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ACYL AND AROMATIC ESTERS AND PALMITOYL β-D-GALACTOSIDE FROM *SUAEDA MARITIMA* (L.) DUMORT.

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ABSTRACT
Suaeda maritima (L.) Dumort. (Chenopodiaceae, Amaranthaceae), occurs as an annual, erect, glaucous or green herb in India, Europe, Mediterranean region, Asia, Australia, North America, Argentina, Egypt and Canada. The plant is used to treat liver diseases; the leaves are taken as a remedy for liver, heart and lipid disorders. The whole plant powder was extracted with methanol and extract was concentrated under reduced pressure to obtain a dark brown viscous mass. It was adsorbed on silica gel (60-120 mesh) and subjected to chromatography over silica gel column packed in petroleum ether. The column was eluted successively with petroleum ether, chloroform and methanol in order of increasing polarity. Three acyl esters characterized as decyl oleate[1], lauryl oleate[2] and stearyl oleate[3], three aromatic esters *viz.*, 3-methoxybenzyl oleate[4], cetyl dihydrocaffeate[5] and stearyl dihydrocaffeate[6] and an acyl galactoside identified as palmitoyl β-D-galactoside[7] were isolated from the whole plant. The structures of all the isolated phytoconstituents have been established on the basis of spectral data analysis and chemical reactions.

KEYWORDS: *Suaeda maritima*, whole plant, isolation, acyl esters, aromatic esters, palmitoyl β-D-galactoside, characterization.

INTRODUCTION
Suaeda maritima (L.) Dumort., syn. *S. fernaldii* Standley, *Chenopodium maritimum* L, (Chenopodiaceae, Amaranthaceae), known as moras, annual sea-blite and herbaceous seepweed, is found in Canary Islands, India, Europe, Mediterranean, Caucasus, Asia, Australia, North America, Argentina., Egypt and Canada. It occurs as an annual, prostrate to ascending, erect, glaucous or green herb, with prostrate, decumbent, light brown, simple or branched stems, slightly woody at base; leaves ascending or spreading, fleshy, succulent, green-red; blade linear, subterete; flowers bisexual, apex obtuse; seeds monomorphic, lenticular, reddish brown or black, reticulate. The species grows gregariously and covers large scale in the frequently inundated river flat lands. It is distributed throughout the coastal areas and in the saltmarshes in India and south-eastern Asian coasts.[1] Seablite can grow naturally, so it is the low cost vegetable with high nutritional value. Its young leaves can be used as a fresh or cooked vegetable. The cooked seablite is quite salty, so it should be cooked with other types of vegetable to reduce salty taste. In southern India, seablite is pickled in vinegar or used for cooking and domestic animal food.[2,3] In India and Saudi Arabia, the plant is recommended to treat liver diseases.[4-6] The leaves are taken as a remedy for liver, heart and lipid disorders.[5] The plant contained quercetin and kaempferol, their glycosides, and methyl ferulate.[7] Aliphatic and aromatic esters from the plant stem have been reported.[8] This manuscript describes the isolation and characterization of four aromatic esters along with aliphatic esters from the whole plant of *S. maritima*.

EXPERIMENTAL
General procedures: Melting points were measured on a thermoelectrically operated Perfit apparatus and are uncorrected. UV spectra were determined on Shimadzu-120 double beam spectrophotometer with methanol as a solvent. IR spectra were recorded in KBr pellet on Shimadzu FTIR-8400 spectrophotometer. ^{1}H NMR (400 MHz) spectra were scanned by Bruker spectrospin NMR instrument using TMS as internal standard. ESI mass spectra were recorded on a Jeol D-300 spectrometer. For column chromatography, silica gel (60-120 mesh, Merck, Mumbai, India) was used. Thin-layer chromatography was performed on silica gel G 60 F_{254} precoated TLC plates (Merck, Mumbai, India). The spots were visualized by exposure to iodine vapors and UV radiations (254 and 366 nm).

Plant Material: The whole plant of *S. maritima* was collected from Ennore, Tamil Nadu and identified by Prof. M. P. Sharma, Department of Botany, Faculty of Science, Jamia Hamdard, New Delhi. A voucher specimen is deposited in the herbarium of the Faculty of Pharmacy, Jamia Hamdard, New Delhi.

Extraction and Isolation: The air-dried whole plant (2 kg) of *S. maritima* was coarsely powdered and extracted exhaustively in a Soxhlet apparatus with methanol for 72 hr. The methanolic extract was concentrated under reduced pressure to obtain a dark brown viscous mass (123 g). A small portion of the extract was analyzed chemically to determine the presence of different chemical constituents. The viscous dark brown mass was adsorbed on silica gel (60-120 mesh) for column chromatography, after being dissolved in a small quantity of methanol for preparation of slurry. The slurry (200 g) was air- dried 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, and 1:3), chloroform and the mixture of chloroform and methanol (99:1, 97:3, 95:5). Various fractions were collected separately and matched by TLC to check homogeneity. Similar fractions having the same R_f values were combined and purified to get the following compounds.

Decyl oleate(1): Elution of the column with petroleum ether produced pale yellow sticky mass of **1**, 125 mg (0.067 % yield), IR υ_{max} (KBr): 2937, 2841, 1722, 1642, 1463, 1394, 1186, 1020, 723 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.33 (2H, m, H-9, H-10), 4.22 (2H, t, J = 6.9 Hz, CH_2-1′), 2.38 (2H, m, CH_2-2), 2.02 (2H, m, CH_2-11), 1.93 (2H, m, CH_2-8), 1.56 (2H, m, CH_2), 1.52 (2H, m, CH_2), 1.35 (2H, m, CH_2), 1.23 (32H, brs, 16 × CH_2), 0.87 (3H, t, J = 6.5 Hz, Me-18), 0.83 (3H, t, J = 6.6 Hz, Me-10′); +ve ESI MS *m/z* (rel. int.): 422 $[M]^+$ ($C_{28}H_{54}O_2$) (2.7).

Lauryl oleate(2): Further elution of the column with petroleum ether afforded pale yellow sticky mass of **2**, 147 mg , UV λmax (MeOH) 207 nm (log ε 4.1); IR υ_{max} (KBr): 2927, 2851, 1723, 1648, 1456, 1424, 1286, 1226, 1120, 912, 726 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.34 (1H, m, H-9), 5.32 (1H, m, H-10), 4.03 (2H, t, J =7.2 Hz, H_2-1′), 2,50 (2H, t, J =7.2 Hz, H_2-2), 2.27 (2H, m, H_2-8), 2.02 (2H, m, CH_2-11), 1.56 (2H, m, CH_2), 1.49 (2H, m, CH_2), 1.30 (8H, brs, 4 x CH_2), 1.25 (34H, brs, 17 × CH_2), 0.86 (3H, t, J = 6.6 Hz, Me-18), 0.83 (3H, t, J = 6.2 Hz, Me-14′); +ve ESI MS *m/z* (rel. int.): 450 $[M]^+$ ($C_{30}H_{58}O_2$), (18.9).

Stearyl oleate(3): Elution of the column with petroleum ether – chloroform (3:1) afforded a pale yellow gummy mass of **3**, 139 mg , UV λmax (MeOH) 207 nm (log ε 4.1); IR υ_{max} (KBr): 2923, 2855, 1722, 1650, 1456, 1371, 1286, 1221, 1162, 1090, 721 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.31 (1H, m, H-9), 5.29 (1H, m, H-10), 4.06 (2H, t, J = 7.3 Hz, H_2-1′), 2.29 (2H, t, J = 7.2 Hz, H_2-2), 2.19 (2H, m, H_2-8), 2.05 (2H, m, CH_2-11), 1.64 (2H, m, CH_2), 1.54 (2H, m, CH_2), 1.30 (6H, brs, 3 x CH_2), 1.23 (44H, brs, 22 × CH_2), 0.85 (3H, t, J = 6.5 Hz, Me-18), 0.82 (3H, t, J = 6.1 Hz, Me-18′); +ve ESI MS *m/z* (rel. int.): 534 $[M]^+$ ($C_{36}H_{70}O_2$) (8.9).

3-Methoxybenzyl oleate (4): Elution of the column with petroleum ether - chloroform (1:1) yielded pale yellow crystals of **4**, 166 mg, m. p. 113-115° C, UV λmax (MeOH) 207, 269 nm (log ε 2.6, 3.8); IR ν_{max} (KBr): 2927, 2851, 1722, 1649, 1524. 1452, 1377, 1249, 1135, 1027, 826, 726 cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.47 (1H, d, J = 2.7 Hz, H-2), 6.63 (1H, m, H-4), 6.57 (1H, m, H-5), 6.60 (1H, m, H-6), 5.32 (2H, m, H-9′, H-10′), 4.22 (2H, s, H_2 -7), 3.31 (3H, s, OMe), 2.47 (2H, t, J =7 .4 Hz, CH_2-2′), 2.26 (2H, m, CH_2-8′), 2.08 (2H, m, CH_2-11′), 1.64 (2H, m, CH_2), 1.55 (2H, brs, CH_2), 1.31 (2H, m, CH_2), 1.22 (16H, brs, 8 × CH_2), 0.83 (3H, t, J = 6.5 Hz, Me-18′), ESI MS *m/z* (*rel. int.*): 402 [M]+ ($C_{26}H_{42}O_3$) (11.4).

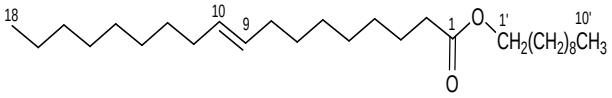
Cetyl dihydrocaffeate (5): Elution of the column with chloroform yielded redish brown crystals of **5**, 109 mg, m.p. 101-103° C, UV λmax (MeOH) 208, 278 nm (log ε 1.6, 3.3); IR ν_{max} (KBr): 3366, 3245, 2925, 2850, 1723, 1645, 1425, 1375, 1259, 1175, 1042, 726 cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.38 (1H, d, J = 2.8 Hz, H-2), 7.15 (1H, m, H-5), 6.56 (1H, m, H-6), 4.21 (2H, t, J = 7.1 Hz, CH_2 -1′), 2.67 (2H, t, J =7.4 Hz, CH_2-7), 2.46 (2H, d, J = 7.5 Hz, CH_2-8), 1.63 (2H, m, CH_2), 1.56 (2H, brs, CH_2), 1.33 (2H, m, CH_2), 1.22 (22H, brs, 11 × CH_2), 0.88 (3H, t, J = 6.5 Hz, Me-14′); ESI MS *m/z* (*rel. int.*): 406 [M]+ ($C_{25}H_{42}O_4$) (8.9).

Stearyl dihydrocaffeate (6): Elution of the column with chloroform – methanol (49:1) gave yellow semisolid of **6**, 135 mg (0.068 % yield); m.p. 110-113° C, UV λmax (MeOH) 206, 277 nm, (log ε 2.3, 3.7); IR νmax (KBr): 3392, 3284, 2945, 2849, 1725, 1647, 1556, 1435, 1387, 1235, 1187, 1045, 882 cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.35 (1H, d, J = 2.5 Hz, H-2), 7.15 (1H, m, H-5), 6.65 (1H, m, H-6), 4.25 (1H, t, J = 7.3 Hz, CH_2 -1′), 2.69 (2H, t, *J* = 7.4 Hz, CH_2-7), 2.48 (2H, t, J = 7.5 Hz, CH_2-8), 1.61 (2H, m, CH_2), 1.55 (2H, m, CH_2), 1.34 (2H, m, CH_2), 130 (2H, brs, CH_2), 1.22 (24H, brs,12 × CH_2), 0.82 (3H, t, J = 6.2 Hz, Me-18′), ESI MS *m/z* (*rel. int.*): 434 $[M]^+$ ($C_{27}H_{46}O_4$) (4.1).

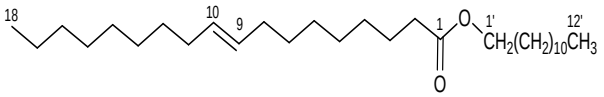
Palmitoyl β-D-galactoside (7): Elution of the column with chloroform-methanol (19:1) produced colourless crystals of **7**, 207 mg , m. p. 131-134° C, UV λmax (MeOH) 205 nm (log ε 4.8); IR υ_{max} (KBr): 3410, 3335, 2943, 2835, 1721, 1648, 1458, 1371, 1298, 1223, 1013, 726 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.23 (1H, d, J = 7.3 Hz, H-1′), 4.49 (1H, m, H-5′), 3.86 (1H, m, H-2′),3.76 (1H, m, H-3′), 3.68 (1H, m, H-4′), 3.16 (2H, brs, H_2-6′), 2.59 (2H, t, J = 7.2 Hz, H_2-2), 1.52 (2H, m, CH_2), 1.25 (24H, brs, 12 × CH_2), 0.84 (3H, t, J = 6.3 Hz, Me-16); +ve ESI MS *m/z* (rel. int.): 418 $[M]^+$ ($C_{22}H_{42}O_7$) (3.2).

RESULTS AND DISCUSSION

The compounds **1** - **3** were the common acyl esters characterized as decyl oleate (**1**), lauryl oleate (**2**) and stearyl oleate (**3**).



Decyl oleate(1)



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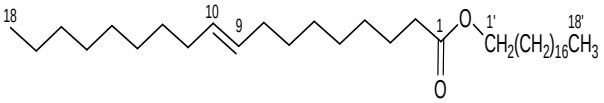
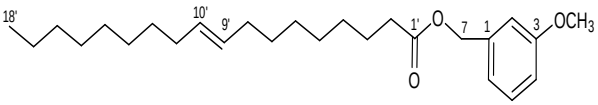


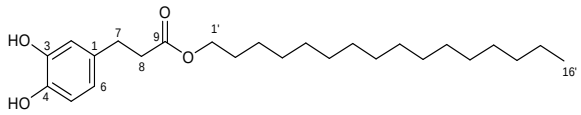
Stearyl oleate (3)

Compound **4,** named 3-methoxybenzyl oleate, had UV absorption maximum at 269 nm for aromatic compounds and IR absorption bands for ester function (1722 cm^{-1}), aromaticity (1649, 1524, 1027 cm^{-1}) and long aliphatic chain (726 cm^{-1}). Its mass spectrum showed a molecular ion peak at *m/z* 402 constituent with the molecular formula of an aromatic ester, $C_{26}H_{42}O_3$. The ^{1}H-NMR spectrum of **4** exhibited a one-proton doublet at δ 7.47 (J = 2.7 Hz) and three one-proton multiplets at δ 6.63, 6.57 and 6.60 assigned to aromatic meta-coupled H-2 and other aromatic H-4, H-5 and H-6 protons, respectively, a two-proton multiplet at δ 5.32 ascribed to vinylic H-9′ and H-10′ protons, a two-proton singlet at δ 4.22 acoounted to oxymethylene H_2-7 protons, a three-proton singlet at δ 3.31 due to methoxy protons, a two-proton triplet at δ 2.47 (J =7 .4 Hz) attributed to methylene H_2-2′ protons adjacent to the ester carbon, other methylene proton signals as two-proton multiplets between δ 2.26 - 1.31 and as a broad singlet at δ 1.22 (16H) and a three - proton triplet at δ 0.83 (J = 6.5 Hz) associated with terminal primary methyl C-18′ protons. On the basis of these evidences, the structure of **4** has been characterized as 3-methoxybenzyl oleate, a new aromatic ester.



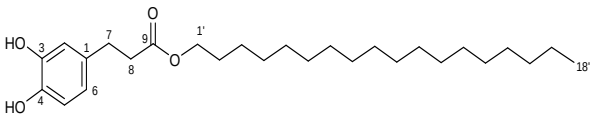
3-Methoxybenzyl oleate (4)

Compound **5,** named cetyl dihydrocaffeate, showed UV absorption maximum at 278 nm for aromatic compounds and IR absorption bands for hydroxyl groups (3366, 3245 cm^{-1}), ester function (1723 cm^{-1}), aromaticity (1645, 1552, 1042 cm^{-1}) and long aliphatic chain (726 cm^{-1}). Its mass spectrum displayed a molecular ion peak at *m/z* 406 constituent with a molecular formula of an aromatic ester, $C_{25}H_{42}O_4$. The ^{1}H-NMR spectrum of compound **5** exhibited a one-proton doublet at δ 7.38 (J = 2.8 Hz) and two one-proton multiplets at δ 7.15 and 6.56 assigned to meta-coupled aromatic H-2 and other aromatic H-5 and H-6 protons, respectively. Three two-proton triplets at δ 4.21 (J = 7.1 Hz), 2.67 (J = 7.4 Hz,) and 2.46 (J = 7.5 Hz,) were ascribed to oxymethylene H_2-1′, methylene H_2-7 protons attached to the aromatic ring and methylene H_2-8 adjacent to the ester group, respectively. The other methylene proton signals appeared from δ 1.63 to 1.22. A three-proton triplet at δ 0.88 (J = 6.5 Hz) was accounted to terminal C-16′ primary methyl protons. These spectral data analysis led to formulate the structure of **5** as *n*-hexadecanyl dihydrocaffeate.



Cetyl dihydrocaffeate (5)

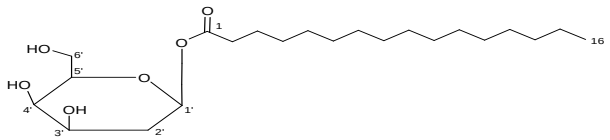
Compound **6,** named stearyl dihydrocaffeate, exhibited UV absorption maximum for aromatic compounds (277 nm) and IR absorption bands for hydroxyl groups (3392, 3284 cm^{-1}), ester function (1725 cm^{-1}), aromaticity (1647, 1556, 1045 cm^{-1}) and long aliphatic chain (882 cm^{-1}). Its mass spectrum displayed a molecular ion peak *m/z* 434 constituent with the molecular formula of an aromatic ester $C_{27}H_{46}O_4$. The ^{1}H-NMR spectrum of **6** displayed a one-proton doublet at δ 7.35 (J = 2.5 Hz) and two one-proton multiplets at δ 7.15 and 6.65 assigned to aromatic H-2, H-5 and H-6 protons, respectively, three two-proton triplets at δ 4.25 (J = 7.3 Hz), 2.69 (J = 7.4 Hz) and 2.48 (J = 7.5), ascribed to oxymethylene H_2 -1′, methylene H_2-7 linked to the aromatic ring and methylene H_2-8 nearby the ester group, respectively, other methylene protons between δ 1.61 – 1.22 and a three-proton triplet at δ 0.82 (J = 6.2 Hz) accounted to terminal primary C-18′ methyl protons. On the basis of these spectral data analysis the structure of **6** has been established as *n*-octadecanyl dihydrocaffeate.



Stearyl dihydrocaffeate (6)

Compound **7,** designated as named palmitoyl β-D-galactoside, showed IR absorption bands for hydroxyl groups (3410, 3335 cm^{-1}), ester function (1721 cm^{-1}) and long aliphatic chain (726 cm^{-1}). Its mass spectrum displayed a molecular ion peak at *m/z* 418 constituent to a molecular formula of an acyl ester, $C_{22}H_{42}O_7$. The ^{1}H-NMR spectrum of **7** exhibited a one-proton doublet at δ 5.23 (J = 7.3 Hz) assigned to anomeric H-1′ proton, other sugar protons as multiplets between δ 4.49 - 3.68 and a broad singlet at δ 3.16 due to hydroxymethylene H_2-6′ protons, methylene protons nearby ester group as a two-proton triplet at δ 2.59 (J = 7.2 Hz), as a two-proton multiplet at δ 1.52, as a broad singlet at δ 1.25 (24H) and as a three-proton triplet at δ 0.84 (J = 6.3 Hz) accounted

to terminal primary methyl Me-16 protons. Acid hydrolysis of **7** yielded palmitic acid (m.p. 61 - 63° C) and D-galactose (R_f 0.16, *n*-butanol-acetic acid-water, 4:1:5, v/v). On the basis of these evidences, the structure of compound **7** has been characterized as *n*-hexadecanoyl β-D-galactopyranoside**.**



Palmitoyl-β-D-galactoside (7)

CONCLUSION

Phytochemical investigation of a methanolic extract of the whole plant of *Suaeda maritima* resulted in the isolation of three acyl and three aromatic esters and palmitoyl β-D-galactoside. This work has enhanced understanding about the phytoconstituents of the plant. These compounds may be used as chromatographic markers for standardization of the whole plant.

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