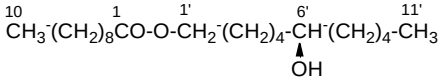
The compounds **6** was a known higher aliphatic alkane characterized as 1-triacontanol (Fig. 2) [29, 30].



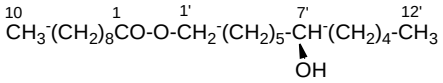
Palmityl oleate **(2)**



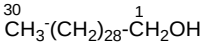
Glyceryl-1-linoleiyl-2-dotriacontanyl-3-linoleniate **(3)**



6′β-Hydroxyundecanylcapriate **(4)**



7′β-Hydroxydodecanylcapriate **(5)**



n-Triacontanol **(6)**

*Figure 2: Chemical constituents **2** to **6** isolated from the leaves of Leea indica (Burm.f.) Merr.*

Conclusion

Phytochemical investigation of the whole plant of *Eryngium caeruleum* led to isolate a fatty acid ester identified as triacontyl palmitate (triacontylhexadecanoate, myricyl palmitate, **1**). The leaves of *Leea indica* afforded three fatty acid esters characterized as hexadecyl (Z)-octadec-9-enoate (palmityl oleate, **2**), 6′β-hydroxyundecanyl*n*-decanoate(**4**) and 7′β-hydroxydodecanyl*n*-decanoate(**5**), a new mixed glyceride glyceryl-1-linoleio-2-dotriacontanyl -3-linoleniate (**3**) and a known higher aliphatic alcohol, viz., 1-triacontanol (**6**). This work has enhanced understanding about the chemical constituents of the undertaken plants. Further research is recommended to screen bioactivities of the isolated phytoconstituents with a view for supplementing conventional drug development especially in developing countries.

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