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## Phytochemical Investigation of the Fruits of *Capparis decidua* (Forsk.) Edgew.

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### ABSTRACT

*Capparis decidua* (Forssk.) Edgew. (Capparaceae) is a branching shrub or small tree found in the subtropical and tropical regions of southern Asia and Africa. Its fruits are small, many-seeded, ovoid, pink berries used to relieve constipation and other stomach ailments. Phytochemical investigation of the fruits led to the isolation of five new compounds characterized as 3,4-dimethoxy-5-hydroxybenzaldehyde-5-O- $\alpha$ -D-galacturonopyranosyl-(2a $\rightarrow$ 1b)-O- $\alpha$ -D-galacturonopyranosyl-2b-octadec-9',12'-dienoate-3b-octadec-9'',12''-dienoate-4b-octadec-9''',12'''-dienoate (3,4-dimethoxy-5-hydroxybenzaldehyde digalacturonotrilinoleate, **5**), 3,4-dimethoxy-5-hydroxybenzaldehyde-5- $\alpha$ -D-galacturonofuranosyl-(2 $\rightarrow$ 1)-2'- $\alpha$ -D-galacturonofuranosyl-2''-octadec-9''',12''',15'''-trienoate (3,4-dimethoxy-5-hydroxybenzaldehyde digalacturonolinolenate, **6**), stigmast-5-en-3 $\beta$ -ol-3-O- $\beta$ -D-galacturonopyranosyl-2'-octadec-9'',12''-dienoate ( $\beta$ -sitosterol- $\beta$ -D-galacturonolinoleate, **7**), *n*-octadec-9-enoyl-O- $\alpha$ -D-galacturonofuranosyl-(2a $\rightarrow$ 1b)-O- $\alpha$ -D-galacturonofuranosyl-(2b $\rightarrow$ 1c)-O- $\beta$ -D-glucopyranosyl-(6c $\rightarrow$ 1d)-O- $\beta$ -D-glucopyranosyl-6d $\rightarrow$ 1e)-O- $\beta$ -D-glucopyranoside (oleilyldigalacturonotriglucoside, **8**) and  $\alpha$ -D-galacturono-furanosyl-(2a $\rightarrow$ 1b)-O- $\beta$ -D-arabinopyranosyl-(2b $\rightarrow$ 1c)-O- $\beta$ -D-arabinopyranosyl-(2c $\rightarrow$ 1d)-O- $\beta$ -D-arabinopyranosyl-(2d $\rightarrow$ 1e)-O- $\beta$ -D-arabinopyranoside (galacturonotetra-arabinoside, **9**) together with the known compounds glyceryl-1,2,3-trilinoleate (trilinolein, **1**), glyceryl-1-oleic-2,3-distearate (glyceryl oleodistearin, **2**), glyceryl-1-linolenic-2-oleic-3-stearate (glyceryl linoleno-oleiostearin, **3**) and *n*-tetracosanyl stearate (**4**). The structures of these phytoconstituents have been established on the basis of spectral data analysis and chemical reactions.

## INTRODUCTION

*Capparis decidua* (Forssk.) Edgew., syn. *C. aphylla* Roth (Capparaceae), commonly known as karel, karer, karu and caper plant, is a densely branching shrub or small tree found in the subtropical and tropical regions of southern Asia and Africa including Egypt, Ethiopia, India, Iran, Jordan, Nigeria, Pakistan, Senegal, Somalia, South Africa and Sudan. It occurs as a slender plant, up to 6 m high, with many green leafless branches, small, light brown paired spines on the twigs at each node; leaves are very minute; flowers are pink in colour, red-veined, in small groups along the leafless shoots, in the axils of the spines; fruits are small many-seeded ovoid or sub-globulous, slightly mucronate pink berries of cherry size and shape, become blackish when dry<sup>1,2</sup>. The plant parts are used as an appetizer, aphrodisiac, carminative, emmenagogue, tonic and to treat asthma, anorexia, cough, diabetes, jaundice, joint pain, parasitic worms, rheumatism and wounds. Pickled fruits are taken to relieve constipation and other stomach ailments. The bark is useful to reduce inflammation and acute pain. The roots are considered as an antibacterial, aphrodisiac, anodyne, anthelmintic, carminative, digestive, expectorant, stimulant, sudorific, thermogenic and useful in arthritis, dyspepsia, constipation, lumbago, odontalgia, amenorrhoea and dysmenorrhoea<sup>3</sup>. The root bark is used to cure gout, rheumatism, cough, dropsy, palsy, asthma, intestinal worms, intermittent fever and the powder is applied externally on malignant ulcer. Juice of the fresh plant is dropped to kill worms in the ear. The buds are utilized to subside boils<sup>1-6</sup>.

The flowers, fruits, stem and seeds contained *n*-pentacosane, *n*-triacontane, isothiocyanate glucoside, glucocapparin, stachydrine, spermidine alkaloids,  $\beta$ -carotene and  $\beta$ -sitosterol. The roots yielded  $\beta$ -sitosterol, isocodonocarpine, alkanes, *n*-triacontanol,  $\beta$ -carotene, ascorbic acid, proteins, capparin, capparinin, capparinin and phthalic acid. The root bark possessed oxygenated heterocyclic compounds<sup>7-18</sup>. This paper describes the isolation and characterization of five new compounds from the fruits of *C. deciduas* collected from Barmer, Rajasthan.

## MATERIALS AND METHODS

### General procedures

Melting points were determined on a Perfit melting point apparatus (Ambala, Haryana, India) and are uncorrected. IR spectra were recorded on KBr discs using a Jasco FTIR-410 spectrophotometer. UV spectra were measured on Shimadzu UV-1601 spectrophotometer in

methanol.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained using Bruker Advance DRX 400 spectropin and Bruker Advance DRX 100 spectropin instruments (Karlsruhe, Germany), respectively, using TMS as an internal standard. FAB mass spectra were recorded on a Jeol D-300 spectrometer. Column chromatography was performed on silica gel 60-120 mesh (Merck, Mumbai, India) and silica gel G coated TLC plates (Merck, Mumbai, India) were used for thin-layer chromatography. Spots were visualized by exposing to iodine vapors and UV radiation and spraying with ceric sulfate solution.

### **Plant material**

The fruits of *C. decidua* were collected from Abrasar village, district Barmer (Rajasthan). The drug sample was authenticated by Dr. H. B. Singh, Raw Material Herbarium and Museum (RHMD), National Institute of Science Communication and Information Resources (NISCAIR), New Delhi. A voucher specimen was deposited in the RHMD, NISCAIR, New Delhi with reference number NISCAIR/RHMD/Consult/-2010-11/1464/62.

### **Extraction and isolation**

The air-dried fruits (2.2 kg) of *C. decidua* were 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 (610 g, 27.3 % yield). Small portion of the extract was analyzed chemically to determine the presence of different chemical constituents. The 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 a slurry. The slurry 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, 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:

#### **Trilinolein (1)**

Elution of the column with petroleum ether - chloroform (1:1) furnished a pink semisolid mass of **1**, purified by preparative TLC using petroleum ether - chloroform (1:1), 3.4 g (0.154

% yield);  $R_f$ : 0.74 (petroleum ether-chloroform, 1:1); m. p. : 42-44<sup>0</sup>C; UV  $\lambda_{max}$  (MeOH): 204 nm (log  $\epsilon$  5.2); IR  $\nu_{max}$  (KBr): 2925, 2853, 1742, 1401, 1379, 1259, 1184, 721  $cm^{-1}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.45 (3H, m, H-10', H-10'' H-10'''), 5.43 (3H, m, H-12', H-12'' H-12'''), 5.41 (3H, m, H-9', H-9'' H-9'''), 5.33 (3H, m, H-13', H-13'', H-13'''), 4.36 (1H, dd, J = 6.0, 6.0 Hz, H-2), 4.22 (2H, d, J = 6.0 Hz, H<sub>2</sub>-1), 4.16 (2H, d, J = 6.0 Hz, H<sub>2</sub>-3), 2.84 (2H, dd, J = 7.1, 7.1 Hz, H<sub>2</sub>-2''), 2.40 (2H, dd, J = 7.2, 7.2 Hz, H<sub>2</sub>-2'), 2.36 (2H, dd, J = 5.6, 6.0 Hz, H<sub>2</sub>-3'''), 2.13 (2H, m, H<sub>2</sub>-12'), 2.11 (2H, m, H<sub>2</sub>-12''), 2.09 (2H, m, H<sub>2</sub>-12'''), 1.68 (6H, m, H<sub>2</sub>-8', H<sub>2</sub>-8'', H<sub>2</sub>-8'''), 1.66 (6H, m, H<sub>2</sub>-14', H<sub>2</sub>-14'', H<sub>2</sub>-14'''), 1.37 (12H, brs, 6 x CH<sub>2</sub>), 1.35 (16H, brs, 8 x CH<sub>2</sub>), 1.33 (20H, brs, 10 x CH<sub>2</sub>), 0.95 (3H, t, J = 6.0 Hz, Me-18''), 0.92 (3H, t, J = 6.2 Hz, Me-18'''); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  173.23 (C-1', C-1''), 172.79 (C-1'''), 131.93 (C-9'), 130.69 (C-9''), 130.51 (C-9'''), 130.09 (C-10'), 129.97 (C-10''), 129.81 (C-10'''), 129.71 (C-12'), 129.69 (C-12''), 128.86 (C-13'), 128.10 (C-13''), 127.91 (C-13'''), 71.57 (C-2), 68.91 (C-1), 62.10 (C-3), 34.20 (C-2'), 34.05 (C-2'', C-2'''), 31.94 (C-11'), 31.80 (C-11''), 31.34 (C-11'''), 29.78 (CH<sub>2</sub>), 29.71 (CH<sub>2</sub>), 29.69 (9 x CH<sub>2</sub>), 29.64 (CH<sub>2</sub>), 29.53 (CH<sub>2</sub>), 29.51 (CH<sub>2</sub>), 29.49 (CH<sub>2</sub>), 29.46 (CH<sub>2</sub>), 29.33 (CH<sub>2</sub>), 29.29 (CH<sub>2</sub>), 29.20 (CH<sub>2</sub>), 29.13 (CH<sub>2</sub>), 29.06 (CH<sub>2</sub>), 29.01 (CH<sub>2</sub>), 28.25 (CH<sub>2</sub>), 27.74 (CH<sub>2</sub>), 25.65 (CH<sub>2</sub>), 25.34 (CH<sub>2</sub>), 24.33 (CH<sub>2</sub>), 22.70 (CH<sub>2</sub>), 22.67 (CH<sub>2</sub>), 22.59 (CH<sub>2</sub>), 19.17 (Me-18'), 19.07 (Me-18''), 14.12 (Me-18'''); +ve FAB MS  $m/z$  (rel. int.): 866 [M]<sup>+</sup> (C<sub>57</sub>H<sub>86</sub>O<sub>6</sub>) (1.2), 263 (10.8), 280 (23.8).

### Glyceryl oleodistearin (2)

Elution of the column with petroleum ether - chloroform (1:3) yielded a pale yellow semisolid mass of **2**, purified by preparative TLC using petroleum ether - chloroform (1:3), 1.7 g (0.077 % yield);  $R_f$  value: 0.26 (petroleum ether - chloroform, 1:3); m. p.: 48-50 °C; UV  $\lambda_{max}$  (MeOH): 208, 284 nm (log  $\epsilon$  5.1, 1.1); IR  $\nu_{max}$  (KBr): 2926, 2853, 1737, 1645, 1443, 1381, 1261, 1072, 931, 722  $cm^{-1}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.34 (1H, m, H-10'', H-9'), 5.01 (1H, m, H-10'), 4.47 (1H, m, H-2), 4.27 (2H, m, H<sub>2</sub>-1), 4.09 (2H, m, H<sub>2</sub>-3), 2.31 (2H, m, H<sub>2</sub>-2'), 2.27 (2H, m, H<sub>2</sub>-2''), 2.20 (2H, m, H<sub>2</sub>-2'''), 2.02 (2H, m, H<sub>2</sub>-8'), 1.84 (2H, m, H<sub>2</sub>-11'), 1.66 (2H, m, CH<sub>2</sub>), 1.60 (2H, m, CH<sub>2</sub>), 1.29 (22H, brs, 10 x CH<sub>2</sub>), 1.25 (54H, brs, 27 x CH<sub>2</sub>), 1.00 (6H, m, Me-18', Me-18''), 0.98 (3H, t, J = 6.1 Hz, Me-18'''); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  172.26 (C-1'), 172.15 (C-1''), 170.12 (C-1'''), 130.04 (C-9'), 114.11 (C-10'), 69.03 (C-2), 67.57 (C-1), 62.32 (C-3), 41.21 (C-2'), 37.72 (C-2''), 34.79 (C-2'''), 34.48 (C-8'), 33.04 (C-11'), 31.95 (CH<sub>2</sub>), 31.80 (CH<sub>2</sub>), 31.66 (CH<sub>2</sub>), 29.72 (CH<sub>2</sub>), 29.53 (CH<sub>2</sub>), 29.36 (CH<sub>2</sub>), 29.14 (CH<sub>2</sub>), 29.01 (CH<sub>2</sub>), 27.29 (CH<sub>2</sub>), 25.57 (CH<sub>2</sub>), 24.88 (CH<sub>2</sub>), 23.22 (CH<sub>2</sub>), 22.71 (CH<sub>2</sub>), 14.15 (Me-18'),

14.11 (Me-18''), 14.07 (Me-18'''); +ve FAB MS  $m/z$  (*rel. int.*): 888 [M]<sup>+</sup> (C<sub>57</sub>H<sub>108</sub>O<sub>6</sub>) (2.1), 267 (13.6), 265 (9.3).

### Glyceryllinolenoleiostearin (3)

Elution of the column with chloroform afforded a yellow semisolid mass of **3**, purified by preparative TLC using petroleum ether - chloroform (1:19), 389 mg (0.018 % yield); R<sub>f</sub>: 0.40 (chloroform); m. p. 78-80 °C, UV  $\lambda_{\max}$  (MeOH): 205 nm (log  $\epsilon$  4.3); IR  $\nu_{\max}$  (KBr): 2923, 2852, 1743, 1106, 1463, 1376, 1260, 1185, 1008, 800, 720 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.82 (1H, m, H-12'), 5.37 (1H, m, H-13'), 5.35 (1H, m, H-10'), 5.33 (2H, m, H-15', H-13''), 5.26 (1H, m, H-9'), 5.08 (1H, m, H-16'), 5.08 (1H, m, H-9''), 4.96 (1H, m, H-10''), 4.93 (1H, m, H-12''), 4.30 (1H, dd, J = 4.4, 4.4 Hz, H-2), 4.20 (1H, d, J = 4.4 Hz, H<sub>2</sub>-1a), 4.17 (1H, d, J = 4.4 Hz, H<sub>2</sub>-1b), 4.12 (1H, d, J = 4.4 Hz, H<sub>2</sub>-3a), 4.09 (1H, d, J = 4.0 Hz, H<sub>2</sub>-3b), 2.77 (2H, m, H<sub>2</sub>-2'), 2.34 (2H, m, H<sub>2</sub>-2''), 2.30 (2H, m, H<sub>2</sub>-2'''), 2.03 (2H, m, H<sub>2</sub>-11'), 2.01 (2H, m, H<sub>2</sub>-14'), 1.97 (2H, m, H<sub>2</sub>-11''), 1.62 (4H, m, H-8', H-17'), 1.61 (4H, m, H<sub>2</sub>-8'', H<sub>2</sub>-14''), 1.29 (24H, brs, 12 x CH<sub>2</sub>), 1.25 (32H, brs, 16 x CH<sub>2</sub>), 0.89 (3H, t, J = 6.4 Hz, Me-18'), 0.86 (3H, t, J = 6.8 Hz, Me-18''), 0.84 (3H, t, J = 6.4 Hz, Me-18'''); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  173.93 (C-1') 173.32 (C-1''), 173.18 (C-1'''), 139.27 (C-13'), 130.23 (C-12'), 130.02 (C-15''), 129.94 (C-10'), 129.64 (C-10''), 129.72 (C-12''), 128.09 (C-9'), 127.91 (C-9''), 115.67 (C-13'') 114.08 (C-16'), 72.13 (C-2), 68.40 (C-1), 65.06 (C-3), 34.30 (C-2'), 34.19 (C-2''), 34.12 (C-2'''), 33.64 (C-11'), 32.62 (C-14'), 31.94 (C-11'), 31.60 (C-11''), 31.54 (C-14''), 29.71 (CH<sub>2</sub>), 29.64 (10 x CH<sub>2</sub>), 29.55 (CH<sub>2</sub>), 29.52 (CH<sub>2</sub>), 29.38 (CH<sub>2</sub>), 29.34 (CH<sub>2</sub>), 29.29 (CH<sub>2</sub>), 29.17 (CH<sub>2</sub>), 29.14 (CH<sub>2</sub>), 29.11 (CH<sub>2</sub>), 29.02 (CH<sub>2</sub>), 28.97 (CH<sub>2</sub>), 28.79 (CH<sub>2</sub>), 27.23 (CH<sub>2</sub>), 27.21 (CH<sub>2</sub>), 26.01 (CH<sub>2</sub>), 25.64 (CH<sub>2</sub>), 24.89 (CH<sub>2</sub>), 22.70 (CH<sub>2</sub>), 22.47 (CH<sub>2</sub>), 22.39 (CH<sub>2</sub>), 18.23 (Me-18', Me-18'', Me-18'''); +ve FAB MS  $m/z$  (*rel. int.*): 874 [M]<sup>+</sup> (C<sub>57</sub>H<sub>94</sub>O<sub>6</sub>) (1.9), 267 (12.6), 263 (8.9), 261 (7.6).

### n-Tetracosanyl stearate (4)

Elution of the column with chloroform gave a colourless amorphous powder of **4**, recrystallized from acetone - methanol (1:1), 2.13 g (0.096 % yield), R<sub>f</sub>: 0.32 (chloroform - methanol, 19:1), m. p.: 69-70 °C; UV  $\lambda_{\max}$  (MeOH): 204 nm (log  $\epsilon$  5.1); IR  $\nu_{\max}$  (KBr): 2917, 2849, 1731, 1645, 1462, 1377, 1172, 1086, 720 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.08 (2H, t, J = 8.4 Hz, H-1'), 2.75 (2H, t, J = 4.8 Hz, H<sub>2</sub>-2), 2.41 (2H, m, CH<sub>2</sub>), 2.10 (2H, m, CH<sub>2</sub>), 1.69 (2H, m, CH<sub>2</sub>), 1.33 (68H, brs, 34 x CH<sub>2</sub>), 0.96 (3H, t, J = 6.0 Hz, Me-18), 0.93 (3H, t, J = 6.3 Hz,

Me-24');  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  172.15 (C-1), 62.85 (C-1'), 51.95 (C-2), 31.94 ( $\text{CH}_2$ ), 29.21 ( $29 \times \text{CH}_2$ ), 29.37 ( $\text{CH}_2$ ), 29.26 ( $\text{CH}_2$ ), 29.17 ( $\text{CH}_2$ ), 28.99 ( $\text{CH}_2$ ), 28.77 ( $\text{CH}_2$ ), 27.33 v 24.89 ( $\text{CH}_2$ ), 22.70 ( $\text{CH}_2$ ), 14.13 (Me-18), 14.12 (Me-24'); +ve FAB MS  $m/z$  (*rel. int.*): 620 [ $\text{M}$ ] $^+$  ( $\text{C}_{42}\text{H}_{84}\text{O}_2$ ) (2.3), 353 (11.6), 267 (17.5).

### 3,4-Dimethoxy-5-hydroxybenzaldehyde digalacturonotrilinoleate (5)

Elution of the column with chloroform - methanol (99:1) gave a pale yellow semisolid mass of **5**, purified by preparative TLC using chloroform - methanol (99:1), 1.21 g (0.055 % yield);  $R_f$ : 0.1 (chloroform - methanol, 99:1); m. p. : 65-70 °C; UV  $\lambda_{\text{max}}$  (MeOH): 203, 282 nm (log  $\epsilon$  3.8, 1.6); IR  $\nu_{\text{max}}$  (KBr): 3410, 3343, 3227, 2923, 2852, 1741, 1711, 1690, 1620, 1520, 1463, 1376, 1175, 1022, 967, 771, 720  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  9.65 (1H, s, H-7), 7.29 (1H, d, J = 3.0 Hz, H-2), 6.59 (1H, d, J = 3.0 Hz, H-6), 4.61 (1H, d, J = 4.8 Hz, H-1a), 4.19 (1H, dd, J = 4.8, 6.5 Hz, H-2a), 3.73 (1H, m, H-3a), 3.48 (1H, m, H-4a), 4.25 (1H, d, J = 7.2 Hz, H-5a), 4.57 (1H, d, J = 4.8 Hz, H-1b), 3.78 (1H, dd, J = 4.8, 8.4 Hz, H-2b), 3.75 (1H, m, H-3b), 3.54 (1H, m, H-4b), 4.23 (1H, d, J = 5.6 Hz, H-5b), 2.42 (2H, t, J = 7.2 Hz, H<sub>2</sub>-2'), 1.37 (10H, m, H<sub>2</sub>-3' to H<sub>2</sub>-7'), 2.11 (2H, m, H<sub>2</sub>-8'), 2.92 (2H, m, H<sub>2</sub>-11'), 5.45 (1H, m, H-9'), 5.43 (2H, m, H-10', H-12'), 5.41 (1H, m, H-13'), 1.71 (2H, m, H<sub>2</sub>-14'), 1.33 (6H, m, H<sub>2</sub>-15', H<sub>2</sub>-16', H<sub>2</sub>-17'), 0.96 (3H, t, J = 6.4 Hz, Me-18'), 2.39 (2H, t, J = 7.6 Hz, H<sub>2</sub>-2''), 1.34 (10H, m, H<sub>2</sub>-3'' to H<sub>2</sub>-7''), 2.13 (2H, m, H<sub>2</sub>-8''), 5.39 (2H, m, H-9'', H-10''), 2.82 (2H, m, H<sub>2</sub>-11''), 5.37 (2H, m, H-12'', H-13''), 1.74 (2H, m, H<sub>2</sub>-14''), 1.30 (6H, m, H<sub>2</sub>-15'', H<sub>2</sub>-16'', H<sub>2</sub>-17''), 0.93 (3H, t, J = 6.1 Hz, Me-18''), 2.33 (2H, t, J = 7.4 Hz, H<sub>2</sub>-2'''), 1.31 (10H, m, H<sub>2</sub>-3''' to H<sub>2</sub>-7'''), 2.10 (2H, m, H<sub>2</sub>-8'''), 5.33 (2H, m, H-9''', H-10'''), 2.78 (2H, m, H<sub>2</sub>-11'''), 5.31 (2H, m, H-12''', H-13'''), 1.71 (2H, m, H<sub>2</sub>-14'''), 1.27 (6H, m, H<sub>2</sub>-15''', H<sub>2</sub>-16''', H<sub>2</sub>-17'''), 0.89 (3H, t, J = 6.8 Hz, Me-18'''), 3.88 (3H, brs, OMe), 3.79 (3H, brs, OMe);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  138.25 (C-1), 132.17 (C-2), 160.82 (C-3), 152.36 (C-4), 139.16 (C-5), 130.85 (C-6), 205.16 (C-7), 109.96 (C-1a), 68.66 (C-2a), 62.14 (C-3a), 65.01 (C-4a), 70.12 (C-5a), 179.46 (C-6a), 109.89 (C-1b), 78.43 (C-2b), 67.26 (C-3b), 66.05 (C-4b), 72.10 (C-5b), 177.71 (C-6b), 174.02 (C-1'), 38.16 (C-2'), 32.61 (C-3'), 30.56 (C-4'), 29.81 (C-5'), 29.79 (C-6'), 29.71 (C-7'), 34.09 (C-8'), 130.49 (C-9'), 130.40 (C-10'), 51.9052.07 (C-11'), 128.46 (C-12'), 114.08 (C-13'), 34.09 (C-14'), 29.53 (C-15'), 28.05 (C-16'), 22.68 (C-17'), 14.17 (C-18'), 173.81 (C-1''), 34.30 (C-2''), 32.61 (C-3''), 29.66 (C-4''), 29.61 (C-5''), 29.34 (C-6''), 28.45 (C-7''), 33.93 (C-8''), 130.31 (C-9''), 130.23 (C-10''), 51.87 (C-11''), 128.56 (C-12''), 128.07 (C-13''), 33.63 (C-14''), 29.45 (C-15''), 28.12 (C-16''), 22.56 (C-17''), 14.13 (C-18''), 171.09 (C-1'''), 34.09 (C-2'''),

29.45(C-3'''), 29.41 (C-4'''), 29.35 (C-5'''), 29.21 (C-6'''), 28.65 (C-7'''), 31.94 (C-8'''), 130.33 (C-9'''), 130.26 (C-10'''), 51.89 (C-11'''), 126.11 (C-12'''), 127.93 (C-13'''), 31.53 (C-14'''), 29.99 (C-15'''), 29.01 (C-16'''), 22.67 (C-17'''), 14.07 (C-18'''), 57.53 (OMe), 52.07 (OMe); +ve FAB MS  $m/z$  (*rel. int.*): 1105 [M+H]<sup>+</sup> (C<sub>57</sub>H<sub>117</sub>O<sub>19</sub>) (2.1), 263 (10.6), 165 (12.8).

### 3,4-Dimethoxy-5-hydroxybenzaldehyde digalacturonolinolenate (6)

Elution of the column with chloroform - methanol (97:3) afforded a yellow semisolid mass of **6**, purified by preparative TLC using chloroform-methanol (97:3), 1.4 g (0.063 % yield); R<sub>f</sub>: 0.27 (chloroform - methanol, 24:1); m. p.: 38 - 40°C; UV λ<sub>max</sub> (MeOH): 203, 281 nm (log ε 5.1, 1.9); IR ν<sub>max</sub> (KBr): 3450, 3353, 3245, 2921, 2850, 1740, 1710, 1695, 1516, 1461, 1377, 1220, 1099, 720 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.65 (1H, s, H-7), 7.29 (1H, d, J = 3.0 Hz, H-2), 6.61 (1H, d, J = 3.0 Hz, H-6), 4.57 (1H, d, J = 6.0 Hz, H-1'), 4.35 (1H, dd, J = 5.8, 6.0 Hz, H-2'), 3.98 (1H, m, H-3'), 3.42 (1H, m, H-4'), 4.37 (1H, d, J = 6.2 Hz, H-5'), 4.50 (1H, d, J = 5.2 Hz, H-1''), 4.20 (1H, dd, J = 5.2, 3.6 Hz, H-2''), 3.77 (1H, m, H-3''), 3.37 (1H, m, H-4''), 4.02 (1H, d, J = 6.6 Hz, H-5''), 2.38 (2H, t, J = 7.2 Hz, H<sub>2</sub>-2'''), 1.36 -1.31 (8H, m, H<sub>2</sub>-3''' to H<sub>2</sub>-6'''), 1.68 (2H, m, H<sub>2</sub>-7'''), 2.15 (1H, m, H<sub>2</sub>-8'''), 5.44 - 5.41 (6H, m, H-9''', H-10''', H-12''', H-13''', H-15''', H-16'''), 2.60 (2H, m, H<sub>2</sub>-11'''), 2.45 (2H, m, H<sub>2</sub>-14'''), 2.10 (2H, m, H<sub>2</sub>-17'''), 0.94 (3H, t, J = 6.8 Hz, Me-18'''), 3.85 (3H, brs, OMe), 3.82 (3H, brs, OMe); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 138.56 (C-1), 137.83 (C-2), 160.03 (C-3), 151.71 (C-4), 140.82 (C-5), 114.07 (C-6), 203.82 (C-7), 109.93 (C-1'), 77.40 (C-2'), 71.80 (C-3'), 85.40 (C-4'), 63.39 (C-5'), 179.13 (C-6'), 107.45 (C-1''), 77.09 (C-2''), 70.24 (C-3''), 84.31 (C-4''), 62.32 (C-5''), 178.09 (C-6''), 172.44 (C-1'''), 31.52 (C-2'''), 29.69 (C-3'''), 29.61 (C-4'''), 29.17 (C-5'''), 24.68 (C-6'''), 22.69 (C-7'''), 34.06 (C-8'''), 130.21 (C-9'''), 130.01 (C-10'''), 57.40 (C-11'''), 122.93 (C-12'''), 129.75 (C-13'''), 56.67 (C-14'''), 128.04 (C-15'''), 127.81 (C-16'''), 30.29 (C-17'''), 14.10 (C-18'''), 55.67 (OMe), 52.65 (OMe); +ve FAB MS  $m/z$  (*rel. int.*): 795 [M+H]<sup>+</sup> (C<sub>39</sub>H<sub>55</sub>O<sub>17</sub>) (1.7).

### β-Sitosterol-β-D-galacturonolinoleate (7)

Elution of the column with chloroform - methanol (19:1) furnished a pale yellow semisolid mass of **7**, purified by preparative TLC using chloroform - methanol (19:1), 940 mg (0.042 % yield); R<sub>f</sub>: 0.35 (chloroform - methanol, 19:1); m. p. : 53-55 °C; UV λ<sub>max</sub> (MeOH): 203 nm (log ε 4.8); IR ν<sub>max</sub> (KBr): 3411, 3370, 3265, 2922, 2851, 1734, 1685, 1640, 1462, 1375, 1172, 1085, 768 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.39 (1H, m, H-6), 3.74 (1H, brm, w<sub>1/2</sub> = 18.2

Hz, H-3 $\alpha$ ), 1.02 (3H, brs, Me-19), 0.96 (3H, d, J = 6.8 Hz, Me-21), 0.85 (3H, d, J = 6.4 Hz, Me-26), 0.81 (3H, d, J = 7.2 Hz, Me-27), 0.77 (3H, t, J = 6.6 Hz, Me-29), 0.69 (3H, brs, Me-18), 4.71 (1H, d, J = 7.2 Hz, H-1'), 4.38 (1H, dd, J = 7.2, 6.0 Hz, H-2'), 4.21 (1H, m, H-3'), 3.45 (1H, m, H-4'), 4.67 (1H, m, H-5'), 2.41 (2H, t, J = 7.2 Hz, H<sub>2</sub>-2''), 5.48 (2H, m, H-9'', H-12''), 5.44 (1H, m, H-10''), 5.42 (1H, m, H-13''), 0.89 (3H, t, J = 6.1 Hz, Me-18''), 2.47 – 1.10 (51H, m, 22 x CH<sub>2</sub>, 7 x CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  37.28 (C-1), 31.64 (C-2), 71.12 (C-3), 40.81 (C-4), 140.36 (C-5), 121.03 (C-6), 31.93 (C-7), 31.79 (C-8), 51.95 (C-9), 36.71 (C-10), 21.08 (C-11), 39.77 (C-12), 42.32 (C-13), 56.76 (C-14), 24.89 (C-15), 28.25 (C-16), 56.09 (C-17), 11.98 (C-18), 19.09 (C-19), 36.15 (C-20), 18.78 (C-21), 33.95 (C-22), 26.09 (C-23), 45.83 (C-24), 28.10 (C-25), 19.82 (C-26), 19.14 (C-27), 23.07 (C-28), 11.06 (C-29), 101.69 (C-1'), 79.65 (C-2'), 73.86 (C-3'), 67.49 (C-4'), 76.75 (C-5'), 179.01 (C-6'), 172.25 (C-1''), 38.82 (C-2''), 29.70 (C-3''), 29.48 (C-4''), 29.37 (C-5''), 29.27 (C-6''), 29.12 (C-7''), 37.74 (C-8''), 129.94 (C-9''), 128.50 (C-10''), 34.30 (C-11''), 123.25 (C-12''), 114.62 (C-13''), 30.29 (C-14''), 27.22 (C-15''), 25.64 (C-16''), 22.70 (C-17''), 14.13 (C-18''); 853 [M+H]<sup>+</sup> (C<sub>53</sub>H<sub>89</sub>O<sub>8</sub>) (1.5), 413 (21.6), 398 (10.6), 396 (14.3), 279 (8.1), 271 (6.2), 263 (12.7), 256 (18.3), 198 (16.1).

### Oleiy digalacturonotriglucoside (8)



Elution of the column with chloroform - methanol (9:1) furnished a brown sticky semisolid mass of **8**, purified by preparative TLC using chloroform - methanol (9:1), 2.77 g (0.125 % yield); R<sub>f</sub>: 0.45 (chloroform - methanol, 9:1); m. p. : 53-55 °C; UV  $\lambda_{\max}$  (MeOH): 204, 276 nm (log  $\epsilon$  4.8, 1.6); IR  $\nu_{\max}$  (KBr): 3490, 3375, 3265, 2922, 2851, 1737, 1690, 1649, 1461, 1377, 1170, 1074, 720 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.03 (1H, m, H-9), 5.01 (1H, m, H-10), 2.49 (2H, t, J = 7.3 Hz, H<sub>2</sub>-2''), 2.24 (2H, m, H<sub>2</sub>-8), 1.97 (2H, m, H<sub>2</sub>-11), 1.48 ((2H, m, H<sub>2</sub>-3), 1.25 (6H, brs, 3 x CH<sub>2</sub>), 1.21 (10H, brs, 5 x CH<sub>2</sub>), 1.17 (2H, m, H<sub>2</sub>-16), 1.14 (2H, m, H<sub>2</sub>-17), 0.82 (3H, t, J = 7.6 Hz, Me-18), 4.95 (1H, d, J = 5.2 Hz, H-1a), 3.60 (1H, m, H-2a), 3.55 (1H, m, H-3a), 3.47 (2H, s, H<sub>2</sub>-5a), 4.92 (1H, d, J = 6.8 Hz, H-1b), 3.62 (1H, dd, H-2b), 3.50 (1H, m, H-3b), 3.45 (2H, s, H<sub>2</sub>-5b), 4.87 (1H, d, J = 7.2 Hz, H-1c), 3.54 (1H, m, H-2c), 3.51 (1H, m, H-3c), 3.41 (1H, m, H-4c), 3.96 (1H, m, H-5c), 3.35 (2H, d, J = 11.2 Hz, H<sub>2</sub>-6c), 4.84 (1H, d, J = 7.1 Hz, H-1d), 3.56 (1H, m, H-2d), 3.49 (1H, m, H-3d), 3.40 (1H, m, H-4d), 3.94 (1H, m, H-5d), 3.30 (2H, d, J = 8.4 Hz, H<sub>2</sub>-6d), 4.81 (1H, d, J = 7.2 Hz, H-1e), 3.52 (1H, m, H-2e), 3.46 (1H, m, H-3e), 3.38 (1H, m, H-4e), 3.92 (1H, m, H-5e), 3.16 (2H, d, J = 9.2 Hz, H<sub>2</sub>-6e); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  173.84 (C-1), 52.11 (C-2), 29.51 (C-3), 29.48 (C-4),



29.41 (C-5), 29.32 (C-6), 29.18 (C-7), 49.07 (C-8), 131.29 (C-9), 122.13 (C-10), 48.32 (C-11), 30.28 (C-12), 29.15 (C-13), 29.16 (C-14), 28.43 (C-15), 25.36 (C-16), 22.55 (C-17), 14.38 (C-18), 109.34 (C-1a), 82.34 (C-2a), 73.09 (C-3a), 88.70 (C-4a), 72.22 (C-5a), 176.05 (C-6a), 107.82 (C-1b), 81.23 (C-2b), 73.32 (C-3b), 83.04 (C-4b), 77.33 (C-5b), 176.67 (C-6b), 100.53 (C-1c), 69.34 (C-2c), 68.28 (C-3c), 64.94 (C-4c), 72.93 (C-5c), 62.04 (C-6c), 98.86 (C-1d), 68.66 (C-2d), 68.23 (C-3d), 65.87 (C-4d), 70.37 (C-5d), 61.89 (C-6d), 98.49 (C-1e), 69.74 (C-2e), 67.46 (C-3e), 63.53 (C-4e), 69.87 (C-5e), 60.23 (C-6e); +ve FAB MS  $m/z$  (rel. int.): 1121  $[M+H]^+$  ( $C_{48}H_{81}O_{29}$ ) (2.6), 441 (12.6), 325 (8.4), 265 (19.2), 163 (11.3).

### Galacturonotetra-arabinoside (9)

Elution of the column with chloroform - methanol (17:3) furnished a brown sticky mass of **9**, purified by preparative TLC using chloroform - methanol (1:3), 4.2 g (0.19 % yield);  $R_f$ : 0.77 (chloroform - methanol, 1:3); m. p. : 80-82 °C; UV  $\lambda_{max}$  (MeOH): 204, 276 nm (log  $\epsilon$  4.8, 1.6); IR  $\nu_{max}$  (KBr): 3460, 3357, 3245, 2927, 2845, 1692, 1601, 1391, 1076  $cm^{-1}$ ;  $^1H$  NMR ( $D_2O$ ):  $\delta$  4.91 (1H, d,  $J = 6.3$  Hz, H-1a), 3.87 (1H, m, H-2a), 3.55 (1H, m, H-3a), 3.17 (2H, s, H<sub>2</sub>-5a), 5.35 (1H, d,  $J = 7.2$  Hz, H-1b), 3.96 (1H, m, H-2b), 3.65 (1H, m, H-3b), 3.50 (1H, m, H-4b), 3.76 (2H, d,  $J = 6.1$  Hz, H<sub>2</sub>-5b), 5.16 (1H, d,  $J = 7.1$  Hz, H-1c), 3.94 (1H, m, H-2c), 3.67 (1H, m, H-3c), 3.47 (1H, m, H-4c), 3.67 (2H, d,  $J = 5.6$  Hz, H<sub>2</sub>-5c), 4.89 (1H, d,  $J = 7.0$  Hz, H-1d), 3.92 (1H, m, H-2d), 3.65 (1H, m, H-3d), 3.45 (1H, m, H-4d), 3.63 (2H, d,  $J = 5.8$  Hz, H<sub>2</sub>-5d), 4.85 (1H, d,  $J = 7.3$  Hz, H-1e), 3.85 (1H, m, H-2e), 3.81 (1H, m, H-3e), 3.42 (1H, m, H-4e), 3.60 (2H, d,  $J = 6.2$  Hz, H<sub>2</sub>-5e);  $^{13}C$  NMR ( $D_2O$ ):  $\delta$  110.02 (C-1a), 80.69 (C-2a), 69.35 (C-3a), 84.17 (C-4a), 61.16 (C-5a), 176.72 (C-6a), 103.80 (C-1b), 76.37 (C-2b), 69.49 (C-3b), 69.25 (C-4b), 62.47 (C-5b), 98.01 (C-1c), 76.02 (C-2c), 69.51 (C-3c), 68.79 (C-4c), 62.62 (C-5c), 96.09 (C-1d), 74.17 (C-2d), 71.28 (C-3d), 68.44 (C-4d), 66.47 (C-5d), 92.11 (C-1e), 72.45 (C-2e), 70.99 (C-3e), 68.25 (C-4e), 65.83 (C-5e), +ve FAB MS  $m/z$  (rel. int.): 723  $[M+H]^+$  ( $C_{26}H_{43}O_{23}$ ) (2.2), 266 (11.3), 133 (16.5).

## RESULTS AND DISCUSSION

Compounds **1-4** were the known phytoconstituents characterized as glyceryl-1,2,3-trilinoleate (trilinolein, **1**), glyceryl-1-oleic-2,3-distearate (glyceryl oleodistearin, **2**), glyceryl-1-linolenic-2-oleic-3-stearate (glyceryl linoleno-oleiostearin, **3**) and *n*-tetracosanyl stearate (**4**)<sup>19-21</sup>.

Compound **5**, named 3,4-dimethoxy-5-hydroxybenzaldehyde digalacturonotrilinoleate, gave positive tests for glycosides and had UV absorption maximum at 282 nm for aromaticity. Its IR spectrum showed absorption bands for hydroxyl groups (3410, 3343  $\text{cm}^{-1}$ ), ester functions (1741  $\text{cm}^{-1}$ ), aldehydic group (1711  $\text{cm}^{-1}$ ), carboxylic group (3227, 1690  $\text{cm}^{-1}$ ), unsaturation (1620  $\text{cm}^{-1}$ ), aromatic ring (1520, 1022  $\text{cm}^{-1}$ ) and long aliphatic chains (771, 720  $\text{cm}^{-1}$ ). On the basis of FAB mass and  $^{13}\text{C}$  NMR spectral data, the molecular ion peak of **5** was determined at  $m/z$  1161  $[\text{M}+\text{H}]^+$  consisting of a molecular formula of aromatic aldehydic digalacturonosidic trilinoleate,  $\text{C}_{57}\text{H}_{117}\text{O}_{19}$ . An ion peak arising at  $m/z$  165  $[(\text{MeO})_2\text{C}_6\text{H}_2\text{CHO}]^+$  indicated that dimethoxybenzaldehyde was linked with glycosidic molecule. The ion peak generated at  $m/z$  263  $[\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_7\text{CO}]^+$  indicated that linoleic acid was esterified with the glycosidic unit. The  $^1\text{H}$  NMR spectrum of **5** showed two one-proton doublets at  $\delta$  7.29 ( $J = 3.0$  Hz) and 6.59 ( $J = 3.0$  Hz) and a one-proton singlet at  $\delta$  9.65 assigned to meta-coupled aromatic H-2 and H-6 and aldehydic H-7 protons, respectively. Two one-proton doublets at  $\delta$  4.61 and 4.57 with coupling interactions of 4.8 Hz each were accounted to  $\beta$ -oriented anomeric H-1a and H-1b protons, respectively. The other sugar protons appeared from  $\delta$  4.25 to 3.48. The presence of the sugar H-2a proton in the deshielded region as double doublet at  $\delta$  4.19 ( $J = 4.8, 6.5$  Hz) indicated attachment of another sugar unit at C-2a. The vinylic protons appeared from  $\delta$  5.45 to 5.37. The methylene protons of the fatty acid chains resonated in the range of  $\delta$  2.42-1.33. Three triplets at  $\delta$  0.96 ( $J = 6.4$  Hz), 0.93 ( $J = 6.1$  Hz) and 0.89 ( $J = 6.8$  Hz) integrating three protons each were associated with the terminal C-18', C-18'' and C-18''' primary methyl proton, respectively. Two three-proton broad singlets at  $\delta$  3.88 and 3.79 were due to methoxy protons. The  $^{13}\text{C}$  NMR spectrum of **5** showed signals for aldehydic carbon at  $\delta$  205.16 (C-7), aromatic carbons from  $\delta$  160.82 to 130.85, sugar carboxylic carbons at  $\delta$  179.46 (C-6a) and 177.71 (C-6b), ester carbons at  $\delta$  174.02 (C-1'), 173.81 (C-1'') and 171.09 (C-1'''), vinylic carbons from  $\delta$  130.45 to 114.08, anomeric carbons at  $\delta$  109.96 (C-1a) and 109.89 (C-1b), other sugar carbons between  $\delta$  78.43-65.01, methylene carbons from  $\delta$  52.07 to 22.67, methoxy carbons at  $\delta$  57.53 and 52.07 and methyl carbons at  $\delta$  14.17 (C-18'), 14.13 (C-18'') and 14.07 (C-18'''). Acid hydrolysis of **5** yielded 3,4-dimethoxy-5-hydroxybenzaldehyde (m. p. 65-66 $^\circ$  C)<sup>22</sup>; D-galacturonic acid and linoleic acid ( $R_f$  0.86, benzene-methanol, 19:1). The absolute configuration of D-galacturonic acid was determined by measuring its specific rotation,  $[\alpha]_D^{25} +14.1^\circ$  (aq. sodium hydroxide solution) and comparison of its  $R_f$  0.25 (ethyl acetate-water-pyridine, 2:2:1) with the authentic sugar sample. On the basis of the foregoing account, the structure of **5** has been established as 3,4-dimethoxy-5-hydroxybenzaldehyde-5-O- $\alpha$ -D-

galacturonopyranosyl-(2a→1b)-O- $\alpha$ -D-galacturonopyranosyl-2b-octadec-9',12'-dienoate-3b-octadec-9'',12''-dienoate-4b-octadec-9''',12'''-dienoate. This is a new aromatic aldehydic glycoside.

Compound **6**, designated as 3,4-dimethoxy-5-hydroxybenzaldehyde digalacturonolinolenate, responded for glycosidic tests positively, had UV absorption maximum at 281 nm for aromaticity and IR absorption bands for hydroxyl groups (3450, 3353  $\text{cm}^{-1}$ ), ester function (1740  $\text{cm}^{-1}$ ), aldehydic group (1710  $\text{cm}^{-1}$ ), carboxylic group (3245, 1695  $\text{cm}^{-1}$ ), aromaticity (1516, 1099  $\text{cm}^{-1}$ ) and long aliphatic chain (720  $\text{cm}^{-1}$ ). On the basis of FAB mass and  $^{13}\text{C}$  NMR spectral data, the molecular ion peak of **6** was determined at  $m/z$  795  $[\text{M}+\text{H}]^+$  consistent to the molecular formula of an aromatic aldehydic digalacturonosidic ester,  $\text{C}_{39}\text{H}_{55}\text{O}_{17}$ . The  $^1\text{H}$  NMR spectrum of **6** exhibited two one-proton doublets at  $\delta$  7.29 ( $J = 3.0$  Hz) and 6.61 ( $J = 3.0$  Hz) and a one-proton singlet at  $\delta$  9.65 assigned correspondingly to meta-coupled aromatic H-2 and H-6 and aldehydic H-7 protons. Two one-proton doublets at  $\delta$  4.57 ( $J = 6.0$  Hz) and 4.50 ( $J = 5.2$  Hz) were attributed to anomeric H-1' and H-1'' proton, respectively. The presence of H-2' in the deshielded region as double doublets at  $\delta$  4.20 ( $J = 5.2, 3.6$  Hz) and 4.35 ( $J = 6.0, 5.8$  Hz) suggested that the second sugar unit was located at C-2' and ester group at C-2'', respectively. The other sugar proton signals appeared from  $\delta$  4.37 to 3.37. Two three-proton broad singlets at  $\delta$  3.85 and 3.82 were due to methoxy groups. The vinylic protons of the fatty acid chain appeared as multiplets from  $\delta$  5.43 to 5.40. A two-proton triplet at  $\delta$  2.38 ( $J = 7.2$  Hz) was attributed to methylene H<sub>2</sub>-2''' protons adjacent to the ester function. The other methylene protons appeared between  $\delta$  2.60-1.31. A three-proton triplet at  $\delta$  0.94 ( $J = 6.8$  Hz) was due to primary C-18''' methyl protons. The  $^{13}\text{C}$  NMR spectrum of **6** displayed signals for aldehydic carbon at  $\delta$  203.82 (C-7), aromatic carbons between  $\delta$  160.03-114.07, ester carbon at  $\delta$  172.44 (C-1'''), carboxylic carbons at  $\delta$  179.13 (C-6') and 178.09 (C-6''), anomeric carbons at  $\delta$  109.93 (C-1') and 107.45 (C-1''), other sugar carbons from  $\delta$  85.40 to 62.32, vinylic carbons from  $\delta$  130.21 to 122.93, methoxy carbons at  $\delta$  55.67 and 52.65 and methyl carbon at  $\delta$  14.10 (C-18'''). The presence of the sugar carbon signals in the deshielded region at  $\delta$  77.40 (C-2') and 85.40 (C-4') and at  $\delta$  77.04 (C-2'') and 84.31 (C-4'') suggested furanose ring system of both the sugar units, location of the sugar unit at C-2' and ester linkage at C-2''. Acid hydrolysis of **6** yielded 3,4-dimethoxy-5-hydroxybenzaldehyde (m. p. 65-66° C)<sup>22</sup>; D-galacturonic acid ( $R_f$  0.25, ethyl acetate-water-pyridine, 2:2:1) and linoleic acid ( $R_f$  0.86, benzene - methanol, 19:1). On the basis of spectral data analysis the structure of **6** has been elucidated as 3,4-dimethoxy-5-

hydroxybenzaldehyde-5- $\alpha$ -D-galacturonofuranosyl-(2 $\rightarrow$ 1)-2'- $\alpha$ -D-galacturonofuranosyl -2''-octadec-9''',12''',15'''-trienoate. This is a new aromatic aldehydic glycosidic ester.

Compound **7**, named  $\beta$ -sitosterol- $\beta$ -D-galacturonolinoleate, gave positive tests for glycosides and showed IR absorption bands for hydroxyl groups (3411, 3370  $\text{cm}^{-1}$ ), ester function (1734  $\text{cm}^{-1}$ ), carboxylic group (3265, 1685  $\text{cm}^{-1}$ ), unsaturation (1640  $\text{cm}^{-1}$ ) and aliphatic chain (768  $\text{cm}^{-1}$ ). On the basis of FAB mass and  $^{13}\text{C}$  NMR spectra, the molecular ion peak of **7** was determined at  $m/z$  853  $[\text{M}+\text{H}]^+$  corresponding to the molecular formula of a steroidal glycosidic ester,  $\text{C}_{53}\text{H}_{89}\text{O}_8$ . The ion peaks arising at  $m/z$  413  $[\text{C}_{29}\text{H}_{49}\text{O}]^+$ , 398  $[413 - \text{Me}]^+$ , 396  $[413 - \text{OH}]^+$ , 271  $[413 - \text{side chain}]^+$  and 256  $[271 - \text{Me}]^+$  indicated the presence of  $\beta$ -sitosterol as an aglycone unit. The ion peaks generating at  $m/z$  279  $[\text{CH}_3\text{-C}_9\text{H}_{14}\text{-(CH}_2)_7\text{COO}]^+$  and  $m/z$  263  $[\text{CH}_3\text{-C}_9\text{H}_{14}\text{-(CH}_2)_7\text{CO}]^+$  suggested that linoleic acid was esterified with the glycosidic unit. The  $^1\text{H}$  NMR spectrum of **7** exhibited vinylic proton signals as multiplets at  $\delta$  5.39 (H-6), 5.48 (H-9'', H-12''), 5.44 (H-10'') and 5.42 (H-13''), a one-proton broad signal at  $\delta$  3.74 with half-width of 18.2 Hz assigned to carbinol H-3 $\beta$  proton, anomeric proton as a one-proton doublet at  $\delta$  4.71 ( $J = 7.2$  Hz), other sugar protons as a one-proton doublet at  $\delta$  4.38 ( $J = 7.2, 6.0$  Hz) and as one-proton multiplets at  $\delta$  4.21, 3.45 and 4.67 attributed correspondingly to H-2', H-3', H-4' and H-5' protons, two three-proton broad singlets at  $\delta$  0.69 and 1.02 and three three-proton doublets at  $\delta$  0.96 ( $J = 6.8$  Hz), 0.85 ( $J = 6.4$  Hz) and 0.81 ( $J = 7.2$  Hz), two three-proton triplets at  $\delta$  0.77 ( $J = 6.6$  Hz) and 0.89 ( $J = 6.1$  Hz) ascribed to tertiary C-18 and C-19, secondary C-21, C-26 and C-27 and primary C-29 and C-18'' methyl protons, respectively, all attached to saturated carbons. The other methylene and methine protons appeared from  $\delta$  2.47 to 1.10. The  $^{13}\text{C}$  NMR spectrum showed signals for carboxylic carbon at  $\delta$  179.01 (C-6'), ester carbon at  $\delta$  172.25 (C-1''), vinylic carbons from  $\delta$  140.36 - 114.62, oxymethine carbon at  $\delta$  71.12 (C-3), anomeric carbon at  $\delta$  101.69 (C-1'), other sugar carbons from  $\delta$  79.65 to 67.49 and methyl carbons in the range of  $\delta$  19.01 - 11.06. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR values of the steroidal skeleton were compared with the known steroidal compounds<sup>23,24</sup>. The presence of H-2' proton signal in the deshielded region at  $\delta$  4.38 and C-2' carbon signal at  $\delta$  79.65 suggested that the fatty ester chain was attached at C-2' carbon of the sugar unit. Acid hydrolysis of **7** yielded  $\beta$ -sitosterol, m. p. 135 – 136 $^\circ$  C,  $R_f$  0.34 (chloroform – methanol, 8 : 0.6), D-galacturonic acid and linoleic acid. On the basis of above mentioned evidences, the structure of **7** has been established as stigmast-5-en-3 $\beta$ -ol-3-O- $\beta$ -D-galacturonopyranosyl-2'-octadec-9'',12''-dienoate. This is a new steroidal glycoside.

Compound **8**, named oleiyl digalacturonotriglucoside, gave positive tests for glycosides and showed IR absorption bands for hydroxyl groups ( $3490, 3375 \text{ cm}^{-1}$ ), carboxylic functions ( $3265, 1690 \text{ cm}^{-1}$ ), ester group ( $1737 \text{ cm}^{-1}$ ), unsaturation ( $1649 \text{ cm}^{-1}$ ) and long aliphatic chain ( $720 \text{ cm}^{-1}$ ). On the basis of FAB mass and  $^{13}\text{C}$  NMR spectra, the molecular ion peak of **8** was established at  $m/z$  1121  $[\text{M}+\text{H}]^+$  consistent to the molecular formula of a fatty acid pentaglycoside,  $\text{C}_{48}\text{H}_{81}\text{O}_{29}$ . The ion peaks arising at  $m/z$  441  $[\text{C}_{18}\text{H}_{33}\text{O}-\text{C}_6\text{H}_8\text{O}_6]^+$ , 325  $[\text{C}_{12}\text{H}_{21}\text{O}_{10}]^+$ , 265  $[\text{C}_{18}\text{H}_{33}\text{O}]^+$  and 163  $[\text{C}_6\text{H}_{11}\text{O}_5]^+$  suggested the linkage of hexosoic acid with oleic acid and the presence of hexose units at the terminal of the glycoside. The  $^1\text{H}$  NMR spectrum of **8** showed two one-proton multiplets at  $\delta$  5.03 and 5.01 assigned to vinylic H-9 and H-10 protons, respectively. Five one-proton doublets at  $\delta$  4.95 ( $J = 5.2 \text{ Hz}$ ), 4.92 ( $J = 6.8 \text{ Hz}$ ), 4.87 ( $J = 7.2 \text{ Hz}$ ), 4.84 ( $J = 7.1 \text{ Hz}$ ) and 4.81 ( $J = 7.2 \text{ Hz}$ ) were attributed correspondingly to  $\alpha$ -oriented anomeric H-1a and H-1b and  $\beta$ -oriented H-1c, H-1d and H-1e protons. The other sugar protons resonated from  $\delta$  3.96 to 3.16. The shifting of H-2a and H-2b in the deshielding region at  $\delta$  3.60 and 3.62 suggested location of the sugar units at C-2a and C-2b. The oxymethylene H<sub>2</sub>-6c and H<sub>2</sub>-6d signals appearing in the deshielded region as doublets at  $\delta$  3.35 ( $J = 11.2 \text{ Hz}$ ) and 3.30 ( $J = 8.4 \text{ Hz}$ ) indicated the attachment of hexose units at C-2c and C-6d carbons, respectively. A three-proton triplet at  $\delta$  0.82 ( $J = 7.6 \text{ Hz}$ ) was accounted to terminal C-18 primary methyl protons. The other methylene protons appeared from  $\delta$  2.49 to 1.14. The  $^{13}\text{C}$  NMR spectrum of **8** showed signals for ester carbon at  $\delta$  173.84 (C-1), vinylic carbons at  $\delta$  131.29 (C-9) and 122.13 (C-10), methylene carbons between  $\delta$  52.11-22.55, methyl carbon at  $\delta$  14.38 (C-18), anomeric carbons in the range of 109.34-98.49, carboxylic carbons at  $\delta$  176.05 (C-6a) and 176.67 (C-6b) and other sugar carbon from  $\delta$  88.70 to 60.23. The existence of C-1a and C-4a in the deshielded region at  $\delta$  109.34 and 88.70 and C-1b, and C-4b at  $\delta$  107.82, and 83.04, respectively, supported two furanosidic sugar units in the molecule. The presence of the carbon signals at  $\delta$  82.34 (C-2a), 81.23 (C-2b), 62.04 (C-6c) and 61.89 (C-6d) in the deshielded region suggested the linkages of sugar units at these carbons. Acid hydrolysis of **8** yielded oleic acid ( $R_f$  0.34, 15 % glacial acid), D-galacturonic acid ( $R_f$  0.30) and D-glucose ( $R_f$  0.36, ethyl acetate – acetic acid – water, 3:1:3 v/v). On the basis of above discussion, the structure of **8** has been elucidated as *n*-octadec-9-enoyl-O- $\alpha$ -D-galacturonofuranosyl-(2a $\rightarrow$ 1b)-O- $\alpha$ -D-galacturonofuranosyl-(2b $\rightarrow$ 1c)-O- $\beta$ -D-glucopyranosyl-(6c $\rightarrow$ 1d)-O- $\beta$ -D-glucopyranosyl-(6d $\rightarrow$ 1e)-O- $\beta$ -D-glucopyranoside. It is a new fatty acid pentaglycoside.

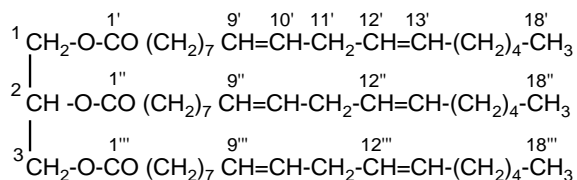
Compound **9**, named galacturonotetra-arabinoside, responded positively for glycoside tests and showed IR absorption bands for hydroxyl groups (3460, 3357, 3245  $\text{cm}^{-1}$ ) and carboxylic function (1692  $\text{cm}^{-1}$ ). On the basis FAB mass  $^{13}\text{C}$  NMR spectra, the molecular ion peak of **9** was determined at  $m/z$  723  $[\text{M}+\text{H}]^+$  consistent to the molecular formula of a pentaglycoside,  $\text{C}_{26}\text{H}_{43}\text{O}_{23}$ . The ion peaks arising at  $m/z$  133  $[\text{C}_5\text{H}_9\text{O}_4]^+$  and 266  $[\text{C}_{10}\text{H}_{17}\text{O}_8]^+$  indicated that  $\text{C}_5$ -monosaccharides were located at one of the terminal of the sugar chain. The  $^1\text{H}$  NMR spectrum of **9** showed five one-proton doublets at  $\delta$  4.91 ( $J = 6.3$  Hz), 5.35 ( $J = 7.2$  Hz), 5.16 ( $J = 7.1$  Hz), 4.89 ( $J = 7.0$  Hz) and 4.85 ( $J = 7.3$  Hz) assigned correspondingly to anomeric  $\alpha$ -oriented H-1a and  $\beta$ -oriented H-1b, H-1c, H-1d and H-1e protons. The other sugar protons appeared from  $\delta$  3.96 to 3.17. The appearance of H-2a, H-2b, H-2c and H-2d in the deshielded region as multiplets at  $\delta$  3.87, 3.96, 3.94 and 3.93 respectively, indicated (2 $\rightarrow$ 1) linkages of the sugar units. The presence of oxygenated methylene H<sub>2</sub>-5b, H<sub>2</sub>-5c, H<sub>2</sub>-5d and H<sub>2</sub>-5e as doublets at  $\delta$  3.76 ( $J = 6.1$  Hz), 3.67 ( $J = 5.6$  Hz), 3.63 ( $J = 5.8$  Hz) and 3.60 ( $J = 6.2$  Hz) supported arabinose/xylose type sugars in the sugar chain. The  $^{13}\text{C}$  NMR spectrum of **9** showed signals for carboxylic carbon at  $\delta$  176.72 (C-6a) and anomeric carbons at  $\delta$  110.02 (C-1a), 103.80 (C-1b), 98.01 (C-1c), 96.01 (C-1d) and 92.11 (C-1e). The presence of the  $\delta$  110.02 (C-1a), 80.69 (C-2a) and 84.17 (C-4a) in the deshielded region indicated furanoside ring system of the one of the sugar unit. The existence of carbon signals in the deshielded region at  $\delta$  80.69 (C-2a), 76.37 (C-2b), 76.02 (C-2c) and 74.17 (C-2d) supported the linkages of the other sugar units as (2 $\rightarrow$ 1). Acid hydrolysis of **9** yielded D-galacturonic acid ( $R_f$  0.30) and D-arabinose ( $R_f$  0.40, ethyl acetate – acetic acid – water, 3:1:3,  $v/v$ ). On the basis of aforementioned discussion the structure of **9** has been formulated as  $\alpha$ -D-galacturonofuranosyl-(2a $\rightarrow$ 1b)-O- $\beta$ -D-arabinopyranosyl-(2b $\rightarrow$ 1c)-O- $\beta$ -D-arabinopyranosyl-(2c $\rightarrow$ 1d)-O- $\beta$ -D-arabinopyranosyl-(2d $\rightarrow$ 1e)-O- $\beta$ -D-arabinopyranoside. This is a new pentaglycoside.

## CONCLUSION

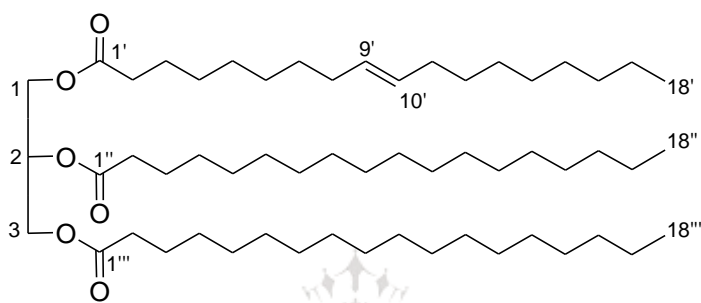
Phytochemical investigation of a methanolic extract of the fruits of *Capparis decidua* gave glycerides, *n*-tetracosanyl stearate, 3,4-dimethoxy-5-hydroxybenzaldehyde digalacturonic esters,  $\beta$ -sitosterol- $\beta$ -D-galacturonic ester, oleiylpentaglycoside and a pentaglycoside. This work has enhanced understanding about the phytoconstituents of the plant. These secondary metabolites can be used as analytical markers for quality control of this plant.

## ACKNOWLEDGMENT

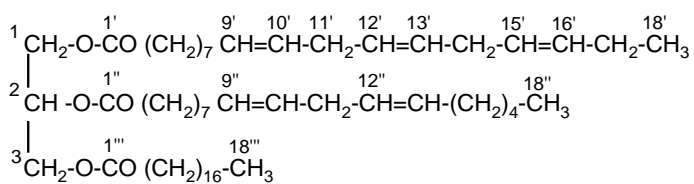
The authors are thankful to the Head, Central Instrumentation Facility, Jamia Hamdard, New Delhi, and Incharge, Arbro Analytical Division, New Delhi for recording spectral data of the compounds.



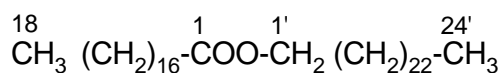
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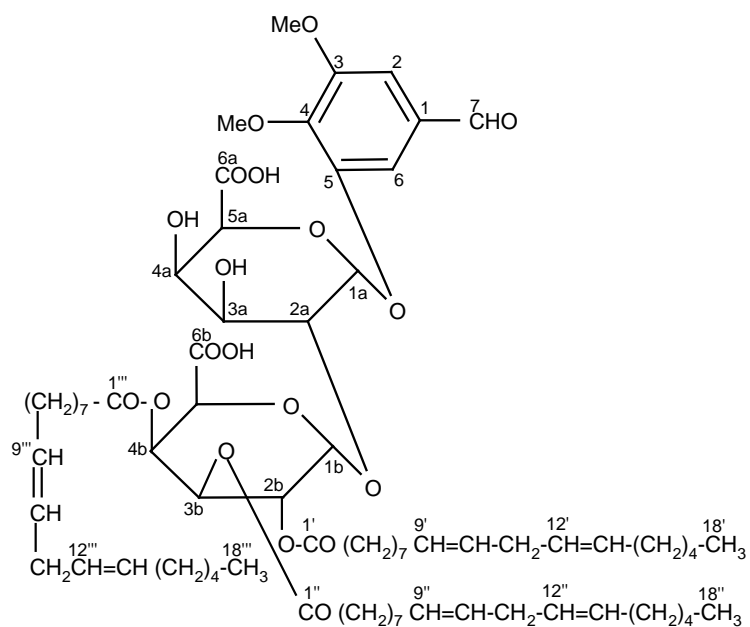
Glyceryl oleodistearin (2)



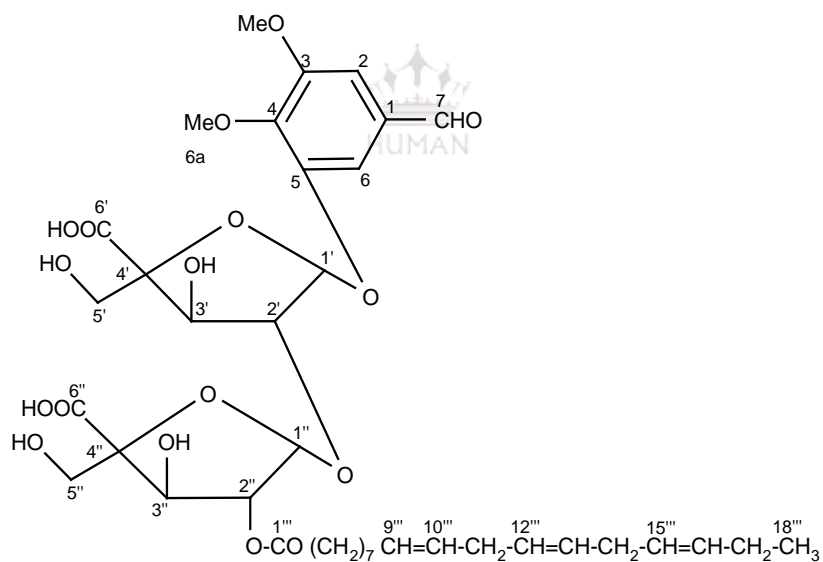
Glyceryl linoleno-oleo stearin (3)



*n*-Tetracosanyl stearate (4)

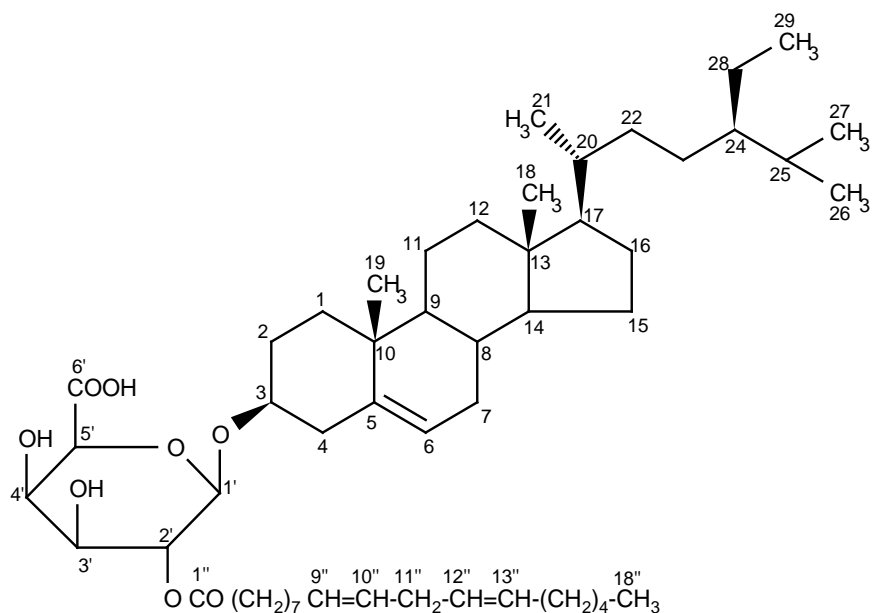


3,4-Dimethoxy-5-hydroxybenzaldehyde digalacturonotrilinoleate (5)

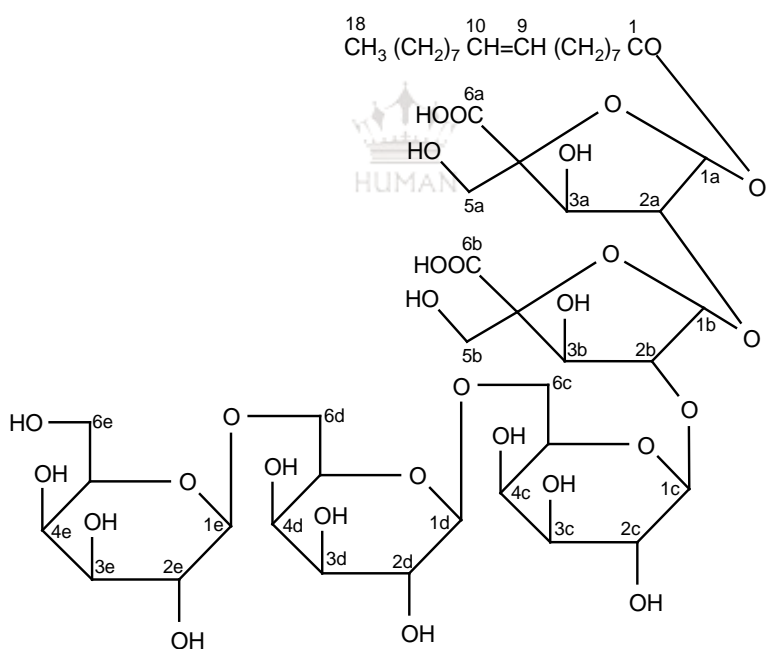


3,4-Dimethoxy-5-hydroxybenzaldehyde digalacturonolinolenate (6)

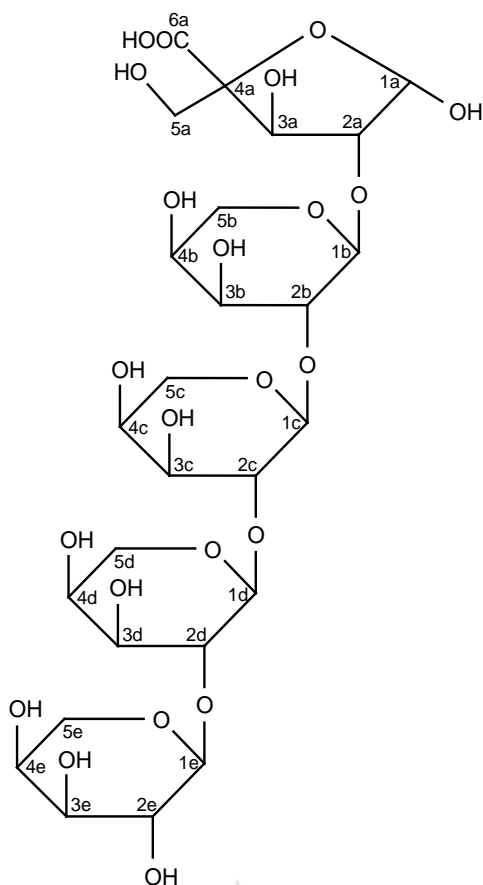




$\beta$ -Sitosterol- $\beta$ -D-galacturonolinoleate (7)



Oleiyl digalacturonotriglucoside (8)



Galacturonotetra-arabinoside (9)

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