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CONSTITUENTS OF THE CHEMICAL HEARTWOOD OF *BERBERIS ARISTATA*, AERIAL PARTS OF *CENTELLA ASIATICA* AND FRUITS OF *CORIANDRUM SATIVUM*

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ABSTRACT

Berberis aristata DC. (family Berberidaceae) is an erect, evergreen, spiny, woody shrub. *Centella asiatica* (L.) Urban (family Apiaceae) is a small slender perennial, spreading herb. *Coriandrum sativum* L. (family Apiaceae) is an erect, many-branched, small, glabrous, bushy, annual herb. The heartwood of *B. aristata* , aerial parts of *C. asiatica* and fruits of *Coriandrum sativum* are used to treat various diseases. This study was planned to isolate phytoconstituents from these plant materials and to characterize their structures. The heartwood of *B. aristata* afforded *n*-docosane (**1**), β-sitosterol (**2**) and 1-hexacosanyl benzoate (**3**). The aerial parts of *C. asiatica* furnished two new fatty acid esters identified as octacosan-1-olyl (Z)-octadec-9-enoiate (*n*-octacosanyl oleate, **4**), a new fatty acid ester and docosan-1-olyl tetracosanoate (*n*-docosanyl lignocerate, **5**). The fruits of *Coriandrum sativum* produced 13α-hydroxystearic acid (**6**). The structures of isolated phytoconstituents were established on the basis of analysis of spectral data and chemical means.

KEYWORDS: *Berberis aristata* heartwood, *Centella asiatica* aerial parts, *Coriandrum sativum* fruits, Phytoconstituents, Isolation, Characterization.

INTRODUCTION

Berberis aristata DC. (family Berberidaceae), commonly known as dāruhaldi, citra, Indian barberry, and tree turmeric, is found in Northern Himalayan region in the Nilgiri and Garhwal mountains and Parasnath hills in Giridih district of Jharkhand, Nepal, Sri Lanka and Europe between an altitude of 1.800 to 2.400 m. It is an erect, evergreen, spiny, woody shrub, 2 -3 m in height, with bark yellow to brown from the outside and deep yellow from the inside, covered with three-branched thorns, spines simple or branched, leaves are arranged in tufts of five to eight, deep green on the dorsal surface and light green on the ventral surface, ovate, stalked, leathery, simple with pinnate venation, toothed; flowers golden yellow, in raceme; ripe fruits are eaten or pickled.

B. aristata possesses alterative, antibacterial, anticancer, antidiabetic, antidiarrheal, antidote, anti-hyperglycaemic, anti-lipidemic, anti-osteoporosis, anti-oxidant, antiperiodic, antipyretic, antiulcerogenic, astringent, bitter, cholagogue, deobstruent, diaphoretic, laxative, hepatoprotective, stomachic and tonic properties. The plant is used in diabetes, diarrhoea, ear problems, gynaecological disorders, HIV-AIDS, haemorrhoids, jaundice, joint pain, liver problems, malarial fever, menorrhagia, ophthalmic infections, osteoporosis, piles, skin diseases, sores, swollen gums and wounds. The roots are used externally to cure eye diseases, a root paste is applied to calm down headache. Bark is piscicide and used to relieve fevers, cough, eye infection, liver complaints, diarrhoea, dysentery, cholera, gastric disorders, enlargement of spleen, and as an antidote.[1-5] The plant contained isoquinoline alkaloids including berberine, palmatine, karachine, palmatine chloride, oxyberberine, tetrahydropalmatine, pseudopalmatinechloride, taxilamine, pakistanine, 1-O-methyl pakistanine, oxycanthine, berbamine and aromoline. Other compounds isolated are flavonoids such as quercetin, meratin and rutin; chlorogenic acid and (E)-caffeic acid, phytosterol and esters.[6-11]

Centella asiatica (L.) Urban, syn. *Hydrocotyle asiatica* L. (family Apiaceae or Umbelliferae), commonly known as mandukparni, jalbrahmi, or Indian pennywort, is distributed in parts of India, Pakistan, China, Southeast Asia, Sri Lanka, Madagascar, South Africa, Eastern Europe and Central America. The plant is a small slender perennial, prostrate, trailing, creeping, scandent, spreading herb, rooting at nodes, stem is glabrous, pink striated and rooting at nodes; leaves fleshy, rosette, orbicular to reniform and dentate; petiole is long, smooth on upper surface and hairy below; flowers are pink and white in fascicled umbels. The fruits are oblong, dull

brown, laterally compressed, pericarp hard, thickened and woody white.

C. asiatica plant has alterative, anti-inflammatory, antidote, astringent, blood-purifier, mild diuretic, emmenagogue, galactagogue, laxative, nervine tonic, and vulnerary properties. The plant is used to treat abdominal distress, amenorrhea, asthma, body aches, boils, burns, colds, dehydration, diarrhoea, bloody dysentery, eczemas, epilepsy, fatigue, fever, female genitourinary tract diseases, jaundice, headaches, hysteria, inflammation, insanity, insomnia, leprosy, lupus, mental illness, nervine disorders, psoriasis, respiratory infections, rheumatism, scleroderma, scrofula, skin diseases, snake bites, syphilis, hookworm and tapeworm infections, toxicity, typhoid, indolent ulcers, venereal diseases, ulcers, and wound healing. It is used as nervine tonic, for improving memory, and mental disorders. It is an ingredient in steam treatment of malaria.[5,12, 13] The leaves for amebiasis, body ache, cough, consumption, convulsions, dysentery, epilepsy, fever, headache, kidney and liver complaints, leprosy, madness, spermatorrhoea, syphilis, skin and tuberculosis. Leaves mixed with *Plantago major* the juice are taken to cure diabetes. Leaf juice used to improve memory, activate the mind, mental retardation, for gastritis, dysentery, and as a blood purifier.[5,12,13]

C. asiatica plant contained asiatic acid, asiaticoside A and B, and madecassosides,[14] essential oil composed of p-cymene-(44%),[15] centellin, asiatic acid, and centellicin,[16] madecassoside, asiaticoside, madecassic acid, centellosides and asiatic acid,[17,18] triterpene and saponin viz., 2α,3β,23-trihydroxyurs-20-en-28-oic acid and 2α,3β,23- trihydroxyurs-20-en-28-oic acid O-α-l-rhamnopyranosy-(1→4)-O-β-dglucopyranosyl(1→6)-O-β-d glucopyranosyl ester,[19] 2α,3β,20,23-tetrahydroxyurs-28-oic acid,[20] indocentoic acid, bayogenin, kaempferol, quercetin, euscaphic acid, terminolic acid, and 3β-6β-23-trihydroxyurs-12-en-28-oic acid,[20] triterpenoid saponins,[21-23] polyacetylenes,[24] flavones ,[25] sterols and lipids.[26] The fatty oil consists of glycerides of palmitic, stearic, lignoceric, and oleic acids. The plant is also rich in vitamin C, vitamin B1, vitamin B2, niacin, carotene, and vitamin A.[13]

Coriandrum sativum L. (family Apiaceae/ Umbelliferae), known as dhania and coriander, is a native of Mediterranean region. It is cultivated in India, Morocco, Russia, Eastern and Southern European countries, France, North Africa, Central America, Mexico, and the United States. It is an erect, many-branched, small, glabrous, bushy, annual herb with pronounced taproot, stem slender, branching, 20–70 cm in height. The leaves are lanceolate, lobed, green or dark green, glabrous on both surfaces, variable in shape and lobed. The flowers are borne in small umbels, white or light pink, asymmetrical. The fruit or seed is ovate globular dry schizocarp with two mericarps and multiple longitudinal ridges on the surface possessing a sweet, slightly pungent, citrus like flavour.

The fruits (seeds) are used as a condiment to prepare curry powders, sausages and seasonings. The fruits possess antibilious, aphrodisiac, carminative, diuretic, emmenagogue, expectorant, galactagogue, refrigerant, sedative, stimulant and stomachic, tonic properties; used against seasonal fever, stomach disorders, indigestion, nausea, dyspeptic complaints, diarrhoea, loss of appetite, convulsion, insomnia and anxiety. A fruit decoction is a good mouthwash for inflamed gums or tonsils. A watery paste of seeds is used as a gargle for the cure of ulcers of the mouth and throat. The green plant is applied to cure measles. Juice of the leaves is given along with black pepper to relieve rheumatism. The cooked leaves are eaten to ameliorate body ache and to expel stomach gas.[5, 27]

The fruits contained an essential oil composed mainly of linalool (60 – 80 %) followed by γ-terpinene, α-pinene, camphor, limonene, neryl acetate, geranyl acetate and p-cymene ; triglyceride oil, petroselinic acid, lipids (28.4%), carotenoids such as beta-carotene, beta-cryptoxanthin epoxide, lutein-5,6-epoxide, violaxanthin and neoxanthin, and aliphatic lactones.[28–33]

Keeping in view the various therapeutic values of the plants and the development of ecofriendly, biodegradable and safer herbal preparations the heartwood of *B. aristata*, aerial parts of *C. asiatica* and fruits of *Coriandrum sativum* were screened for the isolation and characterization of their chemical constituents.

MATERIALS AND METHODS

The protocols of all methodologies (procedures, experimental designs and spectral data analysis) were adopted from the earlier published work.[8, 26]

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 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 vapors and under UV radiations at 254 and 366 nm and spraying with ceric sulphate solution.

Plant materials

The heartwood of *Berberis aristata* , aerial parts of *Centella asiatica* and fruits of *Coriandrum sativum* were purchased from the Khari Baobli market, Delhi and identified by Prof. M. P. Sharma, Department of Botany, School of Chemical and Life Sciences, Jamia Hamdard University, New Delhi. The voucher specimens of the samples are preserved in the herbarium of the Department of Pharmacognosy and Phytochemistry, School of Pharmaceutical Education and Research, Jamia Hamdard, New Delhi.

Extraction and Isolation

One kilogramme (1 kg) each of the heartwood of *Berberis aristata*, aerial parts of *Centella asiatica* and fruits of *Coriandrum sativum* were coarsely powdered and extracted separately and exhaustively with methanol in a Soxhlet apparatus. The extracts were concentrated under reduced pressure to get dark brown masses, 117.6 g, 131.8, and 112.2 g, respectively. The dried residues (100 g each) were dissolved in minimum amount of methanol and adsorbed on silica gel column grade (60-120 mesh) separately to obtain slurries. Each slurry was air-dried and chromatographed over silica gel columns loaded in petroleum ether (b. p. 60 - 80°C) individually. Each column was eluted with petroleum ether, petroleum ether - chloroform (9:1, 3:1, 1:1, 1:3, v/v) and chloroform. Various fractions were collected separately and matched by TLC to check homogeneity. Similar fractions having the same R_f values were combined and crystallized with solvents. The isolated compounds were recrystallized to get pure compounds.

Isolation of phytoconstituents from the heartwood of *Berberis aristata* DC

***n*-Docosane (1)**

Elution of the column with petroleum ether afforded colourless amorphous powder of **1**, recrystallized from acetone: methanol (1:1), m. p. 42- 44 °C; UV λmax (MeOH): 205 nm (log ε 3.1); IR υ_{max} (KBr): 2927, 2845, 1469, 1375, 1223, 1115, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.54 (2H, m, CH_2), 1.32 (2H, m, CH_2), 1.29 (2H, m, CH_2), 1.27 (8H, m, 4 x CH_2), 1.25 (32H, brs, 16 x CH_2), 0.88 (3H, t, J = 6.4 Hz, Me-1), 0.84 (3H, t, J = 6.5 Hz, Me-26); ^{13}C NMR ($CDCl_3$): δ 31.94 (CH_2), 29.96 (11 x CH_2), 29.71 (CH_2), 29.69 (CH_2), 29.53 (CH_2), 29.46 (CH_2), 29.41 (CH_2), 29.38 (CH_2), 25.72 (CH_2), 22.69 (CH_2), 14.13 (Me-1, Me-26); ESI MS *m/z* (rel. int.): 310 $[M]^+$ (C_{22} H_{46}) (19.8).

β-Sitosterol (2)

Elution of the column with petroleum ether - chloroform (1:4) afforded a colourless amorphous powder of **2**, recrystallized from chloroform : methanol (1:1), yield 119 mg, R_f 0.35 (chloroform – methanol, 9: 1); m. p. 136-138 ^{o} C; UV λ max (MeOH): 209 nm (log ε 4.3); IR υ_{max} (KBr): 3435, 2927, 2848, 1636, 1468, 1378, 1262, 1151, 1089, 954 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.34 (1H, m, H- 6), 3.53 (1H, brs, w ½ = 18.1 Hz, H- 3α), 1.01 (3H, brs, Me-19), 0.95 (3H, d, J = 6.3 Hz, Me-21), 0.86 (3H, d, J = 6.7 Hz, Me-27), 0.83 (3H, J = 6.4 Hz, Me-26), 0.78 (3H, t, J = 6.5 Hz, Me-29), 0.68 (3H, brs, Me-18), 2.31 - 1.09 (29H, 11 x CH2 , 7 x CH).

^{13}C NMR ($CDCl_3$): δ 37.35 (C- 1), 31.64 (C- 2), 71.73 (C- 3), 42.15 (C- 4), 141.23 (C- 5), 121.65 (C- 6), 31.96 (C- 7), 31.86 (C- 8), 49.21 (C- 9), 36.72 (C- 10), 21.63 (C- 11), 39.83 (C- 12), 42.36 (C-13), 56.19 (C- 14), 24.23 (C- 15), 28.76 (C- 16), 56.04 (C- 17), 11.91 (C-18), 19.51 (C- 19), 36.17 (C- 20), 18.73 (C- 21), 23.18 (C- 22), 26.15 (C- 23), 45.83 (C-24), 29.51 (C- 25), 19.82 (C- 26), 19.26 (C- 27), 23.41 (C- 28), 11.72 (C-29); +ve FAB MS *m/z* (rel. int.): 414 $[M]^+$ ($C_{29}H_{50}O$) (32.5), 399 (6.3), 396 (13.5), 381 (14.1), 303 (21.4), 273 (14.5, 213 (14.9).

1-Hexacosanyl benzoate (3)

Elution of the column with petroleum ether – chloroform (3:1) gave pale yellow crystals of **3**, recrystallized from methanol - chloroform (1:1), yield 121 mg, m p 139 – 141 ^{o} C, UV λ max (MeOH): 276 nm; IR υ_{max} (KBr): 2951, 2843, 1727, 1635, 1527, 1489, 1343, 1274, 1212, 1075, 973, 911, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$) : δ 7.53 (2H, m, H-2′, H-6′), 7.41 (2H, m, H-3′, H-5′), 7.18 (1H, m, H-4′), 4.25 (1H, t, J=11.3 Hz, H_2-1), 2.21 (2H, m, H_2-2), 1.68 (2H, m, H_2 -3), 1.59 (2H, m, H_2-4), 1.33 (12 H, brs, 6 × CH_2), 1.27 (20H, brs, 10 × CH_2), 1.21 (10 H, brs, 5 × CH_2), 0.89 (3H, t, J = 6.5 Hz, Me-26); ^{13}C NMR ($CDCl_3$): δ 132.51 (C-1′), 128.83 (C-2′), 130.92 (C-3′), 132.38 (C-4′), 130.81 (C-5′), 128.69 (C-6′), 167.78 (C-7′), 65.88 (C-1), 38.05 (C-2), 31.94 (C-3), 30.57 (C-4), 29.38 (5 x CH_2), 29.34 (9 x CH_2), 28.24 (3 x CH_2), 27.72 (C-22), 25.54 (C-23), 22.69 (C-24), 20.19 (C-25), 14.02 (Me-26); +ve ion FAB MS *m/z* (rel. int.): 486 $[M]^+$ ($C_{33}H_{58}O_2$) (12.7), 381 (11.6), 365 (8.9), 121 (25.6), 105 (71.2).

Isolation of phytoconstituents from the aerial parts of *Centella asiatica* L.

***n*-Octacosanyl oleate (4)**

Elution of the column with petroleum ether-chloroform (1:3) gave colorless crystals of **4**, recrystallized from methanol - chloroform (1:1), yield 183 mg; m. p. 63 - 65°C; IR υ_{max} (KBR): 2928, 2851, 1726, 1635, 1463, 1218, 1173, 1032, 927, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.32 (1 H, m, H-9), 5.28 (1 H, m, H-10), 2.29 (2 H, t, J = 7.2 Hz, H_2-2), 2.31 (2H, m, H_2-8), 2.14 (2H, m, H_2-11), 1.73 (2H, m, H_2-3), 1.62 (2H, m, H_2-7), 1.29 (40 H, brs, 20 × CH_2), 1.25 (28 H, brs, 14 × CH_2), 0.89 (3 H, t. J=5.4 Hz, Me-18), 4.45 (2 H, t, J = 7.8 Hz, H_2-1′), 1.35 (2H, m, H_2-2 ′), 0.85 (3 H, t. J=6.5 Hz, Me-28′).

^{13}C NMR ($CDCl_3$): δ 173.15 (C-1), 51.86 (C-2), 38.18 (C-3), 37.63 (C-4), 37.51 (C-5), 29.43 (C-7), 38.82 (C-

8), 121.18 (C-9), 119.96 (C-10), 48.83 (C-11), 36.64 (C-12), 34.33 (C-13), 31.81 (C-14), 31.60 (C-15), 29.01 (C-16), 24.85 (C-17), 13.93 (C-18), 60.11 (C-1′), 36.14 (C-2′), 34.81 (C-3′), 29.46 (C-6, C-4′ to C-22′), 29.11 (C-23′), 29.31 (C-24′), 29.22 (C-25′), 25.53 (C-26′), 22.68 (C-27′), 14.83 (C-28′); ESIMS *m/z* (rel. int.): 674 [M+] ($C_{46}H_{90}O_2$) (12.1), 409 (20.3), 281 (23.6), 265 (9.8).

***n*-Docosanyl lignocerate** (**5**),
Elution of the column with chloroform furnished colorless crystals of **5**, recrystallised from chloroform-methanol (1:1, v/v), yield: 119 mg; m. p. 74 - 76 °C; UV λmax (MeOH): 211 nm (log ε 3.8); IR υ_{max} (KBr) 2931, 2842, 2338, 1725, 1465, 1219, 1054, 931, 751 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.29 (2H, t, J = 6.7 Hz, H_2 -1′), 2.26 (2H, t, J = 7.1 Hz, H_2 -2), 1.55 (2H, m, H_2-3), 1.36 (2H, m, H_2-2′), 1.28 (72H, brs, 38 x CH_2), 0.86 (3H, t, J = 6.3 Hz, Me-24), 0.83 (3H, t, J = 6.6 Hz, Me-22′); ^{13}C NMR ($CDCl_3$): δ 171.32 (C-1), 34.89 (C-2), 32.71 (C-3), 30.64 (C-4), 29.36 (C-5 to C-21), 27.06 (C-22), 25.82 (C-23), 16.21 (C-24), 64.51 (C-1′), 29.27 (C-2′ to C-19′), 25.81 (C-20′), 22.74 (C-21′), 14.76 (C-22′); ESIMS *m/z* (rel. int.): 676 $[M]^+$ ($C_{46}H_{92}O_2$) (12.8), 367 (19.2), 351 (11.9) (10.1), 325 (23.1), 309 (9.5).

Isolation of phytoconstituents from the fruits *Coriandrum sativum* L.

13α-Hydroxystearic acid (6)

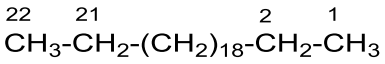
Elution of the column with petroleum ether-chloroform (1:1) furnished colourless crystals of **6**, recrystallized from acetone-methanol (1:1), yield 121 mg, m. p. 63 - 65 °C; IR υmax (KBr): 3310, 3253, 2910, 1695, 1435, 1242, 1114, 941, 725 cm^{-1}; ^1H NMR ($CDCl_3$) : δ 4.05 (1H, m, $w_{1/2}$ = 5.1 Hz, H -13β), 2.29 (2H, t, J = 7.3 Hz, H_2-2), 1.58 (2H, m, H_2 -3), 1.55 (2H, m, H_2 -4), 1.24 (24 H, brs, 12 x CH_2), 0.87 (3H, t, J = 6.9 Hz, Me-18); ^{13}C NMR ($CDCl_3$): δ 181.36 (C-1), 67.55 (C-13), 35.41 (C-2), 32.69 (C-3), 29.86 (C-4), 29.32 (9 x CH_2), 27.57 (C-15), 25.79 (C-16), 22.68 (C-17), 14.16 (C-18); +ve FAB MS *m/z* (rel. int.) : 300 $[M]^+$ ($C_{18}H_{36}O_3$) (4.9), 229 (18.6), 199 (17.6), 101 (20.1), 59 (25.6).

RESULTS AND DISCUSSION

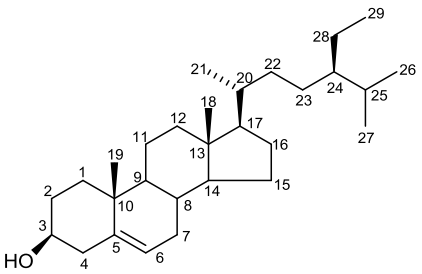
Compound **1** was a known aliphatic constituent identified as *n*-docosane.[34, 35] The structure of compound **2** was elucidated as β-sitosterol.[36, 37]

Compound **3** showed UV absorption maximum at 276 nm for aromatic ring and IR absorption bands for an ester function (1727 cm^{-1}), aromatic ring (1635, 1527 cm^{-1}) and long aliphatic chain (748 cm^{-1}). On the basis of mass and ^{13}C NMR spectra its molecular ion peak was determined at *m/z* 486 consistent with a molecular formula of a phenyl hexacosanyl ester, $C_{33}H_{58}O_2$. The ion peaks arising at *m/z* 105 [C_7′ - O fission, C_6H_5-CO]$^+$, 381 [M – 105, O-CH_2-$(CH_2)_{24}$-CH_3] $^+$, 121 [C_1 - O fission, C_6H_5-COO]$^+$, and 365 [M – 121, CH_2-$(CH_2)_{24}$-CH_3] $^+$ indicated that hexacosanol was esterified with benzoic acid.

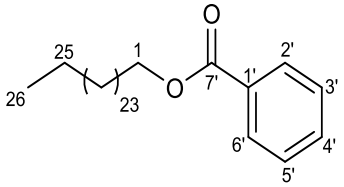
The ^1H NMR spectrum of **3** displayed two two-proton multiplets at δ 7.53 and 7.41 and a one-proton multiplet at δ 7.18 assigned to aromatic H-2′, H-6′, H-3′, H-5′ and H-4′ protons, respectively. A two- proton triplet at δ 4.25 (J = 11.3 Hz) was ascribed to oxymethylene H_2-1 protons. Three two-proton multiplets at δ 2.21, 1.68, and 1.59 were associated with the methylene protons. A three-proton triplet δ 0.89 (J = 6.5 Hz) was attributed to terminal C-26 primary methyl protons. The absence of any signal between δ 7.18 – 4.25 in the ^1H NMR spectrum ruled out the existence of any vinylic proton in the molecule. The ^{13}C NMR spectrum of **3** exhibited signals for ester carbon at δ 167.78 (C-7′), aromatic carbons between δ 132.51 – 128.69, oxymethylene carbon at δ 65.88 (C-1), other methylene carbons from δ 38.05 to 20.19 and methyl carbon at δ 14.02 (C-26). Acid hydrolysis of **3** yielded benzoic acid, m. p. 121 -122°C, and 1-hexacosanol, m. p. 79 – 81 °C, $[M]^+$ at *m/z* 382 ($C_{26}H_{54}O$). On the basis of the aforementioned spectral data and chemical reactions, the structure of **3** has been elucidated as 1-hexacosanyl benzoate, a new aromatic ester.



***n*-Docosane (1)**



β-Sitosterol (2)



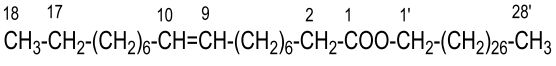
1-Hexacosanyl benzoate (3)

Fig 1: Structural formulae of the chemical constituents 1, 2 and 3 isolated from the *Berberis aristata* heartwood.

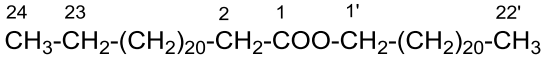
Compound **4** showed IR absorption bands for an ester group (1726 cm^{-1}), unsaturation (1635 cm^{-1}) and long aliphatic chain (731 cm^{-1}). Its mass spectrum displayed a molecular ion peak at *m/z* 674 $[M]^+$ consistent with a molecular formula of a fatty acid ester, $C_{46}H_{90}O_2$. The ion peaks generated due to removal of the acyl group at *m/z* 265 [C_1 - O fission, $CH_3(CH_2)_7$-CH=CH-$(CH_2)_7$CO]$^+$, 409 [M – 265, O-CH_2-$(CH_2)_{26}$-CH_3] $^+$, and 281 [O – C_1′ fission, $CH_3(CH_2)_7$-CH=CH-$(CH_2)_7$COO]$^+$ indicated that oleic acid was esterified with octacosan-1-ol.

The ^{1}H NMR spectrum of **4** exhibited two one-proton multiplets at δ 5.32 (1 H, m, H-9), 5.28 (1 H, m, H-10) assigned to vinylic H-9 and H-10 protons. Two triplets at δ 4.45 (J = 7.8 Hz) and 2.29 (J = 7.2 Hz), integrated for two protons each, were attributed correspondingly to oxymethylene H_2-1′ and methylene H_2 -2 protons adjacent to the ester function. The remaining methylene protons resonated as two-proton multiplets at δ 2.31 (H_2-8), 2.14 (H_2-11), 1.73 (H_2-3), 1.62 (H_2-7), and 1.35 (H_2-2′) and as broad singlets at δ 1.29 (40 H) and 1.25 (28 H). Two three-proton triplets at δ 0.89 (J = 5.4 Hz) and 0.85 (J = 6.5 Hz) were ascribed to primary C-18 and C-28′ methyl protons, respectively. The ^{13}C NMR spectrum of **4** displayed signals for the ester carbon at δ 173.15 (C-1), oxymethylene carbon at δ 60.11 (C-1′), other methylene carbons between δ 51.86 – 22.68 and methyl carbons at δ 13.93 (C-18) and 14.83 (C-28′). On the basis of these spectral data analysis the structure of **4** has been formulated as *n*-octacosan-1-olyl (Z)-octadec-9-enoate (*n*-octacosanyl oleate), a new fatty acid ester (Fig. 2).

Compound **5** exhibited UV absorption maximum at 211 nm for an aliphatic compound and IR absorption bands for an ester group (1725 cm^{-1}) and long aliphatic chain (751 cm^{-1}). Its mass spectrum showed a molecular ion peak at *m/z* 676 $[M]^+$ consistent with a molecular formula of a fatty acid ester, $C_{46}H_{92}O_2$. The ion peaks generated due to removal of the acyl group at *m/z* 351 [C_1 - O fission, $CH_3(CH_2)_{22}$-$CO]^+$, 423 [M – 351, O-CH_2-$(CH_2)_{20}$-$CH_3]^+$, 367 [O – C_1′ fission, $CH_3(CH_2)_{22}$-$COO]^+$ and 309 [M – 367, CH_2-$(CH_2)_{20}$-$CH_3]^+$ suggested that lignoceric acid was esterified with docosan-1-ol.
The ^{1}H NMR spectrum of **5** exhibited two two-proton triplets at δ 4.29 (J = 6.7 Hz) and 2.26 (J = 7.1 Hz) attributed correspondingly to oxymethylene H_2-1′ and methylene H_2 -2 protons adjacent to the ester function. The remaining methylene protons appeared as two-proton multiplets at δ 1.55 and 1.36 and as a broad singlet at δ 1.28 (72H). Two three-proton triplets at δ 0.86 (J = 6.3 Hz) and 0.83 (J = 6.6 Hz) were ascribed to primary C-24 and C-22′ methyl protons, respectively. The ^{13}C NMR spectrum of **5** displayed signals for the ester carbon at δ 171.32 (C-1), oxymethylene carbon at δ 64.51 (C-1′), other methylene carbons between δ 34.89 – 22.74 and methyl carbons at δ 16.21 (C-24) and 14.76 (C-22′). On the basis of above discussion the structure of **5** has been characterized as docosan-1-olyl tetracosanoate (*n*-docosanyl lignocerate), a new fatty acid ester (Fig. 2).



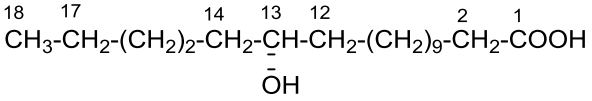
***n*-Octacosanyl oleate (4)**



***n*-Docosanyl lignocerate (5)**

Fig 2: Structural formulae of the chemical constituents 4 and 5 isolated from the *Centella asiatica* aerial parts.

The IR spectrum of compound **6** showed absorption bands for a hydroxyl group (3310 cm^{-1}), carboxylic function (3253, 1695 cm^{-1}) and long aliphatic chain (725 cm^{-1}). Its mass spectrum exhibited a molecular ion peak at *m/z* 300 corresponding to a hydroxystearic acid, $C_{18}H_{36}O_3$. The ion fragments arising at *m/z* 199 [C_{12} – C_{13} fission, $CH_2(CH_2)_{10}$-$COOH]^+$, 101 [M – 199]$^+$ and *m/z* 229 [C_{14} – C_{13} fission, CH(OH)-$CH_2(CH_2)_{10}$-$COOH]^+$ indicated that the hydroxyl group was located on C-13 carbon atom. An ion peak produced at *m/z* 59 [C_2 – C_3 fission, CH_2-$COOH]^+$ suggested the attachment of the carboxylic function at the terminal carbon. The ^{1}H NMR spectrum of **6** displayed a one-proton multiplet at δ 4.05 with half-width of 5.1 Hz assigned to beta-oriented oxymethine H -13 proton. A two-proton triplet at δ 2.29 (J = 7.3 Hz) was ascribed to methylene H_2-2 adjacent to the carboxylic group. The other methylene protons appeared as two-proton multiplets at δ 1.58 (H_2 -3) and 1.55 (H_2 -4) and as a singlet at δ 1.24 (24 H). A three-proton triplet at δ 0.87 (J = 6.9 Hz) was accounted to terminal C-18 primary methyl protons. The ^{13}C NMR spectrum of **6** exhibited signals for the carboxylic carbon at δ 181.36 (C-1), carbinol carbon at δ 67.55 (C-13), methylene carbons from δ 35.41 to 22.68 and methyl carbon at δ 14.16 (C-18). The absence of any signal beyond δ 4.05 in the ^{1}H NMR spectrum and carbon signals between δ 181.36 - 67.55 in the ^{13}C NMR spectrum ruled out the existence of any vinylic linkage in the molecule. On the basis of these spectral data analysis, the structure of **6** has been elucidated as 13α-hydroxystearic acid, a new hydroxyfatty acid (Fig. 3).



13α-Hydroxystearic acid (6)

Fig 3: Structural formula of the chemical constituent 6 isolated from the fruits of *Coriandrum sativum* L.

CONCLUSION

Phytochemical investigation of a methanolic extract of the heartwood of *Berberis aristata* afforded *n*-docosane (**1**), β-sitosterol (**2**) and 1-hexacosanyl benzoate (**3**). The aerial parts of *Centella asiatica* furnished two new fatty acid esters identified as octacosan-1-olyl (Z)-octadec-9-enoiate (*n*-octacosanyl oleate, **4**), a new fatty acid ester and docosan-1-olyl tetracosanoate (*n*-docosanyl lignocerate, **5**). The fruits of *Coriandrum sativum* produced 13α-hydroxystearic acid (**6**). This work has enhanced understanding about the phytoconstituents of these plants. These secondary metabolites can be used as analytical markers for quality control of these herbal drugs. 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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REFERENCES

1. Kirtikar KR, Basu BD. Indian Medicinal Plants, I. International Book Distributors, Dehradun, 2005; 1064.
2. Anonymous. The Wealth of India: A dictionary Indian Raw Materials and Industrial Products, Raw Materials, A; National Institute of Science Communication and Information Resources (CSIR), New Delhi, 2007; 135.
3. Khare CP, Indian Medicinal Plants, An Illustrated Dictionary, Springer-Verlag Berlin/Heidelberg, 2007; 88.
4. Sharma K, Bairwa R, Chauhan N, Shrivastava B, Saini NK. *Berberis aristata*: A review. International Journal of Research in Ayurveda & Pharmacy, 2011; 2(2): 383-388.
5. Quattrocchi U. CRC World Dictionary of Medicinal and Poisonous Plants: Common Names, Scientific Names, Eponyms, Synonyms, and Etymology. CRC Press, Boca Raton, Florida, 2012; p p. 565, 882, 1131.
6. Bhartwaj D, Kaushik N. Phytochemical and pharmacological studies in genus *Berberis*, Phytochemistry Reviews, 2012; 11 (4): 523–542.
7. Potdar D, Hirwani RR, Dhulap S. Phyto-chemical and pharmacological applications of Berberis aristata. Fitoterapia. 2012; 83(5): 817-30. doi: 10.1016/j.fitote.2012.04.012.
8. Ahamad J, Naquvi KJ, Ali M, Mir SR. New isoquinoline alkaloids from the stem bark of *Berberis aristata*, Indian J Chemistry, 2014; 53B: 1237 – 1241.
9. Katiyar D, Singh RK, Singh S, Singh D, Singh V. Isolation and characterization of n-docosane from heartwood of *Berberis aristata*. Int J Pharmaceutical Science & Res, 2011; 2(2): 331-335.
10. Katiyar D, Singh V, Gilani SJ, Goel R, Vats A, Bajaj U. Isolation and characterization of stigmast-5-en-3β-ol from heartwood of *Berberis aristata*, Int. J. Drug Dev. & Res., 2014; 6 (1): 92-98.
11. Katiyar D, Dixit PK, Singh V, Gilani SJ, Goel R (2015) N-Tetracosanyl benzoate: A novel phytoconstituent of *Berberis aristata* DC. Med Aromat Plants, 2015; 4: 4: 210. doi:10.4172/2167-0412.1000210.
12. Khare CP. Indian Medicinal Plants, An Illustrated Dictionary, 2007; Springer-Verlag Berlin/Heidelberg, 2007; 136 – 137.
13. Jamil SS, Nizami Q, Salam M. *Centella asiatica* (Linn.) Urban-a review. Nat Prod Radiance, 2007; 6(2): 158-170.
14. James JT, Dubery IA. Pentacyclic triterpenoids from the medicinal herb, *Centella asiatica* (L.) Urban. Molecules, 2009; 14(10): 3922-3941.
15. Francis SC, Thomas MT. Essential oil profiling of *Centella asiatica* (L.) Urb - A medicinally important herb. South Indian J Biol Sci, 2016; 2(1): 169- 173.
16. Siddiqui BS, Aslam H, Ali ST, Khan S, Begum S. Chemical constituents of *Centella asiatica*. J Asian Nat Prod Res, 2007; 9(3-5): 407-414.
17. Inamdar PK, Yeole RD, Ghogare AB, De Souza NJ. Determination of biologically active constituents in *Centella asiatica*. Journal of Chromatography A, 1996; 742 (1-2): 127-130.
18. Randriamampionona D, Diallo B, Rakotoniriana F, Rabemanantso C, Cheuk K, Corbisier AM, et al. Comparative analysis of active constituents in *Centella asiatica* samples from Madagascar: Application for ex situ conservation and clonal propagation. Fitoterapia, 2008; 78(7- 8): 482-489. DOI: 10.1016/j.fitote.2007.03.016
19. Yu QL, Duan HQ, Gao WY, Takaishi Y. A new triterpene and a saponin from *Centella asiatica*. Chin Chem Lett, 2007; 18(1): 62-64.
20. Yu Q, Duan H-Q, Takaishi Y, and Gao W-Y. A Novel Triterpene from *Centella asiatica*. Molecules, 2006; 11(9): 661-665. https://doi.org/10.3390/11090661.
21. Jiang ZY, Zhang XM, Zhou J, Chen JJ. New triterpenoid glycosides from *Centella asiatica*. Helv. Chim. Acta, 2005; 88: 297–303.
22. Matsuda H, Morikawa T, Ueda H, Yoshikawa M. Medicinal foodstuffs. XXVI. Inhibitors of aldose reductase and new triterpene and its oligoglycoside, centellasapogenol A and centellasaponin A, from *Centella asiatica* (Gotu Kola). Heterocycles, 2001b; 55: 1499–1504.
23. Kuroda M, Mimaki Y, Harada H, Sakagami H, Sashida Y. Five new triterpene glycosides from *Centella asiatica*. Nat. Med., 2001; 55: 134–138.
24 Schulte KE, Ruecker G, Abdul Bary E. Constituents of medical plants. XXVII. Polyacetylenes from *Hydrocotyle asiatica*. Arch. Pharm., 1973; 306: 197–209.
25. Prum N, Illel B, Raynaud J. Flavonoid glycosides from *Centella asiatica* L. (Umbelliferaea). Pharmazie; 1983; 38: 423.
26. Kapoor R, Ali M, Mir SR. Phytochemical investigation of *Centella asiatica* aerial parts. Oriental J. Chem., 2003; 19: 485–486.
27. Mahleyuddin NN, Moshawih S, Ming LC, Zulkifly HH, Kifli N, Loy MJ, Sarker MMR, Al-Worafi YM, Goh BH, Thuraisingam S, Goh HP. *Coriandrum sativum* L.: A Review on Ethnopharmacology, Phytochemistry, and Cardiovascular Benefits. Molecules, Dec 30, 2021; 27(1): 209. doi: 10.3390/molecules27010209.
28. Ravi R, Prakash M, Bhat KK. Aroma characterization of coriander (*Coriandrum sativum* L.) oil samples, Eur Food Res Technol, 2007; 225: 367-374.
29. Neffati M, Marzouk B. Changes in essential oil and fatty acid composition in coriander (*Coriandrum*

sativum L.) leaves under saline conditions, Ind Crops Prod, 2008; 28: 137-142.
30. Bhuiyan MNI, Begum J, Sultana M. Chemical composition of leaf and seed essential oil of *Coriandrum sativum* L. from Bangladesh, Bangladesh J Pharmacol, 2009; 4: 150-153.
31. Ebrahimi SN, Hadian J, Ranjbar H. Essential oil compositions of different accessions of *Coriandrum sativum* L. from Iran, Nat Prod Res., 2010; 24(14): 1287–1294. doi: 10.1080/14786410903132316.
32. Sriti J, Wannes WA, Talou T, Vilarem G, Marzouk B. Chemical composition and antioxidant activities of Tunisian and Canadian coriander (*Coriandrum sativum* L.) fruit, J Essent Oil Res., 2011; 23: 7-15.
33. Naquvi KJ, Ali M, Ahmad J. Two new aliphatic lactones from the fruits of *Coriandrum sativum* L. Org Med Chem Lett. 2012; 2(1): 28. doi: 10.1186/2191-2858-2-28.
34. Romeo R, Lemmon EW. Equations of state for *n*-hexadecane and *n*- docosane. International Journal of Thermophysics, 2022; 43: 146; https://doi.org/10.1007/s10765-022-03059-0.
35. Fredi G, Dirè S, Callone E, Ceccato R, Mondadori F, Pegoretti A. Docosane - Organosilica microcapsules for structural composites with thermal energy storage/release capability, Materials, 2019; 12: 1286. doi:10.3390/ma12081286.
36. Ali M, Sultana S, Mir SR. Isolation of sterols, triterpenoids and a sesquiterpene from the leaves of *Ficus nitida* Thunb. International Journal of Pharmaceutical Chemical Research, 2017; 3(2): 190-195.
37. Sultana S, Ali M, Jameel M, Aliphatic constituents from the leaves of *Dillenia indica* L., *Halothamus bottae* Jaub. and *Xylosma longifolium* Clos, Chemistry Research Journal, 2018; 3(3): 109-117.