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New fatty acid glycosides from the seeds of *Cicer arietinum*

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Abstract

The phytochemical investigation of the seeds of *Cicer arietinum* Linn (Papilionaceae) afforded eight new fatty acid glycosides identified as *n*-octadec-9-enoyl- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranoside (ciceroleioside) 1, *n*-docos-11-enoyl- β -D-glucopyranosyl-(2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranoside (ciceretolioside) 2, *n*-eicos-11,14-dienoyl- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranoside (ciceroleioside) 4, *n*-decanoyl- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranoside (ciceraprioside) 5, *n*-octadec-9,12-dienoyl acid- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranoside (cicerlinoleioside) 6, *n*-tetradecanoyl- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranoside (cicermyristioside) 8, *n*-octadecanoyl- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranoside (cicerstearioside) 9 and *n*-octadec-9,12-dienoyl- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranoside (cicerostereolein) 3, Stigmasta-5,22-dien-3 β -D-glucopyranoside (stigmasterol- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranoside (cicerostereolein) 3, Stigmasta-5-en-3-O- β -D-glucopyranoside (β -sitosterol glucoside) 11 and α -D-glucopyranosyl-(2 \rightarrow 1)- α -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranoside (triglycoside) 12. Their stereostructures have been elucidated on the basis of spectral data analyses and chemical reactions.

Keywords: *Cicer arietinum*; Papilionaceae; fatty acid glycosides; structure elucidation

Introduction

Cicer arietinum Linn. (Papilionaceae), commonly known as chickpea, is an erect or spreading much-branched annual herb which is a native to south western Asia and is now extensively cultivated as a winter crop throughout northern India^[1]. It is a multipurpose crop and is used in more diverse food preparation than any other pulse. The seeds are used in almost all forms starting from fresh greens to dried split grains and flour^[2]. The seeds are efficacious as an anthelmintic, appetizers, stimulant, tonic and aphrodisiac. They are also prescribed for the treatment of bronchitis, burning sensation, leprosy, skin diseases, blood disorders, throat problems, biliousness and diseases of liver and spleen^[3]. Earlier studies of *C. arietinum* have shown the presence of sterols, flavonoids and volatile components^[4-6]. The present paper describes the isolation and structural elucidation of seven new fatty acid glycosides along with known compounds from the seeds of this plant.

Experimental Section

General experimental procedure

Melting points were determined on a Perfit melting point apparatus and are uncorrected. FT IR: Jasco FT/IR-5000; UV: Lambda Bio 20 Spectrophotometer, MeOH; ¹H-NMR (400 MHz): Advance DRY 400, Bruker spectropin, CDCl₃; ¹³C NMR (75 MHz): Advance DRY 100, Bruker spectropin, CDCl₃ with TMS as an internal standard; MS: FAB ionization on Jeol-JMS-DX 303; CC: silica gel (Qualigens), 60-120 mesh; TLC: silica gel G (Qualigens). Spots were visualized by exposure to iodine vapors, UV radiation and by spraying reagents.

Plant material

The seeds of *C. arietinum* were purchased from the local market of Delhi. The samples were identified by Dr. M.P. Sharma, Taxonomist, Department of Botany, Faculty of Science, Jamia Hamdard, New Delhi.

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Extraction and isolation

The seeds (2 kg) were coarsely powdered and extracted in a Soxhlet apparatus with methanol for 72 h. The methanolic extract was concentrated on a steam bath and dried under reduced pressure to get a dark brown mass (210 g). The extract was dissolved in a minimum amount of methanol and adsorbed on silica gel (60-120 mesh) for preparation of slurry. The air-dried slurry was chromatographed over the silica-gel column packed in petroleum ether (60-80 °C). The column was eluted with petroleum ether, chloroform and methanol in their various combinations in order of increasing polarity to isolate the following compounds:

Ciceroleioside (1)

Elution of the column with petroleum ether yielded a light brown mass of **1**, recrystallized from methanol, 1.61 g (0.080% yield); R_f : 0.77 (petroleum ether); m.p.: 67-68 °C; UV λ_{max} (MeOH): 209 nm (log ϵ 5.3); IR ν_{max} (KBr): 3460, 3390, 3352, 3260, 3190, 2926, 2854, 1739, 1645, 1460, 1350, 1233, 1145, 1072 cm^{-1} ; 1H NMR (DMSO- d_6): Table 1; ^{13}C NMR (DMSO- d_6): Table 2; +ve FAB MS m/z (*rel. int.*): 870 $[M]^+$ ($C_{40}H_{70}O_{20}$) (1.3), 265 (16.3), 149 (22.6), 131 (13.5).

Hydrolysis of **1**: Compound **1** (35 mg) was dissolved in aqueous ethanol (5 ml), dil. HCl (3 ml) added and the reaction mixture refluxed for 1 h. The solution was dried under reduced pressure and the residue was dissolved in $CHCl_3$ (5 ml). The $CHCl_3$ layer was washed with H_2O (2 \times 5 ml), dried over anhydrous Na_2SO_4 and concentrated. It was chromatographed over silica gel TLC (petroleum ether: $CHCl_3$, 1:1) with a standard solution of oleic acid. The residue after separating the acid fraction was dissolved with water and chromatographed over paper with standard solution of β -L-arabinose and D-glucose. *n*-Butanol: H_2O : AcOH (4:1:5, top layer) was used as the developing solvent system. The paper was sprayed with aniline hydrogen phthalate. The sugars were identified as D-glucose and β -L-arabinose.

Cicercetoleioside (2)

Further elution of the column with petroleum ether yielded a light brown mass of **2**, recrystallized from methanol, 2.02 g (0.101% yield); R_f : 0.86 (petroleum ether); m.p.: 143-145 °C; UV λ_{max} (MeOH): 206 nm (log ϵ 5.3); IR ν_{max} (KBr): 3465, 3402, 3360, 3280, 2926, 2855, 1738, 1645, 1450, 1365, 1195, 1146, 1073 3390, 1073 cm^{-1} ; 1H NMR (DMSO- d_6): Table 1; ^{13}C NMR (DMSO- d_6): Table 2; +ve FAB MS m/z (*rel. int.*): 1058 $[M]^+$ ($C_{49}H_{86}O_{24}$) (1.3), 737 (3.1), 575 (11.6), 413 (2.8), 321 (10.2), 281 (10.9), 167 (41.4), 149 (39.5).

Hydrolysis of **2**: Compound **2** (35 mg) was dissolved in aqueous ethanol (5 ml), dil. HCl (3 ml) added and the reaction mixture refluxed for 1 h. After usual work up as for **1** cetoleic acid, D-glucose and β -L-arabinose were identified.

Glycerostearolein (3)

Elution of the column with petroleum ether-chloroform (1:1) mixture furnished colorless solid mass of **3**, recrystallized from methanol, 636 mg (0.032% yield); R_f : 0.72 (petroleum ether: chloroform; 9:1); m.p.: 54-55 °C; UV λ_{max} (MeOH): 211 nm (log ϵ 4.8); IR ν_{max} (KBr): 3434, 2919, 2850, 1737, 1647 cm^{-1} ; 1H NMR (DMSO- d_6): δ 5.31 (1H, m, H-9''), 5.19 (1H, m, H-10''), 3.50 (1H, m, H-2), 3.34 (4H, brs, H₂-1, H₂-3), 2.50 (4H, brs, H₂-2', H₂-2''), 2.03 (2H, m, H₂-8') 1.91 (2H, m, H₂-11'), 1.35 (2H, m, CH₂), 1.23 (20H, brs, 10 \times CH₂), 1.16 (30 H, brs, 15 \times CH₂), 0.85 (3H, t, J = 6.1 Hz, Me-18'), 0.76 (3H, t, J = 6.3 Hz, Me-18''); +ve FAB MS m/z (*rel. int.*): 622 $[M]^+$ ($C_{39}H_{74}O_5$) (4.9).

Cicereicosanoide (4)

Elution of the column with petroleum ether-chloroform (3:1) mixture afforded colorless crystals of **4**, recrystallized from acetone, 769 mg (0.038% yield); R_f : 0.56 (petroleum ether: chloroform; 3:7); m.p.: 153-154 °C; UV λ_{max} (MeOH): 210 nm (log ϵ 5.3); IR ν_{max} (KBr): 3510, 3407, 3365, 3255, 2921, 1738, 1617, 1417, 1258, 1142, 1071, 801 cm^{-1} ; 1H NMR (DMSO- d_6): Table 1; ^{13}C NMR (DMSO- d_6): Table 2; +ve FAB MS m/z (*rel. int.*): 896 $[M]^+$ ($C_{42}H_{72}O_{20}$) (5.3), 604 (14.7), 307 (10.5), 291 (9.6), 149 (18.9), 137 (41.3).

Hydrolysis of **4**: Compound **4** (35 mg) was dissolved in aqueous ethanol (5 ml), dil. HCl (3 ml) added and the reaction mixture refluxed for 1 h. After usual work up as for **1**, D-glucose and β -L-arabinose were identified.

Cicercaprioside (5)

Mother liquor of **4** on further crystallization gave colorless crystals of **5**, recrystallized from methanol, 1.37 g (0.068% yield); R_f : 0.82 (petroleum ether: chloroform; 3:7); m.p.: 110-111 °C; UV λ_{max} (MeOH): 210 nm (log ϵ 5.3); IR ν_{max} (KBr): 3490, 3388, 3260, 2922, 2850, 1741, 1457, 1419, 1236, 1144, 1071, 801 cm^{-1} ; 1H NMR (DMSO- d_6): Table 1; ^{13}C NMR (DMSO- d_6): Table 2; +ve FAB MS m/z (*rel. int.*): 760 $[M]^+$ ($C_{32}H_{56}O_{20}$) (4.3), 281 (15.6), 155 (68.9), 149 (65.3).

Hydrolysis of **5**: Compound **5** (35 mg) was dissolved in aqueous ethanol (5 ml), dil. HCl (3 ml) added and the reaction mixture refluxed for 1 h. After usual work up as for **1**, capric acid, D-glucose and β -L-arabinose were identified.

Cicerlinoleioside (6)

Elution of the column with chloroform yielded pale yellow crystals of **6**, recrystallized from acetone, 947 mg (0.047% yield); R_f : 0.54 (chloroform: acetone; 3:1); m.p.: 80 °C; UV λ_{max} (MeOH): 210 nm (log ϵ 5.6); IR ν_{max} (KBr): 3520, 3435, 3365, 2922, 1742, 1632, 1445, 1143, 1072 cm^{-1} ; 1H NMR (DMSO- d_6): Table 1; ^{13}C NMR (DMSO- d_6): Table 2; +ve FAB MS m/z (*rel. int.*): 868 $[M]^+$ ($C_{40}H_{68}O_{20}$) (10.3), 281 (9.9), 263 (11.2), 149 (53.6), 137 (79.8), 111 (12.3), 97 (16.3). Hydrolysis of **6**: Compound **6** (35 mg) was dissolved in aqueous ethanol (5 ml), dil. HCl (3 ml) added and the reaction mixture refluxed for 1 h. After usual work up as for **1**, linoleic acid, D-glucose and β -L-arabinose were identified.

Stigmasterol- β -D-glucopyranoside (7)

Further elution of the column with chloroform yielded colorless amorphous powder of **7**, recrystallized from methanol, 1.13 g (0.056% yield); R_f : 0.72 (toluene: ethyl formate: formic acid; 5:5:1.5); m.p.: 280-282 °C; UV λ_{max} (MeOH): 247 nm (log ϵ 5.7); IR ν_{max} (KBr): 3471, 2928, 2852, 1638, 1465, 1381, 1260, 1171 cm^{-1} ; 1H NMR (DMSO- d_6): δ 5.35 (1H, brs, H-5), 5.30 (1H, m, H-22), 5.06 (1H, m, H-23), 4.50 (1H, brs, H-1'), 4.28 (1H, m, H-5'), 4.16 (1H, m, H-2'), 3.92 (1H, m, H-3'), 3.55 (1H, m, $w_{1/2}$ = 18.5 Hz, H-3), 3.51 (1H, brs, H-4'), 3.32 (2H, brs, H₂-6'), 1.00 (3H, brs, Me-19), 0.91 (3H, d, J = 6.1 Hz), 0.84 (3H, d, J = 6.0 Hz, Me-27), 0.80 (3H, d, J = 6.1 Hz), 0.68 (3H, brs, Me-18); ^{13}C NMR (DMSO- d_6): 140.56 (C-5), 130.01 (C-22), 128.28 (C-23), 121.71 (C-6), 107.49 (C-1'), 85.68 (C-5'), 68.23 (C-3'), 65.08 (C-4); +ve FAB MS m/z (*rel. int.*): 574 $[M]^+$ ($C_{35}H_{58}O_6$) (6.8).

Ciceramyristioside (8)

Further elution of the column with chloroform yielded pale yellow crystals of **8**, recrystallized from methanol, 637 mg (0.318% yield); R_f : 0.62 (chloroform: methanol; 9:1); m.p.: 120-121 °C; UV λ_{max} (MeOH): 210 nm (log ϵ 5.1); IR ν_{max}

(KBr): 3510, 3418, 3370, 2924, 2850, 1742, 1652, 1457, 1343, 1238, 1146, 1072 cm^{-1} ; ^1H NMR (DMSO- d_6): Table 1; ^{13}C NMR (DMSO- d_6): Table 2; +ve FAB MS m/z (*rel. int.*): 948 $[\text{M}]^+$ ($\text{C}_{41}\text{H}_{72}\text{O}_{24}$) (2.1), 575 (19.6), 413 (18.2), 211 (2.3), 149 (21.9).

Hydrolysis of **8**: Compound **8** (35 mg) was dissolved in aqueous ethanol (5 ml), dil. HCl (3 ml) added and the reaction mixture refluxed for 1 h. After usual work up as for **1**, myristic acid, D-glucose and β -L-arabinose were identified.

Cicestearioside (9)

Elution of the column with chloroform-methanol (99:1) furnished pale yellow crystals of **9**, recrystallized from methanol, 982 mg (0.049% yield); R_f : 0.66 (chloroform: methanol; 7:3); m.p.: 173-174 $^\circ\text{C}$; UV λ_{max} (MeOH): 210 nm ($\log \epsilon$ 5.3); IR ν_{max} (KBr): 3410, 3389, 3260, 2923, 1741, 1415, 1346, 1234, 1141, 1071 cm^{-1} ; ^1H NMR (DMSO- d_6): Table 1; ^{13}C NMR (DMSO- d_6): Table 2; +ve FAB MS m/z (*rel. int.*): 872 $[\text{M}]^+$ ($\text{C}_{40}\text{H}_{72}\text{O}_{20}$) (5.2), 605 (11.3), 149 (18.6), 133 (6.2).

Hydrolysis of **9**: Compound **9** (35 mg) was dissolved in aqueous ethanol (5 ml), dil. HCl (3 ml) added and the reaction mixture refluxed for 1 h. After usual work up as for **1**, stearic acid, D-glucose and β -L-arabinose were identified.

Cicerotadecatrienoside (10)

Further elution of the column with chloroform-methanol (99:1) mixture gave pale yellow crystals of **10**, recrystallized from methanol, 462 mg (0.023% yield); R_f : 0.78 (chloroform: methanol; 7:3); m.p.: 86-87 $^\circ\text{C}$; UV λ_{max} (MeOH): 209 nm ($\log \epsilon$ 5.1); IR ν_{max} (KBr): 3420, 3396, 3265, 2923, 2855, 1740, 1652, 1457, 1419, 1236, 1144, 1070, 802 cm^{-1} ; ^1H NMR (DMSO- d_6): Table 1; ^{13}C NMR (DMSO- d_6): Table 2; +ve FAB MS m/z (*rel. int.*): 1000 $[\text{M}]^+$ ($\text{C}_{45}\text{H}_{76}\text{O}_{24}$) (2.6), 397 (33.6), 263 (13.5), 133 (19.2).

Hydrolysis of **10**: Compound **10** (35 mg) was dissolved in aqueous ethanol (5 ml), then dil. HCl (3 ml) added and the reaction mixture refluxed for 1 h. After usual work up as for **1**, oleic acid, D-glucose and β -L-arabinose were identified.

Table 1: ^1H NMR spectral data of the new isolated fatty acid glycosides.

Position	1	2	4	5	6	8	9	10
1	---	---	---	---	---	---	---	---
2	2.72 brs	2.51 d (7.1), 2.49 d (7.1)	2.51 d (7.0), 2.49 d (7.0)	2.48 brs	2.50 brs	2.50 brs	2.51 d (3.0), 2.50 d (3.0)	2.50 d (6.6), 2.48 d (6.6)
3	1.98 m	2.25 m	1.49 m	1.93 m	1.92 m	1.50 m	2.08 m	1.91 m
4	1.48 m	1.48 m	1.22 m	1.48 m	1.48 m	1.25 brs	1.90	1.23 brs
5	1.23 brs	1.22 m	1.22 m	1.19 brs	1.22 brs	1.25 brs	1.22 brs	1.23 brs
6	1.23 brs	1.22 m	1.22 m	1.19 brs	1.22 brs	1.25 brs	1.22 brs	1.23 brs
7	1.23 brs	1.22 m	1.22 m	1.19 brs	1.22 brs	1.22 brs	1.22 brs	1.19 brs
8	2.51 m	1.22 m	1.22 m	1.16 brs	2.25 m	1.22 brs	1.22 brs	2.26 m
9	5.35 m	1.99 m	1.22 m	1.16 brs	5.30 m	1.22 brs	1.22 brs	5.31 m
10	5.30 m	2.68 m	1.99 m	0.85 t (6.3)	5.18 m	1.22 brs	1.22 brs	5.18 m
11	2.26 m	5.30 m	5.30 m	---	2.72 m	1.22 brs	1.22 brs	2.72 m
12	1.23 brs	5.18 m	5.19 m	---	5.18 m	1.22 brs	1.22 brs	5.16 m
13	1.23 brs	2.50 m	2.25 m	---	5.16 m	1.22 brs	1.22 brs	5.18 m
14	1.23 brs	1.90 m	5.19 m	---	2.11 m	0.84 t (6.2)	1.22 brs	2.11 m
15	1.23 brs	1.22 m	5.17 m	---	1.22 brs	---	1.22 brs	1.48 m
16	1.23 brs	1.22 m	1.96	---	1.22 brs	---	1.22 brs	1.23 brs
17	1.23 brs	1.22 m	1.22 m	---	1.19 brs	---	1.22 brs	1.23 brs
18	0.85 t (6.2)	1.22 m	1.22 m	---	0.84 t (6.1)	---	0.84 t (6.1)	0.85 t (6.3)
19	---	1.13 m	1.17 m	---	---	---	---	---
20	---	1.11 m	0.84 t (6.5)	---	---	---	---	---
21	---	1.05 m	---	---	---	---	---	---
22	---	0.84 t (6.3)	---	---	---	---	---	---
1a	5.18 d (7.5)	5.06 d (7.1)	4.96 d (7.1)	5.15 d (7.1)	5.12 d (7.3)	5.18 d (7.1)	5.19 d (6.9)	5.07 d (7.1)
2a	4.57 dd (7.5, 6.5)	4.16 m	4.56 m	4.58 m	4.27 m	4.69 m	4.65 dd (3.6, 6.9)	4.44 m
3a	3.77 m	3.86 m	3.81 m	3.67 m	3.60 m	3.52 m	3.69 m	3.54 m
4a	3.45 m	3.81 m	3.73 m	3.79 m	3.69 m	3.69 m	3.81 m	3.37 m
5a	4.71 brm	4.75 m	4.65 m	4.67 m	4.70 m	4.72 m	4.76 m	4.70 m
6a	3.13 brs	3.03 d (10.5), 3.01 d (10.5)	3.08 d (9.0), 3.06 d (9.0)	3.10 d (9.5), 3.08 d (9.5)	3.08 d (9.1), 3.05 d (9.1)	3.09 d (9.5), 3.06 d (9.5)	3.06 d (9.2), 3.03 d (9.2)	3.12 d (9.3), 3.10 d (9.3)
1b	4.95 brs	4.90 d (6.9)	4.92 d (7.1)	4.90 d (7.0)	4.89 d (6.8)	4.88 brs	4.89 brs	4.88 brs
2b	4.57 dd (7.5, 6.5)	4.27 m	4.56 m	4.58 m	4.27 m	4.65 m	4.69 dd (3.6, 6.9)	4.42 m
3b	3.77 m	3.74 m	3.86 m	3.67 m	3.60 m	3.54 m	3.74 m	3.54 m
4b	3.45 m	3.69 m	3.69 m	3.79 m	3.74 m	3.81 m	3.81 m	3.37 m
5b	4.71 brm	4.72 m	4.65 m	4.67 m	4.68 m	4.72 m	4.72 m	4.53 m
6b	3.13 brs	3.09 d (9.3), 3.06 d (9.3)	3.03 d (9.5), 3.01 d (9.5)	3.10 d (9.5), 3.08 d (9.5)	3.12 d (10.5), 3.09 d (10.5)	3.09 d (9.5), 3.06 d (9.5)	3.09 d (9.5), 3.07 d (9.5)	3.12 d (9.3), 3.10 d (9.3)
1c	4.95 brs	4.86 brs	4.72 d (6.9)	4.87 d (7.1)	4.83 d (6.8)	4.88 brs	5.16 d (6.9)	4.88 brs
2c	4.55 dd (7.1)	4.65 m	4.47 m	4.55 m	4.43 m	4.63 m	4.29 m	4.42 m
3c	3.68 m	4.03 m	4.15 m	3.97 m	3.81 m	3.74 m	4.25 m	3.47 m

4c	3.45 m	4.71 m	4.56 m	4.25 m	4.65 m	4.29 m	4.58 m	3.69 m
5c	4.71 brm	3.42 d (12.0), 3.20 d (12.0)	3.20 d (11.1), 3.16 d (11.1)	3.13 d (10.2), 3.11 d (10.2)	3.12 d (10.5), 3.09 d (10.5)	3.20 d (10.5), 3.20 d (10.5)	3.16 d (11.1), 3.12 d (11.1)	3.17 m, 3.20 m
1d	4.95 brs	4.86 brs	4.69 d (6.8)	5.87 d (7.1)	4.87 d (7.0)	4.85 brs	4.89 brs	4.81 brs
2d	4.28 dd (7.1)	4.58 m	4.47 m	4.55 m	4.43 m	4.55 m	4.40 m	4.39 m
3d	3.68 m	4.27 m	4.27 m	3.81 m	3.86 m	3.74 m	3.86 m	3.47 m
4d	3.45 m	4.70 m	4.56 m	4.25 m	4.46 m	4.46 m	4.55 m	3.69 m
5d	4.71 brm	3.16 d (12.0), 3.12 d (12.0)	3.12 d (9.3), 3.09 d (9.3)	3.13 d (10.2), 3.18 d (10.2)	3.20 d (10.3), 3.17 d (10.3)	3.15 d (11.2), 3.12 d (11.2)	3.16 d (11.1), 3.12 d (11.1)	3.17 m, 3.20 m
1e	---	4.86 brs	---	---	---	4.85 brs	---	4.81 brs
2e	---	4.46 m	---	---	---	4.55 m	---	4.27 m
3e	---	4.25 m	---	---	---	3.69 m	---	3.47 m
4e	---	4.71 m	---	---	---	4.46 m	---	3.81 m
5e	---	3.16 d (12.0), 3.12 d (12.0)	---	---	---	3.15 d (10.5), 3.12 d (10.5)	---	3.17 m, 1.20 m

Coupling constants in Hertz (Hz) are mentioned in parenthesis.

Table 2. ^{13}C NMR spectral data of the new isolated fatty acid glycosides.

Position	1	2	4	5	6	8	9	10
1	172.13	173.01	171.01	172.31	171.93	173.05	171.19	172.17
2	53.23	53.21	54.13	32.70	45.16	33.53	33.53	31.29
3	29.07	33.45	31.02	29.10	28.72	29.05	31.48	29.59
4	29.07	31.33	29.07	29.10	78.72	29.05	29.05	29.02
5	29.07	29.07	29.07	28.97	29.04	29.05	29.05	29.02
6	29.07	29.07	29.07	28.85	29.04	29.05	29.05	29.02
7	28.72	29.07	28.87	26.70	29.04	29.05	29.05	28.71
8	33.58	29.07	28.87	25.59	33.47	28.72	29.05	30.98
9	129.72	29.07	26.64	22.36	129.10	28.72	29.05	129.57
10	127.77	31.33	33.47	17.95	127.73	28.45	29.05	127.72
11	31.33	129.69	129.70	---	54.13	26.63	29.05	33.37
12	28.71	127.77	129.10	---	129.07	25.53	28.72	129.11
13	28.71	133.63	36.99	---	127.39	22.09	28.72	127.35
14	26.67	28.74	127.79	---	32.16	18.01	28.41	29.59
15	25.25	28.71	127.41	---	26.61	---	26.73	24.99
16	24.46	28.69	31.34	---	24.40	---	24.38	24.41
17	22.12	28.66	25.06	---	21.98	---	22.16	22.08
18	13.96	25.26	24.31	---	18.30	---	14.03	14.59
19	---	24.46	22.09	---	---	---	---	---
20	---	22.12	13.68	---	---	---	---	---
21	---	22.14	---	---	---	---	---	---
22	---	13.97	---	---	---	---	---	---
1a	104.07	104.07	104.09	104.11	104.04	104.07	104.05	104.03
2a	71.63	72.41	72.88	72.93	71.85	72.38	72.86	72.83
3a	66.21	66.19	68.59	68.91	68.85	69.70	68.58	69.85
4a	68.60	68.88	66.21	68.64	68.56	68.88	68.85	66.16
5a	74.32	75.65	74.31	75.14	75.63	75.63	74.29	75.62
6a	60.53	60.02	60.54	60.58	60.03	60.03	60.05	60.09
1b	91.78	98.99	91.76	91.82	91.73	91.76	91.75	91.73
2b	72.79	72.88	71.60	71.66	72.85	72.87	71.60	72.34
3b	69.70	68.42	69.70	69.74	69.67	68.58	66.58	69.99
4b	69.73	69.33	68.89	66.25	66.17	66.19	69.68	68.56
5b	72.88	74.86	55.10	74.38	74.28	74.31	74.29	74.28
6b	60.01	60.53	60.03	60.05	60.49	60.52	60.50	60.68
1c	98.97	91.78	98.98	96.98	98.96	98.97	98.96	99.97
2c	77.56	77.57	77.58	77.16	77.55	77.55	77.53	77.58
3c	68.88	71.99	68.89	71.21	71.17	71.60	71.18	71.16
4c	83.52	83.52	83.52	83.55	82.54	83.50	82.40	83.48
5c	60.57	60.74	62.73	60.77	60.68	60.71	60.70	60.49
1d	96.77	96.88	96.88	96.84	96.85	98.95	96.84	99.95
2d	77.10	77.08	77.01	77.51	77.04	77.55	77.05	77.58
3d	71.19	71.61	71.20	70.06	69.99	71.18	70.02	71.57
4d	82.56	82.57	82.41	82.58	83.49	82.56	83.50	82.55
5d	62.18	61.24	60.73	62.23	62.14	60.71	62.17	60.68
1e	---	98.99	---	---	---	96.85	---	96.87
2e	---	76.77	---	---	---	77.04	---	77.06
3e	---	70.03	---	---	---	70.01	---	72.34
4e	---	82.55	---	---	---	82.40	---	82.38
5e	---	62.17	---	---	---	62.16	---	62.13

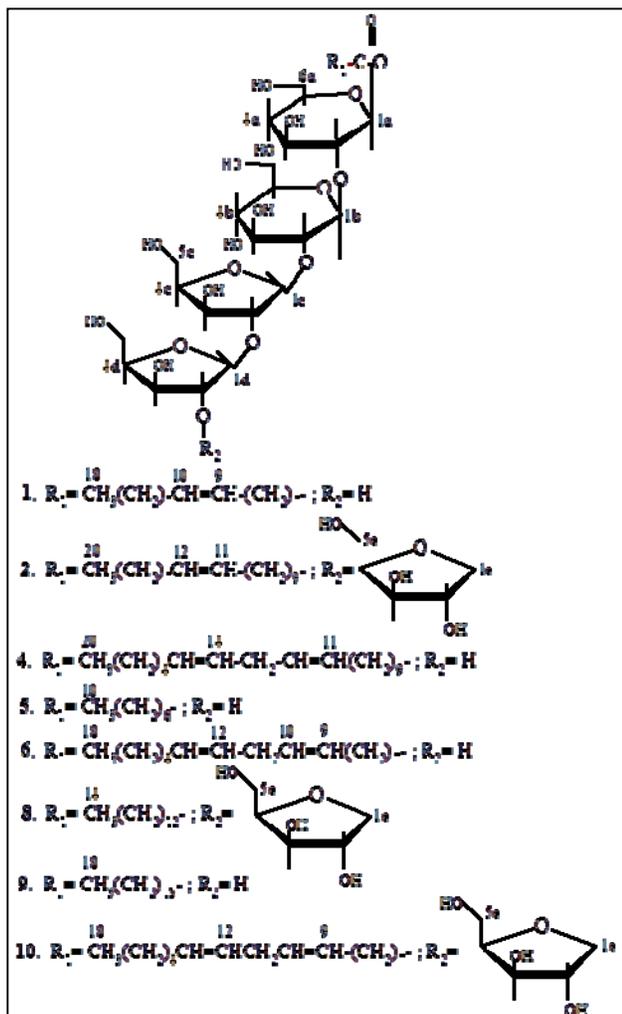


Fig 1: Structures of the new isolated fatty acid glycosides

β -sitosterol glucoside (11)

Elution of the column with chloroform-methanol (19:1) mixture gave colorless amorphous powder of 11, recrystallized from methanol, 920 mg (0.046% yield); R_f : 0.53 (C_6H_6 : CHCl_3 : MeOH ; 5:4:1); m.p.: 270-272 °C; UV λ_{max} (MeOH): 268 nm ($\log \epsilon$ 4.5); IR ν_{max} (KBr): 3450, 2955, 2363, 1610, 1460, 1375, 1255, 1155, 1100, 1080, 1020, 796 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$): δ 5.33 (1H, brs, H-6), 4.90 (1H, d, $J = 9.61$ Hz, H-1), 4.44 (1H, d, $J = 6.0$ Hz, H-5'), 4.23 (1H, m, H-4), 4.20 (1H, dd, $J = 7.63, 6.0$ Hz, H-2'), 3.63 (1H, m, H-3'), 3.34 (1H, brm, $w_{1/2} = 16.50$ Hz, H-3 α), 3.04 (2H, brs, H-2-6'), 0.95 (3H, brs, Me-19), 0.91 (3H, d, $J = 6.5$ Hz, Me-21), 0.89 (3H, d, $J = 7.0$ Hz, Me-29), 0.82 (3H, d, $J = 5.69$ Hz, Me-26), 0.80 (3H, d, $J = 6.39$ Hz, Me-27), 0.65 (3H, brs, Me-18); ^{13}C NMR ($\text{DMSO}-d_6$): δ 76.57 (C-3), 139.95 (C-5), 121.35 (C-6), 100.68 (C-1'), 73.22 (C-2'), 76.57 (C-3'), 70.55 (C-4'), 78.18 (C-5'), 62.06 (C-6'); +ve FAB MS m/z (*rel. int.*): 576 [$\text{M}]^+$ ($\text{C}_{35}\text{H}_{60}\text{O}_6$) (N.O.), 413 [$\text{M}-\text{sugar}]^+$ ($\text{C}_{29}\text{H}_{50}\text{O}$) (4.3).

Triglycoside (12)

Elution of the column with chloroform-methanol (4:1) mixture afforded colorless crystals of 12, recrystallized from ethanol, 540 mg (0.027% yield); R_f : 0.80 (chloroform: methanol; 7:3); m.p.: 158-160 °C; IR ν_{max} (KBr): 3563, 3425, 3398, 3260, 3180, 2936, 1434, 1350, 1239, 1128, 1063, 993, 912, 859 cm^{-1} ; +ve FAB MS m/z (*rel. int.*): 474 [$\text{M}]^+$ ($\text{C}_{17}\text{H}_{30}\text{O}_{15}$) (6.3).

Results and discussion

The compound 3, 7, 11 and 12 are the known phytoconstituents identified as glycerostearolein, stigmasterol- β -D-glucopyranoside, β -sitosterol glucopyranoside and triglycoside, respectively, on the basis of spectral data analysis, comparison of physical constants and chemical reactions.

Compound 1, named ciceroleioside, was obtained as a light brown mass from petroleum ether eluants. It responded positively to the tests of glycosides. Its IR spectrum displayed characteristic absorption band for hydroxyl group (3460, 3390, 3352, 3260, 3190 cm^{-1}), ester group (1739 cm^{-1}) and unsaturation (1645 cm^{-1}). On the basis of mass and ^{13}C NMR spectra its molecular weight was established as 870 consistent with a molecular formula of C_{18} fatty acid tetra glycosides, $\text{C}_{40}\text{H}_{70}\text{O}_{20}$. A prominent ion peaks generating at m/z 265 [$\text{CO}-\text{O}$ fission] $^+$ indicated that oleic acid was attached to terminal glycoside chain. The ion fragments arising at m/z 149 ($\text{C}_5\text{H}_9\text{O}_5$) and 131 ($\text{C}_5\text{H}_9\text{O}_4$) supported the location of the arabinose moiety at the terminal side of the glycoside chain. The ^1H NMR spectrum of 1 exhibited two one-proton multiplets at δ 5.35 and δ 5.30 ascribed to vinylic H-9 and H-10 protons. A one-proton doublet at δ 5.18 with coupling interactions of 7.5 Hz and a three-proton broad signal at δ 4.95 were assigned to anomeric protons H-1a and to H-1b, H-1c and H-1d. A four-proton broad multiplet at δ 4.71 was accounted to carbinol H-5a, H-5b, H-4c and H-4d. A two-proton double doublet at δ 4.57 ($J = 7.5, 6.5$ Hz) and two one-proton double doublets at δ 4.55 ($J = 7.1, 6.6$ Hz) and δ 4.28 ($J = 7.1, 6.6$ Hz) were ascribed to carbinol H-2a, H-2b and to H-2c and H-2d and their location in the deshielded region suggested glycosidic linkage between C-2 to C-1. The remaining sugar protons resonated between δ 3.77-3.13. A two proton broad signal at δ 2.72 was attributed to H₂-2 methylene protons adjacent to the ester group. Two multiplets at δ 2.51 and 2.26, both integrated for two-protons, were associated correspondingly with the H₂-8 and H₂-11 methylene protons adjacent to the vinylic C-9 and C-10 carbons. A three-proton triplet at δ 0.85 ($J = 6.2$ Hz) was ascribed to terminal C-18 primary methyl protons. The remaining methylene protons appeared at δ 1.98 (2H), δ 1.48 (2H) and δ 1.23 (20H). The ^{13}C NMR spectrum of 1 displayed important signals for ester carbon at δ 172.13 (C-1), vinylic carbons at δ 129.72 (C-9) and 127.77 (C-10), methyl carbon at δ 13.96 (Me-18) and methylene carbons between δ 53.23-22.12. The four anomeric carbons appeared between δ 104.07-91.78 indicating the location of four sugar moieties in the glycosidic chain. The carbon signals at δ 83.52 (C-4c) and δ 82.52 (C-4d) supported the presence of two L-arabinofuranoside residues in the glycoside. The carbinol signals in the deshielded region at δ 71.63 (C-2a), 72.79 (C-2b), 77.56 (C-2c) and 77.10 (C-2d) indicated (2 \rightarrow 1) linkages of the sugar residues. The hydroxymethylene carbons appeared at δ 60.53 (C-6a), δ 60.01 (C-6b), δ 60.57 (C-5c) and δ 62.18 (C-5d). The remaining carbinol carbons of the sugar residues resonated between δ 74.32-66.21. The ^{13}C NMR values of the sugar residues were compared with the ^{13}C NMR chemical shifts of sugar parts [7]. The $^1\text{H}-^1\text{H}$ cosy spectrum of 1 showed correlation of H-9 with H-10 and H₂-3, H-1a with H-2a; H-2a with H-3a and H-1b; H-2c with H-1c; H-3c and H-1d; and H-4d with H-3d and H₂-5d. The HMBC spectrum of 1 exhibited interactions of C-9 with H-10, H₂-8 and H₂-11; C-1 with H₂-2 and H-1a; C-2b with H-1b and H-1c; C-2c with H-1c and H-1d; and C-4d with H-3d and H₂-5d. Acid hydrolysis of 1 yielded oleic acid, β -D-glucose and β -L-

arabinose (TLC-comparable). On the basis of above mentioned discussion the structure of **1** has been established as *n*-octadec-9-enoyl- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1) - β -L-arabinofuranosyl-(2 \rightarrow 1) - β -L-arabinofuranoside.

Compound **2**, named cicercetoleoside, was obtained from the petroleum ether eluants as a light brown mass. It gave positive tests for glycosides. Its IR spectrum displayed characteristic absorption band for hydroxyl group at 3465, 3402, 3360, 3280 cm^{-1} , ester group at 1738 cm^{-1} and unsaturation at 1645 cm^{-1} . On the basis of mass and ^{13}C NMR spectra its molecular weight was established as 1058 consistent with a molecular formula of C_{22} fatty acid penta glycoside, $\text{C}_{49}\text{H}_{86}\text{O}_{24}$. A prominent ion peaks generating at m/z 321 [CO-O fission] $^{+}$ indicated that cetoleic acid was attached to terminal glycoside chain. The ion fragments arising at m/z 149 ($\text{C}_5\text{H}_9\text{O}_5$), 281 ($\text{C}_{10}\text{H}_{17}\text{O}_9$) and 413 ($\text{C}_{15}\text{H}_{25}\text{O}_{13}$) supported the location of the three arabinose moieties at the terminal side of the glycoside chain. The ion peaks at m/z 737 (Glu-Glu-Ara-Ara-Ara) and 575 (Glu-Ara-Ara-Ara) indicated the attachment of two glucose moieties in the glycone moiety. The ^1H NMR spectrum of **2** exhibited two one-proton multiplets at δ 5.30 and δ 5.18 ascribed to vinylic H-11 and H-12 protons. Two one-proton doublet at δ 5.06 and δ 4.90 with coupling interactions of 7.1 and 6.9 Hz, respectively, and a three-proton broad signal at δ 4.86 were assigned to anomeric protons H-1a, H-1b and to H-1c, H-1d and H-1e, respectively. Three one-proton multiplet δ 4.75, δ 4.72 and δ 4.70 and a two-proton multiplet at δ 4.71 were accounted to carbinol H-5a, H-5b, H-4c and to H-4d and H-4e. Five one-proton multiplet at δ 4.16, δ 4.27, δ 4.65, δ 4.58 and δ 4.46 were attributed to carbinol H-2a, H-2b, H-2c, H-2d and H-2e and their location in the deshielded region suggested the attachment of the glycosidic linkages between C-2 to C-1. The remaining sugar protons resonated between δ 3.86-3.01. Two one-proton doublets at δ 2.51 ($J = 7.1$ Hz) and δ 2.49 ($J = 7.1$ Hz) were associated with H₂-2 methylene proton adjacent to the ester group. Two multiplets at δ 2.68 and δ 2.50, both integrated for two-protons each, were accumulated correspondingly to the H₂-10 and H₂-13 methylene protons adjacent to the vinylic C-11 and C-12 carbons. A three-proton triplet at δ 0.84 ($J = 6.3$ Hz) was ascribed to terminal C-22 primary methyl protons. The ^{13}C NMR spectrum of **2** displayed important signals for ester carbon at δ 173.01, vinylic carbons at δ 129.69 (C-10) and 127.77 (C-11), methyl carbon at δ 13.97 (Me-22) and methylene carbons between δ 53.21-22.12. The five anomeric carbons appeared between δ 104.07-91.78 indicating the location of five sugar moieties in the glycosidic chain. The carbon signals at δ 83.52 (C-4c), δ 82.57 (C-4d) and δ 82.55 (C-4e) suggested the presence of three L-arabinofuranoside residues in the glycoside. The carbinol signals in the deshielded region at δ 72.41 (C-2a), δ 72.88 (C-2b), δ 77.57 (C-2c), δ 77.08 (C-2d) and δ 76.77 (C-2e) indicated (2 \rightarrow 1) linkages of the sugar residues. The hydroxymethylene carbons appeared at δ 60.02 (C-6a), δ 60.53 (C-6b), δ 60.74 (C-5c), δ 61.24 (C-5d) and δ 62.17 (C-5e). The remaining carbinol carbons of the sugar residues resonated between δ 75.65-66.19. The ^{13}C NMR values of the sugar residues were compared with the ^{13}C NMR chemical shifts of sugar parts [7]. The ^1H - ^1H cosy spectrum of **2** showed correlations of H-11 with H₂-10, H-12 and H₂-13; H-2a with H-1a and H-1b; H-2b with H-1b and H-1c; H-2c with H-1c and H-1d; H-2d with H-3d and H-1e; and H-4e with H-3e and H₂-5e. The HMBC spectrum of **2** exhibited interactions of C-11 with H-12 and H₂-10; C-1 with H₂-2 and H-1a; C-2a with H-1b; C-2b with

H-2b and H-1c; C-2c with H-1c and H-1d; C-2d with H-1d and H-1e; and C-4e with H-3e and H₂-5e. Acid hydrolysis of **2** yielded cetoleic acid, β -D-glucose and β -L-arabinose (TLC comparable). On the basis of the foregoing discussion the structure of **2** has been elucidated as *n*-docos-11-enoyl- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl -(2 \rightarrow 1) - β -L-arabinofuranoside.

Compound **4**, designated as cicereicosanoside, was obtained from petroleum ether-chloroform (3:1) eluants as a colorless crystalline mass. It gave positive tests for glycosides. Its IR spectrum displayed characteristic absorption band for hydroxyl groups at 3510, 3407, 3365, 3255 cm^{-1} , ester group at 1738 cm^{-1} and unsaturation at 1617 cm^{-1} . Its molecular weight was established as 896 consistent with a molecular formula of a C_{20} fatty acid glycoside, $\text{C}_{42}\text{H}_{72}\text{O}_{20}$. The prominent ion peaks generating at m/z 291 [CO-O fission] $^{+}$ and 307 [$\text{C}_{19}\text{H}_{71}\text{COO}$] $^{+}$ indicated that C_{20} acid was attached to the terminal glycoside chain. The ion fragment arising at m/z 137 ($\text{C}_5\text{H}_9\text{O}_4$) supported the location of the vinylic linkages at C₁₁ and C₁₄ positions. The ion peak at m/z 604 was due to the glycosidic linkage containing two glucose and two arabinose moieties. The ion peak at m/z 149 arising to arabinose moiety supported its location at the terminal side of the glycoside linkage. The ^1H NMR spectrum of **4** exhibited two one-proton multiplets at δ 5.30 and δ 5.17 were ascribed to vinylic H-11 and H-15 protons. A two-proton multiplet at δ 5.19 was assigned to vinylic H-12 and H-14. Four one-proton doublet at δ 4.69 ($J = 7.1$), δ 4.92 ($J = 7.1$), δ 4.72 ($J = 6.9$) and δ 4.69 ($J = 6.8$) were attributed to anomeric protons H-1a, H-1b, H-1c and H-1d, respectively. Two multiplets at δ 4.65 and δ 4.56, both integrated for two protons each, were accounted to carbinol protons H-5a, H-5b and to H-4c and H-4d. Two multiplets at δ 4.56 and δ 4.47, integrated for two protons each, were ascribed to carbinol protons H-2a and H-2b, and to H-2c and H-2d and their location in the deshielded region suggested glycosidic linkage between C-2 to C-1. The remaining sugar protons resonated between δ 4.15-3.01. Two one-proton doublets at δ 2.51 ($J = 7.0$ Hz) and 2.49 ($J = 7.0$ Hz) were attributed to H₂-2 methylene proton adjacent to the ester group. Three multiplets at δ 1.99, δ 2.25 and δ 1.96, each integrated for two-protons, were associated correspondingly with the H₂-10 and H₂-13 and to H₂-16 methylene protons adjacent to the vinylic C-11 and C-12 and C-15 carbons. A three-proton triplet at δ 0.84 ($J = 6.5$ Hz) was ascribed to terminal C-20 primary methyl protons. The ^{13}C NMR spectrum of **4** displayed important signals for ester carbon at δ 171.01, vinylic carbons at δ 129.70 (C-11), 129.10 (C-12), 127.79 (C-14) and 127.41 (C-15), methyl carbon at δ 13.68 (Me-20) and methylene carbons between δ 54.13-22.09. The four anomeric carbons appeared between δ 104.09-91.76 indicating the location of four sugar moieties in the glycosidic chain. The carbon signals at δ 83.52 (C-4c) and δ 82.41 (C-4d) suggested the presence of two L-arabinofuranoside residues in the glycoside. The carbinol signals in the deshielded region at δ 72.88 (C-2a), δ 71.60 (C-2b), δ 71.20 (C-2c) and δ 77.01 (C-2d) indicated (2 \rightarrow 1) linkages of the sugar residues. The hydroxymethylene carbons appeared at δ 60.54 (C-6a), δ 60.03 (C-6b), δ 62.73 (C-5c) and δ 60.73 (C-5d). The remaining carbinol carbons of the sugar residues resonated between δ 77.58-66.21. The ^{13}C NMR values of the sugar residues were compared with the ^{13}C NMR chemical shifts of sugar parts [7]. The ^1H - ^1H cosy spectrum of **4** showed correlations of H-11 with H₂-10 and H-12; H-15 with H₂-16 and H-14; H-2a with H-1a, H-3a and H-1b; H-2b with H-1b

and H-1c; H-2c with H-1c and H-1d; and H-4d with H-3d and H₂-5d. The HMBC spectrum of **4** exhibited interactions of C-11 with H₂-10 and H-12; C-15 with H-14; C-1 with H-1a; C-2b with H-1b and H-1c; C-2c with H-1c and H-1d; and C-4d with H-3d and H₂-5d. Acid hydrolysis of **4** yielded eicosanoic acid, β-D-glucose and β-L-arabinose (TLC comparable). On the basis of spectral data analysis and chemical reactions, the structure of **4** has been established as *n*-eicos-11, 14-dienoyl-β-D-glucopyranosyl (2→1)-β-D-glucopyranosyl-(2→1)-β-L-arabinofuranosyl - (2→1)-β-L-arabinofuranoside.

Compound **5**, named ciceraprioside, was obtained from mother liquor of **4** as a colorless crystalline mass. It gave positive tests for glycosides. Its IR spectrum displayed characteristic absorption band for hydroxyl group at 3490, 3388, 3260 cm⁻¹ and ester group at 1741 cm⁻¹. On the basis of mass and ¹³C NMR spectra its molecular weight was established as 760 consistent with a molecular formula of C₁₀ fatty acid tetraglycoside.

A prominent ion peaks generating at m/z 155 [CO-O fission]⁺ indicated that capric acid was attached to terminal glycoside chain. The ion fragments arising at m/z 281 (C₁₀H₁₇O₉) and 149 (C₅H₉O₅) supported the location of the two arabinose moieties at the terminal side of the glycoside chain. The ¹H NMR spectrum of **5** exhibited four one-proton doublets at δ 5.15 (*J* = 7.1 Hz), δ 4.90 (*J* = 7.0 Hz), δ 4.87 (*J* = 7.1 Hz) and δ 5.87 (*J* = 7.1 Hz) were assigned to anomeric protons H-1a, H-1b, H-1c and H-1d, respectively. Two multiplets at δ 4.67 and δ 4.25, both integrated for two protons each, were accounted to carbinol H-5a and H-5b and to H-4c and H-4d, respectively. Two two-proton multiplets at δ 4.58 and δ 4.55 were ascribed to carbinol H-2a, H-2b and to H-2c and H-2d oxygenated methine protons and their location in the deshielded region suggested glycosidic linkage between C-2 to C-1. The remaining sugar protons resonated between δ 3.97-3.08. A two-proton broad signal at δ 2.48 was associated with H₂-2 methylene protons adjacent to the ester function. The methylene protons appeared at δ 1.93 (2H), 1.48 (2H), 1.19 (6H) and 1.16 (4H). A three-proton triplet at δ 0.85 (*J* = 6.3 Hz) was ascribed to terminal C-10 primary methyl protons. The ¹³C NMR spectrum of **5** displayed important signals for ester carbon at δ 172.31, methyl carbon at δ 17.95 (Me-10) and methylene carbons between δ 29.10-22.36. The four anomeric carbons appeared between δ 104.11-91.82 indicating the location of four sugar moieties in the glycosidic chain. The carbon signals at δ 83.52 (C-4c) and δ 82.41 (C-4d) suggested the presence of two L-arabinofuranoside residues in the glycoside. The carbinol signals in the deshielded region at δ 72.93 (C-2a), δ 71.66 (C-2b), δ 77.16 (C-2c) and δ 77.51 (C-2d) indicated (2→1) linkages of the sugar residues. The hydroxymethylene carbons appeared at δ 60.58 (C-6a), δ 60.05 (C-6b), δ 60.77 (C-5c) and δ 62.23 (C-5d). The remaining carbinol carbons of the sugar residues resonated between δ 75.14-66.25. The ¹³C NMR values of the sugar residues were compared with the ¹³C NMR chemical shifts of sugar parts [7]. The HMBC spectrum of **5** exhibited correlations of C-1 with H₂-2 and H-1a; C-2b with H-1b and H-1c; C-2c with H-1c and H-1d; and C-4d with H-3d and H₂-5d. Acid hydrolysis of **5** yielded capric acid, β-D-glucose and β-L-arabinose (TLC comparable). On the basis of above mentioned discussion the structure of **5** has been characterized as *n*-decanoyl β-D-glucopyranosyl (2→1)-β-D-glucopyranosyl-(2→1)-β-L-arabinofuranosyl - (2→1)-β-L-arabinofuranoside.

Compound **6**, named cicerlinoleoside, was obtained from chloroform as pale yellow crystals. It gave positive tests for

glycosides and decolourized bromine water suggesting unsaturated nature of the molecule. Its IR spectrum displayed characteristic absorption bands for hydroxyl groups at 3520, 3435, 3365 cm⁻¹, ester group at 1742 cm⁻¹ and unsaturation at 1632 cm⁻¹. On the basis of mass and ¹³C NMR spectra its molecular weight was established as 868 consistent with a molecular formula of C₁₈ fatty acid tetra glycoside, C₄₀H₆₈O₂₀. A prominent ion peak generating at m/z 263 [CO-O fission]⁺ indicated that linoleic acid was attached to terminal glycoside chain. The ion peaks arising at m/z 137 [C₉-C₁₀ fission]⁺, 111 [C₁₀-C₁₁ fission]⁺ and 97 [C₁₁-C₁₂ fission]⁺ indicated the existence of the vinylic linkage at C-9 and C-12 of the fatty acid. The ion fragments forming at m/z 149 (C₅H₉O₅) and 281 (C₁₀H₁₇O₉) supported the location of the arabinose moiety at the terminal side of the glycoside chain. The ¹H NMR spectrum of **6** exhibited two one-proton multiplets at δ 5.30 and δ 5.16 were ascribed to vinylic H-9 and H-13 protons. A two-proton multiplet at δ 5.18 was attributed to vinylic H-10 and H-12. Four one-proton doublets at δ 5.12 (*J* = 7.3), δ 4.89 (*J* = 6.8), δ 4.83 (*J* = 6.8) and δ 4.87 (*J* = 7.0) were assigned to anomeric protons H-1a, H-1b, H-1c and H-1d, respectively. Four one-proton multiplets at δ 4.70, δ 4.68, δ 4.65 and δ 4.46 were accounted correspondingly to carbinol H-5a, H-5b, H-4c and H-4d. Two multiplets at δ 4.27 and δ 4.43, both integrated for two proton each, were ascribed to carbinol H-2a, H-2b and to H-2c and H-2d and their location in the deshielded region suggested glycosidic linkage between C-2 to C-1. The remaining sugar protons resonated between δ 3.86-3.05. A one-proton broad signal at δ 2.50 was attributed to H₂-2 methylene protons adjacent to the ester group. Three multiplets at δ 2.25, δ 2.72 and δ 2.11, integrated for two-protons each, were associated correspondingly with the H₂-8 and H₂-11, H₂-11 and H₂-14 methylene protons adjacent to the vinylic C-9, C-10 and C-13 vinylic carbons. A three-proton triplet at δ 0.84 (*J* = 6.1 Hz) was ascribed to terminal C-18 primary methyl protons. The remaining methylene protons appeared at 1.92 (2H), 1.48 (2H), 1.22 (10H) and 1.19 (2H). The ¹³C NMR spectrum of **6** displayed important signals for ester carbon at δ 171.93, vinylic carbons at δ 129.10 (C-9), 127.73 (C-10), 129.07 (C-12) and 127.39 (C-13), methyl carbon at δ 18.30 (Me-18) and methylene carbons between δ 45.16-21.98. The four anomeric carbons appeared between δ 104.09-91.73 indicating the location of four sugar moieties in the glycosidic chain. The carbon signals at δ 82.54 (C-4c) and δ 83.49 (C-4d) suggested the presence of two L-arabinofuranoside residues in the glycoside. The carbinol signals in the deshielded regions at δ 71.85 (C-2a), δ 72.85 (C-2b), δ 77.55 (C-2c) and δ 77.04 (C-2d) indicated (2→1) linkages of the sugar residues. The hydroxymethylene carbons appeared at δ 60.03 (C-6a), δ 60.49 (C-6b), δ 60.68 (C-5c) and δ 62.14 (C-5d). The remaining carbinol carbons of the sugar residues resonated between δ 77.63-68.56. The ¹³C NMR values of the sugar residues were compared with the ¹³C NMR chemical shifts of sugar parts [7]. The HMBC spectrum of **6** showed correlations of C-9 with H₂-8 and H-10; C-13 with H₂-14 and H-12; C-1 with H-1a; C-2a with H-3c, H-1b and H-1c; C-2c with H-1c and H-1d; and C-4d with H-3d and H₂-4e. Acid hydrolysis of **6** yielded linoleic acid, β-D-glucose and β-L-arabinose (TLC comparable). On the basis of foregoing discussion the structure of **6** has been formulated as *n*-octadec-9, 12-dienoyl-β-D-glucopyranosyl (2→1)-β-D-glucopyranosyl-(2→1)-β-L-arabinofuranosyl - (2→1)-β-L-arabinofuranoside.

Compound **8**, designated as cicermyristioside, was obtained from chloroform eluants as a pale yellow crystalline mass. It

gave positive tests for glycosides. Its IR spectrum displayed characteristic absorption band for hydroxyl groups at 3510, 3418, 3370 cm^{-1} , ester group at 1742 cm^{-1} . On the basis of mass and ^{13}C NMR spectra its molecular weight was established as 948 consistent with a molecular formula of C_{14} fatty acid penta glycosides, $\text{C}_{41}\text{H}_{72}\text{O}_{24}$. A prominent ion peaks generating at m/z 211 [CO-O fission] $^{+}$ indicated that myristic acid was attached to terminal glycoside chain. The ion fragments arising at m/z 413 ($\text{C}_{15}\text{H}_{25}\text{O}_{13}$) and 149 ($\text{C}_3\text{H}_9\text{O}_4$) supported the location of three arabinose moiety at the terminal side of the glycoside chain. The ion peak at m/z 575 was generated due to removal of $\text{C}_{21}\text{H}_{35}\text{O}_{18}$ (Ara-Ara-Ara-Glu) unit. The ^1H NMR spectrum of **8** exhibited a one-proton doublet at δ 5.18 with coupling interaction of 7.1 Hz and a two-broad signals at δ 4.88 and δ 4.85, both integrated for two protons each, were assigned to anomeric protons H-1a and H-1b, H-1c and to H-1d and H-1e, respectively. Two two-proton multiplets at δ 4.72 and δ 4.46 and one-proton multiplet at δ 4.29 were accounted to carbinol H-5a, H-5b and to H-4d, H-4e and H-4c, respectively. Three one-proton multiplets at δ 4.69, δ 4.65 and δ 4.63 and a two-proton multiplet at δ 4.55 were ascribed to carbinol H-2a, H-2b, H-2c and to H-2d and H-2e and their location in the deshielded region suggested glycosidic linkage between C-2 to C-1. The remaining sugar protons resonated between δ 3.81-3.06. A three-proton triplet at δ 0.84 ($J = 6.2$ Hz) was ascribed to terminal C-14 primary methyl protons. A two-proton broad signal at δ 2.50 was associated with the H₂-2 methylene protons adjacent to the ester group. The remaining methylene protons appeared at δ 1.50 (2H), 1.25 (6H) and 1.22 (14 H). The ^{13}C NMR spectrum of **8** displayed important signals for ester carbon at δ 173.05, methyl carbon at δ 18.01 (Me-14) and methylene carbons between δ 33.53-22.09. The five anomeric carbons appeared between δ 104.07-91.76 indicating the location of five sugar moieties in the glycosidic chain. The carbon signals at δ 83.50 (C-4c), δ 82.56 (C-4d) and 82.40 (C-4e) suggested the presence of three L-arabinofuranoside residues in the glycoside. The carbinol signals in the deshielded region at δ 72.38 (C-2a), δ 72.87 (C-2b), δ 77.55 (C-2c), δ 77.55 (C-2d) and δ 77.04 (C-2e) indicated (2 \rightarrow 1) linkages of the sugar residues. The hydroxymethylene carbons appeared at δ 60.03 (C-6a), δ 60.52 (C-6b), δ 60.71 (C-5c), δ 60.71 (C-5d) and δ 62.16 (C-5e). The remaining carbinol carbons of the sugar residues resonated between δ 75.63-68.88. The ^{13}C NMR values of the sugar residues were compared with the ^{13}C NMR chemical shifts of sugar parts [7]. The HMBC spectrum of **8** exhibited interactions of C-14 with H₂-13; C-1 with H-1a and H₂-2; C-1a with H-1b; C-2b with H-1b and H-1c; C-2c with H-1d; C-2d with H-1d and H-1e; and C-4e with H-3e and H₂-5e. Acid hydrolysis of **8** yielded myristic acid, β -D-glucose and β -L-arabinose (TLC comparable). On the basis of above mentioned discussion the structure of **8** has been established as *n*-tetradecanoyl- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranoside. Compound **9**, named cicerstearioside, was obtained from chloroform-methanol (99:1) eluants as a pale yellow crystalline mass. It gave positive tests for glycosides. Its IR spectrum displayed characteristic absorption band for hydroxyl group at 3410, 3389, 3260 cm^{-1} , and ester group at 1741 cm^{-1} . On the basis of mass and ^{13}C NMR spectra its molecular weight was established as 872 consistent with a molecular formula of C_{18} fatty acid glycosides, $\text{C}_{40}\text{H}_{72}\text{O}_{20}$. A prominent ion peak generating at m/z 605 [$\text{C}_{18}\text{a-O}$ fission] $^{+}$ indicated that stearic acid was

attached to terminal glycoside chain. The ion fragments arising at m/z 149 ($\text{C}_5\text{H}_9\text{O}_5$) and 133 ($\text{C}_5\text{H}_9\text{O}_4$) supported the location of the arabinose moiety at the terminal side of the glycoside chain. The ^1H NMR spectrum of **9** showed two one-proton doublets at δ 5.19 and 5.16 with coupling interactions of 6.9 Hz each and a two-proton broad signal at δ 4.89 were assigned to anomeric protons H-1a, H-1c and to H-1b and H-1d. Four one-proton multiplets at δ 4.76 δ 4.72, δ 4.58, δ 4.55 were accounted to carbinol protons H-5a, H-5b, H-4c and H-4d, respectively. Two one-proton doublet at δ 4.65 ($J = 3.6$, 6.9 Hz) and δ 4.69 ($J = 3.6$, 6.9 Hz) and two one-proton multiplet at δ 4.29 and δ 4.40 were ascribed to carbinol H-2a, H-2b and to H-2c and H-2d and their location in the deshielded region suggested glycosidic linkage between C-2 to C-1. The remaining sugar protons resonated between δ 4.25-3.03. A three-proton triplet at δ 0.84 ($J = 6.1$ Hz) was ascribed to terminal C-18 primary methyl protons. Two one-proton doublets at δ 2.51 ($J = 3.0$ Hz) and 2.50 ($J = 3.0$ Hz) were accommodated in H₂-2 methylene protons adjacent to the ester group. The remaining methylene protons appeared at δ 1.90 (2H) and 1.22 (26H). The ^{13}C NMR spectrum of **9** displayed important signals for ester carbon at δ 171.19, methyl carbon at δ 14.03 (Me-14) and methylene carbons between δ 33.53-22.16. The four anomeric carbons appeared between δ 104.05-91.75 indicating the location of four sugar moieties in the glycosidic chain. The carbon signals at δ 82.40 (C-4c) and δ 83.50 (C-4d) suggested the presence of two L-arabinofuranoside residues in the glycoside. The carbinol signals in the deshielded region at δ 72.86 (C-2a), δ 71.60 (C-2b), δ 77.53 (C-2c), δ 77.05 (C-2d) indicated (2 \rightarrow 1) linkages of the sugar residues. The hydroxymethylene carbons appeared at δ 60.05 (C-6a), δ 60.50 (C-6b), δ 60.70 (C-5c) and δ 62.17 (C-5d). The remaining carbinol carbons of the sugar residues resonated between δ 74.29-68.58. The ^{13}C NMR values of the sugar residues were compared with the ^{13}C NMR chemical shifts of sugar parts [7]. The HMBC spectrum of **9** showed correlations of C-18 with H₂-17; C-1 with H₂-2 and H-1a; C-2a with H-1b; C-2b with H-2b and H-1c; C-2c with H-1d; and C-4d with H-3d and H₂-5d. Acid hydrolysis of **9** yielded stearic acid, β -D-glucose and β -L-arabinose (TLC comparable). On the basis of above mentioned discussion the structure of **9** has been identified as *n*-octadecanoyl- β -D-glucopyranosyl (2 \rightarrow 1)- β -D-glucopyranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1)- β -L-arabinofuranosyl-(2 \rightarrow 1). -----Compound **10**, named cicerotadecatrienoside, was obtained from chloroform-methanol (99:1) eluants as a pale yellow crystalline mass. It gave positive tests for glycosides. Its IR spectrum displayed characteristic absorption bands for hydroxyl group at 3420, 3396, 3265 cm^{-1} , ester group at 1740 cm^{-1} and at unsaturation 1652 cm^{-1} . On the basis of mass and ^{13}C NMR spectra its molecular weight was established as 1000 consistent with a molecular formula of C_{18} fatty acid penta glycoside, $\text{C}_{45}\text{H}_{76}\text{O}_{24}$. A prominent ion peaks generating at m/z 263 [CO-O fission] $^{+}$ indicated that linoleic acid was attached to terminal glycoside chain. The ion fragments arising at m/z 265 ($\text{C}_5\text{H}_9\text{O}_5$) and 133 ($\text{C}_{10}\text{H}_{17}\text{O}_8$) supported the location of two arabinose moieties at the terminal side of the glycoside chain. The ^1H NMR spectrum of **10** exhibited a two one-proton multiplets at δ 5.31 and 5.16 and a two-proton multiplet at δ 5.18 were ascribed to vinylic H-9 and H-12 and to H-10 and H-13 protons, respectively. A one-proton doublet at δ 5.07 with coupling interactions of 7.1 Hz and two broad signals at δ 4.88 and δ 4.81, both integrated for two protons each, were assigned to anomeric protons H-1a and to H-1b,

H-1c and to H-1d and H-1e, respectively. Three one-proton multiplets at δ 4.70, δ 4.53, δ 3.81 and a two-proton multiplet at 3.69 were accounted to carbinol H-5a, H-5b, H-4e and to H-4c and H-4d. Three one-proton multiplets at δ 4.44, 4.39 and 4.27 and a two-proton multiplet at δ 4.42 were ascribed to carbinol H-2a, H-2d, H-2e and to H-2b and H-2c and their location in the deshielded regions suggested glycosidic linkage between C-2 to C-1. The remaining sugar protons resonated between δ 3.54-3.10. Two one-proton doublets at δ 2.50 ($J = 6.6$ Hz) and 2.48 ($J = 6.6$ Hz) were attributed to H₂-2 methylene proton adjacent to the ester group. Three one-proton multiplets at δ 2.26, 2.72 and 2.11, integrated for two-protons each, were associated correspondingly with the H₂-8, H₂-11 and H₂-14 methylene protons adjacent to the vinylic C-9 and C-10 and C-13 vinylic carbons. A three-proton triplet at δ 0.85 ($J = 6.3$ Hz) was ascribed to terminal C-18 primary methyl protons. The remaining methylene protons resonated at δ 1.91 (2H), 1.23 (10H), 1.19 (2H) and 1.48 (2H). The ¹³C NMR spectrum of **10** displayed important signals for ester carbon at δ 172.17, vinylic carbons at 129.57 (C-9), 127.72 (C-10), 129.11 (C-12) and 127.35 (C-13), methyl carbon at δ 14.59 (Me-18) and methylene carbons between δ 33.37-22.08. The five anomeric carbons appeared between δ 104.03-91.73 indicating the location of five sugar moieties in the glycosidic chain. The carbon signals at δ 83.48 (C-4c), δ 82.55 (C-4d) and δ 82.38 (C-4e) suggested the presence of three L-arabinofuranoside residues in the glycoside. The carbinol signals in the deshielded region at δ 72.83 (C-2a), δ 72.34 (C-2b), δ 77.58 (C-2c, C-2d) and 77.06 (C-2e) indicated (2→1) linkages of the sugar residues. The hydroxymethylene carbons appeared at δ 60.09 (C-6a), δ 60.68 (C-6b), δ 60.49 (C-5c), δ 60.68 (C-5d) and δ 62.13 (C-5e). The remaining carbinol carbons of the sugar residues resonated between δ 75.62-66.16. The ¹³C NMR values of the sugar residues were compared with the ¹³C NMR chemical shifts of sugar parts [7]. The HMBC spectrum of **10** exhibited correlations of C-9 with H-10 and H₂-8; C-13 with H-12, H₂-11 and H₂-14; C-1 with H₂-2 and H-1a; C-2a with H-1b; C-2b with H-1c; C-2c with H-1d; C-2d with H-3d and H-1e; and C-4e with H-3e and H₂-5e. Acid hydrolysis of **10** yielded linoleic acid, β -D-glucose and β -L-arabinose (TLC comparable). On the basis of above mentioned discussion the structure of **10** has been established as *n*-octadec-9, 12-dienoyl- β -D-glucopyranosyl (2→1)- β -D-glucopyranosyl-(2→1)- β -L-arabinofuranosyl-(2→1)- β -L-arabinofuranosyl-(2→1)- β -L-arabino furanoside.

References

1. Van der Maesen LJG. In: The Chickpea. (ed.) Saxena MC & Singh KB. Oxford, UK: CAB International, 1987, 11.
2. Aggarwal SS, Tamrakar BP, Paridhavi M. A Textbook of Clinically useful Herbal Drugs. Delhi: Shri Ram Enterprises, 2004, 141.
3. The Wealth of India. A dictionary of Indian raw materials and industrial products, Publication and Information Directorate. New Delhi: CSIR. 1992; III:526-554.
4. Siddiqui S. Studies in the constituents of Chana (*Cicer arietinum* L.). Journal of Scientific and Industrial Research. 1945; 4:68-70.
5. Hosel W, Berz W. Flavonoids from *Cicer arietinum* L. Phytochemistry. 1970; 9:2053-2056.
6. Borger G, Berz W. Flavonoids from *Cicer arietinum* L. Phytochemistry. 1988; 27:3714-3715.
7. Agrawal PK, Jain DC, Gupta RK, Thakur RS. Carbon-13 NMR spectroscopy of steroidal saponin and steroidal saponins. Phytochemistry. 1985; 24:2479-2497.