ORIGINAL ARTICLE

New phytoconstituents from the aerial parts of *Fumaria parviflora* Lam

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ABSTRACT

Fumaria parviflora Lam. (Fumariaceae) is an annual herb found throughout the world. Traditionally it has great significance in various disorders. In folk medicine of Turkey it is used against hepato-biliary dysfunction and imported from Iran. In Charaka and Sushruta, it is recommended for treatment of fevers, blood disorders, chronic skin diseases, urinary diseases and cough. The compounds were isolated from methanolic extract of the plants by column chromatography using silica gel (60-120 mesh) as stationary phase and structure of the isolated compounds have been established on the basis of spectral data analysis and chemical reactions. Phytochemical investigation of its aerial parts led to the isolation of five new compounds characterized as (5αH,11αH)-8-oxo-homoiridolide (1), *n*-docosanyl-2-*O*-β-*D*-glucopyranosyl salicylate (2), 2-methyl-6-hydroxymethylenedodecan-10-oyl-12, 15-olide14-*O*-β-*D*-xylopyranoside (3), 4-oxo-stigmast-5-en-3β-ol-*D*-glucopyran oside (4) and salicylic acid-*O*-β-*D*-xylopyranoside (5) along with the known compounds α-*D*-glucopyranosyl hexadecanoate (6) and α-*D*-glucopyranosyl-(2 → 1′)-α-*D*-glucopyranoside (7). The isolated compounds are useful as they will provide essential data and information for the further researchers and development of effective analytical marker for identity, purity and quality control of this traditional plant in future.

Key words: Fumariaceae, homaira, homoiridolide, kshetra, phenolic ester glycoside, pitpapra

INTRODUCTION

Fumaria parviflora Lam. (Fumariaceae) is a pale green, small, scandent, much branched annual herb. The plant is distributed over greater part of India as a weed in cultivated crop and appeared during the cold season. It is locally known as 'Pitpapra' in Hindi, 'Kshetra' in Sanskrit and 'Homaira' in Arabic.[1] The genus *Fumaria* (Fumariaceae) consists of 46 species in the world,[2] which grows in wheat fields, plains and low hills in Europe and in many parts of the world including Middle East and South Asia.[3] It is used as fodder in Assam since long time. Extract of the plant is used as valuable bitter tonic, astringent, laxative, diuretic, in dyspepsia and scrofulous skin infections and as alternative medicine.[4] It is reported to contain pentatriacontane (0.5%), alkaloids principally with protopine (0.13%), tannins and sugars. As fumitory and for liver complains it is mainly imported from Iran.[5] In the Unani traditional system it is prescribed to treat gut and respiratory disorders, abdominal cramps, indigestion and asthma[6,7] while in folk medicine of Turkey it has been reported to be used against hepato-biliary diseases.[8] Phytochemical studies on *F. parviflora* revealed the presence of flavonoids, glycosides, tannins, saponins, steroids, triterpenoids, phenols, and alkaloids such as fumarophycine, cryptopine, sinactine, stylopine, bicuculline, adlumine, perfumidine dihydrosanguirine , protopine alkaloids and antimicrobial agent Octacosanol (OC).[2, 9-11, 17] This manuscript describes isolation of phytoconstituents using column chromatographic techniques from the aerial parts of *F. Parviflora* collected from Delhi region.

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MATERIALS AND METHODS

Materials

All chemicals were from Sigma-Aldrich unless otherwise stated. Melting points were determined on a thermoelectrically heated Perfit apparatus (Ambala, India) without correction. IR spectra were recorded using KBr pellets, with a Jasco FT-IR-5000 Spectrometer (FTS 135, Hong Kong). UV spectra were determined with Lambda Bio 20 Spectrophotometer (Perkin Elmer, Schwerzenbach, Switzerland) in methanol. The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker ARX-Spectrometer (Rheinstetten, Germany), with TMS (tetra methyl silane) as an internal standard. Mass-spectrometric detection was carried out on (Synapt Mass spectrometer, Q-TOF-ESI) (Waters Corp., UK) with an electrospray-ionisation (ESI) technique. The ESI source was used in positive ionization mode. Column chromatographic separations were carried out on silica gel (Qualigens, Mumbai, India, 60-120 mesh). Precoated TLC plates Silica gel 60 F_{254} (Merck, Darmstadt, Germany) were used for analytical thin layer chromatography and the spots were visualized by exposure to iodine vapor and UV radiations.

Methods

Plant material

The aerial parts *F. parviflora* were collected from the Herbal Garden, Jamia Hamdard, New Delhi, in month of October and identified by Prof. Javed Ahmad, In-charge of the Herbal Garden, Jamia Hamdard, New Delhi. A specimen voucher of the plant was deposited in the Herbarium, Faculty of Pharmacy, Jamia Hamdard, New Delhi with a reference number PRL-JH/2011/05.

Preparation of extract and isolation

The dried aerial parts of *F. parviflora* (2.5 kg) were coarsely powdered and extracted with methanol for 72 h using a Soxhlet extractor. The methanolic extract was dried under reduced pressure to obtain a dark brown residue (380 g). The residue (concentrated extract, 100 g) was dissolved in minimum amount of methanol and adsorbed on silica gel column grade (60-120 mesh) to obtain slurry. The slurry was dried in air and chromatographed over silica gel loaded column in chloroform. The column was eluted with chloroform-methanol (99:1, 93:7, 19:1, 9:1, and 17:3 *v/v*) to isolate the compounds **1-7**.

RESULTS

(5αH, 11αH)-8-oxo-homoiridolide (1)

Elution of the column with chloroform-methanol (99:1) gave yellow crystals of **1**, recrystallized from acetone, 230 mg (0.23%), R_f 0.4 (chloroform-methanol, 93:7 *v/v*), m.p. 220-221°C, UV λ_{max} (MeOH): 240 nm (log ε 3.8, 1.2). IR λ_{max} (KBr): 3442, 2923, 2841, 1762, 1701, 1646, 1415, 1367, 1260, 1092, 966, 821 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.39 (1H, s, H-3), δ 5.63 (1H, d, *J* = 7.0 Hz, H-1α), δ 4.73 (1H, brs, $w_{1/2}$ = 11.2 Hz, H-6α), δ 3.19 (1H, d, *J* = 5.5 Hz, H-5α), δ 2.87 (1H, brs, $w_{1/2}$ = 13.6 Hz, H-11α), δ 2.10 (2H, m, H_2-7), δ 2.08 (2H, m, H_2-9), δ 2.06 (2H, m, H_2-10). ^{13}C NMR ($CDCl_3$): δ 100.76 (C-1), δ 142.96 (C-3), δ 152.57 (C-4), δ 43.68 (C-5), δ 89.12 (C-6), δ 29.98 (C-7), δ 213.76 (C-8), δ 29.91 (C-9), δ 29.96 (C-10), δ 38.63 (C-11), δ 166.81 (C-12). ESI MS *m/z* (rel. int.): 224 $[M]^+$ ($C_{11}H_{12}O_5$) (3.2).

Glucosyl salicylic ester (2)

Elution of the column with chloroform-methanol (93:7) afforded yellow crystals of **2**, recrystallized from chloroform-methanol (1:1), 250 mg (0.25%), R_f 0.2 (chloroform- methanol, 93:7), m.p. 237-239°C, UV λ_{max} (MeOH): 215, 255, 300. IR λ_{max} (KBr): 3455, 3407, 2932, 2841, 1733, 1645, 1525, 1401, 1372, 1257, 1161, 1023, 798 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.85 (1H, m, H-3), δ 6.78 (1H, m, H-6), δ 6.65 (1H, m, H-5), δ 6.01 (1H, m, H-4), δ 4.71 (1H, d, *J* = 7.5 Hz, H-1''), δ 4.50 (1H, m, H-5''), δ 3.74 (2H, m, H_2-1'), δ 3.49 (1H, m, H-3''), δ 3.70 (1H, m, H-2''), δ 3.34 (1H, m, H- 4''), δ 3.05 (2H, brs, H_2-6''), δ 2.31 (2H, m, H_2-2'), δ 1.71 (2H, m, CH_2), δ 1.36 (2H, m, CH_2), δ 1.24 (34H, brs, 17 × CH_2) δ 0.86 (3H, t, *J* = 6.2 Hz, Me-22). ESI MS *m/z* (rel. int.): 608 $[M]^+$ ($C_{35}H_{60}O_8$) (23.5), 445 (3.1), 428 (29.3), 325 (12.6), 309 (2.2), 299 (2.1), 283 (51.8).

Acid hydrolysis of 2

Compound **2** (30 mg) was dissolved in ethanol (5 mL), dil. HCl (2 mL) added and the reaction mixture heated on a steam bath for 1 hour. The solvent was evaporated under reduced pressure and the residue was dissolved in chloroform to separate *n*-docosanol, co-TLC comparable. The residue was dissolved in water and chromatographed on silica gel TLC plate along with the standard samples of sugars using *n*-butanol-acetic acid-water (4:1:5) as developing solvent system. The sugar was identified as *D*-glucose, R_f 0.12.

2-methyl-6-hydroxymethylenedodecan-10-oyl-12, 15-olide14-*O*-β-*D*-xyloside (3)

Elution of the column with chloroform-methanol (19:1) gave yellow powder of **3**, recrystallized from chloroform-methanol (1:1), 298 mg (0.298%), m.p. 194-95°C, R_f 0.25 (chloroform-methanol, 13:7). UV λ_{max} (MeOH): 221 nm (log ε 3.7), IR λ_{max} (KBr): 3416, 3265, 2928, 2343, 1734, 1642, 1445, 1392 1035 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 5.36 (1H, t, *J* = 4.0 Hz, H-3), δ 4.22 (1H, *J* = 7.1 Hz, H-1'α), δ 4.01 (1H, m, H-2'), δ 3.92 (1H, m, H-3'), δ 3.76 (1H, m H-4'), δ 3.69 (2H, t, *J* = 5.5 Hz, H_2-12), δ 3.51 (2H, brs, H_2-5'), δ 3.37 (2H, d, *J* = 7.0 Hz, H_2-14), δ 2.68 (1H, m, H-10), δ 2.39 (2H, m, H_2-4), δ 2.25 (1H, m, H-6), δ 2.15 (2H, m, H_2-5), δ 2.05 (2H, m, H_2-7), δ 1.75 (2H, m, H_2-8), δ 1.65 (3H, brs, Me-1), δ 1.63 (3H, brs, Me-13), δ 1.49 (2H, m, H_2-9). ^{13}C NMR (DMSO-d_6): δ 22.48 (C-1), δ 130.15 (C-2), δ 121.06 (C-3), δ 42.75 (C-4), δ 41.25 (C-5), δ 39.07 (C-6), δ 32.63 (C-7), δ 31.40 (C-8), δ 28.09 (C-9), δ 54.30 (C-10), δ 29.31 (C-11), δ 60.15 (C-12), δ

23.86 (C-13), δ 66.83 (C-14), δ 174.41 (C-15), δ 101.41 (C-1'), δ 72.61 (C-2'), δ 71.48 (C-3'), δ 69.38 (C-4'), δ 67.17 (C-5'). ESI MS *m/z* (rel. int.): 386 $[M]^+$ ($C_{20}H_{34}O_7$) (4.3).

Acid hydrolysis of 3

Compound 3 (35 mg) was dissolved in ethanol (5 mL), dil. HCl (2 mL) added and the reaction mixture heated on a steam bath for 1 hour. The solvent was evaporated under reduced pressure, the residue dissolved in water and chromatographed on silica gel TLC plate along with the standard samples of sugars using *n*-butanol-acetic acid-water (4:1:5) as developing solvent system. The sugar was identified as *D*-xylose, R_f 0.12.

Parvisterol-3β-*D*-glucoside (4)

Elution of column with chloroform-methanol (19:1) afforded colorless crystals of 4, recrystallized from chloroform-methanol (1:1), 322 mg (0.322%), R_f: 0.7 (chloroform-methanol, 17:3), m.p. 230-231°C, UV λ_{max} (MeOH): 225 nm (log ε 3.8), IR λ_{max} (KBr): 3415, 3165, 2928, 2841, 1693, 1643, 1483, 1378, 1266, 1026, 922, 806 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.32 (1H, m, H-6), δ 5.10 (1H, d, *J* = 7.5 Hz, H-1'), δ 4.37 (1H, m, H-5'), δ 3.81 (1H, dd, *J* = 5.1, 8.5 Hz, H-3α), δ 3.74 (1H, m, H-2'), δ 3.53 (1H, m, H-3'), δ 3.50 (1H, m, H-4'), δ 3.22 (2H, brs, H_2-6'), δ 1.21 (3H, brs, Me-19), δ 0.96 (3H, d, *J* = 6.6 Hz, Me-21), δ 0.87 (3H, d, *J* = 6.3 Hz, Me-26), δ 0.80 (3H, d, *J* = 6.6 Hz, Me-27), δ 0.76 (3H, d, *J* = 6.1Hz, Me-29), δ 0.64 (3H, brs, Me-18). ^{13}C NMR ($CDCl_3$): δ 37.17 (C-1), δ 30.82 (C-2), δ 73.48 (C-3), δ 208.15 (C-4), δ 140.17 (C-5), δ 122.16 (C-6), δ 31.80 (C-7), δ 31.86 (C-8), δ 50.09 (C-9), δ 36.65 (C-10), δ 21.13 (C-11), δ 39.86 (C-12), δ 42.25 (C-13), δ 56.67 (C-14), δ 24.22 (C-15), δ 28.17 (C-16), δ 55.97 (C-17), δ 11.25 (C-18), δ 20.10 (C-19), δ 36.08 (C-20), δ 18.92 (C-21), δ 33.86 (C-22), δ 25.97 (C-23), δ 45.77 (C-24), δ 30.57 (C-25), δ 19.25 (C-26), δ 19.72 (C-27), δ 28.76 (C-28), δ 11.57 (C-29), δ 101.01 (C-1'), δ 76.27 (C-2'), δ 71.37 (C-3'), δ 70.05 (C-4'), δ 79.14 (C-5'), δ 61.87 (C-6'). ESI MS *m/z* (rel. int.): 590 $[M]^+$ ($C_{35}H_{58}O_7$) (1.6).

Acid hydrolysis of 4

Compound 4 (35 mg) was dissolved in ethanol (5 mL), dil. HCl (2 mL) added and the reaction mixture heated on a steam bath for 1 hour. The solvent was evaporated under reduced pressure, the residue was dissolved in water and chromatographed on silica gel TLC plate along with the standard samples of sugars using *n*-butanol-acetic acid-water (4:1:5) as developing solvent system. The sugar was identified as *D*-glucose, R_f 0.12.

Salicylic acid-*O*-β-*D*-xyloside (5)

Elution of the column with chloroform-methanol (9:1) gave brown crystals of 5, recrystallized from chloroform methanol (1:1), 105 mg (0.0.105%), R_f 0.2 (Chloroform-methanol, 3:1), m.p. 284-285°C; UV λ_{max} (MeOH): 228 nm; IR λ_{max} (KBr): 3515, 3445, 3205, 2930, 2845, 1692, 1635, 1545, 1410, 1370, 1165, 1027 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.46 (1H, dd, *J* = 8.5, 3.0 Hz, H-3), δ 6.29 (1H, m, H-6), δ 6.22 (1H, m, H-4), δ 6.19 (1H, m, H-5), δ 4.94 (1H, d, *J* = 7.5 Hz, H-1'), δ 4.24 (1H, m, H-2'), δ 3.77 (1H, m, H-3'), δ 3.54 (1H, m, H-4'), δ 3.46 (2H, d, *J* = 7.5 Hz, H_2-5'). ESI MS *m/z* (rel. int.): 270 $[M]^+$ ($C_{12}H_{14}O_7$) (9.2), 138 (18.2).

Acid hydrolysis of 5

Compound 5 (20 mg) was dissolved in ethanol (5 mL), dil. HCl (2 mL) added and the reaction mixture heated on a steam bath for 1 hour. The solvent was evaporated under reduced pressure and the residue was dissolved in chloroform to separate salicylic acid, co-TLC comparable. The residue was dissolved in water and chromatographed on silica gel TLC plate along with the standard samples of sugars using *n*-butanol-acetic acid-water (4:1:5) as developing solvent system. The sugar was identified as *D*-xylose, R_f 0.20.

Palmityl glucoside (6)

Elution of the column with chloroform-methanol (9:1) gave colorless needles of 6, recrystallized from methanol, 528 mg (0.528%), R_f 0.4, (chloroform-methanol, 13:7), m.p. 160-161°C, UV λ_{max} (MeOH): 240 nm (log ε 3.7). IR λ_{max} (KBr): 3541, 3419, 3260, 2924, 2844, 1721, 1634, 1382, 827, 722 cm^{-1}; ^1H NMR (DMSO-d_6): δ 4.88 (1H, d, *J* = 3.5 Hz, H-1'), δ 3.83 (1H, m, H-5'), δ 3.76 (1H, m, H-2'), δ 3.63 (1H, m, H-3'), δ 3.56 (1H, m, H-4'), δ 3.16 (2H, d, *J* = 6.0 Hz, H_2-6'), δ 2.30 (2H, t, *J* = 7.5 Hz, H_2-2), δ 2.08 (2H, m, CH_2), δ 1.71 (2H, m, CH_2), δ 1.59 (2H, m, CH_2), δ 1.46 (2H, m, CH_2), δ 1.28 (4H, brs, 2 × CH_2), δ 1.18 (14H, brs, 7 × CH_2), δ 0.84 (3H, t, *J* = 6.5 Hz, Me-16). ^{13}C NMR (DMSO-d_6): δ 169.64 (C-1), δ 102.89 (C-1'), δ 75.58 (C-5'), δ 73.16 (C-2'), δ 73.05 (C-3'), δ 72.25 (C-4'), δ 61.02 (C-6'), δ 54.08 (C-2), δ 49.96 (CH_2), δ 38.71 (CH_2), δ 31.16 (CH_2), δ 28.79 (8 × CH_2), δ 25.84 (CH_2), δ 23.06 (CH_2), δ 17.18 (C-16). ESI MS *m/z* (rel. int.): 418 $[M]^+$ ($C_{22}H_{42}O_7$) (2.9), 255 (12.6), 163 (11.6).

Acid hydrolysis of 6

Compound 6 (25 mg) was dissolved in ethanol (5 mL), dil. HCl (2 mL) added and the reaction mixture heated on a steam bath for 1 hour. The solvent was evaporated under reduced pressure and the residue was dissolved in chloroform to separate palmitic acid, co-TLC comparable. The residue was dissolved in water and chromatographed on silica gel TLC plate along with the standard samples of sugars using *n*-butanol-acetic acid-water (4:1:5) as developing solvent system. The sugar was identified as *D*-glucose, R_f 0.12.

α-*D*-diglucoside (7)

Elution of the column with chloroform-methanol (17:3) gave colorless crystals of 7, recrystallized from methanol, 873 mg (0.873%), R_f 0.7 (chloroform-methanol, 13:7), m.p. 290°C, UV λ_{max} (MeOH): 240 nm, IR λ_{max} (KBr): 3455, 3350, 3261, 2910, 1643, 1371, 822 cm^{-1}. ^1H NMR (D_2O): δ 4.93 (1H, d, *J* = 4.0 Hz, H-1α), δ 4.86 (1H, d, *J* = 5.1 Hz, H-1'α),

δ 4.07 (1H, m, H-5), δ 4.04 (1H, m, H-5'), δ 3.99 (1H, m, H-2), δ 3.94 (1H, m, H-2'), δ 3.79 (1H, m, H-3), δ 3.68 (1H, m, H-3'), δ 3.36 (1H, m, H-4), δ 3.30 (1H, m, H-4'), δ 3.05 (2H, d, *J* = 4.5 Hz, H_2-6), δ 3.01 (2H, d, *J* = 7.5 Hz, H_2-6'). ESI MS *m*/*z* (rel. int.): 342 $[M]^+$ ($C_{12}H_{22}O_{11}$) (5.1), 163 (5.3).

DISCUSSION

Compound 1, named fumaria homoiridolide, was obtained as a yellow crystalline powder from chloroform-methanol (99:1) eluants. Its IR spectrum showed characteristic absorption bands for hydroxyl group (3442 cm^{-1}), lactone ring (1762 cm^{-1}), keto group (1701 cm^{-1}), and unsaturation (1646 cm^{-1}). On the basis of mass and ^{13}C NMR spectral data the molecular ion peak was determined at *m*/*z* 224 $[M]^+$ consisting to the molecular formula of a, homoiridolide, $C_{11}H_{12}O_5$. The ^1H NMR spectrum of 1 exhibited a one-proton deshielded singlet at δ 7.39 assigned to vinylic H-3 proton, a one-proton doublet at δ 5.63 (*J* = 7.0 Hz) ascribed dioxygenated methine H-1α proton, a one-proton broad singlet at δ 4.73 with half width of 11.2 Hz attributed to oxygenated methine H-6α proton, a one-proton doublet at δ 3.19 (*J* = 5.5 Hz) accounted to methine H-5α proton, a one-proton broad multiplet at δ 2.87 with half width dimension 13.6 Hz due to methine H-11α proton and three two-proton multiplets at δ 2.10, 2.08 and 2.06 associated with the methylene H_2-7, H_2-9 and H_2-10 protons respectively. The ^{13}C NMR spectrum of 1 displayed signals for lactone carbon at δ 166.81 (C-12), vinylic carbons at δ 142.96 (C-3) and 152.57 (C-4), oxygenated methine carbon at δ 100.76 (C-1) and 89.12 (C-6) oxygenated carbon at δ 213.76 (C-8) and methine and methylene carbons between δ 43.68- 29.91. The ^1H NMR and ^{13}C NMR spectral data of 1 were compared with the reported data of iridoide.[12,13] On the basis of these spectral data the structure of 1 has been established as (5αH, 11αH)-8-oxo-homoiridolide. This is a new homoiridolide.

Compound 2, designated as glucosyl salicylic ester, was obtained as a yellow color crystalline mass from chloroform-methanol (93:7) eluants. Its IR spectrum showed absorption bands for hydroxyl groups (3455, 3407 cm^{-1}), aromatic ring (1645 cm^{-1}), ester group (1733 cm^{-1}), and long aliphatic chain (798 cm^{-1}). It exhibited a molecular ion peak at *m*/*z* 608 in its mass spectrum corresponding to the molecular formula of a phenolic ester glycoside $C_{35}H_{60}O_8$. The ion fragments arising at *m*/*z* 309 $[CH_2(CH_2)_{20}CH_3]^+$, 325 $[OCH_2(CH_2)_{20}CH_3]^+$, 299 $[M-309]^+$ and 283 $[M-325]^+$ indicated that glycosidic salicylic acid was esterified with a C_{22} aliphatic alcohol. The ion peaks generated at *m*/*z* 445 $[M-C_6H_{11}O_5]^+$ and 428 $[C_6H_{12}O_6]^+$ suggested that a C_6 sugar was linked to the molecule. The ^1H NMR spectrum of 2 displayed four one-proton multiplets at δ 6.85, 6.78, 6.65 and 6.01 assigned to aromatic H-3, H-6, H-5 and H-4 protons, respectively. A one-proton doublet at δ 4.71 (*J* = 7.5 Hz) was ascribed to anomeric H-1'' proton. The other sugar protons appeared as one-proton multiplets at δ 4.50, 3.70, 3.49 and 3.34 and as a two proton broad singlet at δ 3.05 attributed oxygenated methine H-5'', H-2'', H-3'', H-4'' and hydroxyl methylene H_2-6'' protons, respectively. A two-proton multiplet at δ 3.74 was accounted to oxygenated methylene H_2-1' protons. The other methylene protons resonated as two-protons multiplets at δ 2.31, 1.71 and 1.36 and as a broad singlet at δ 1.24 (34 H). A three-proton triplet at δ 0.86 (*J* = 6.2 Hz) was due to terminal C-22 primary methyl protons. Acid hydrolysis of 2 yields *D*-glucose and salicylic acid. On the basis of these evidences the structure of 2 was established as *n*-dodecosanyl-2-*O*-β-*D*-glucopyranosyl salicylate. This is a new phenolic ester glycoside.

Compound 3, named parvisesquiterpinic xyloside, was obtained as a yellow powder from chloroform-methanol (19:1) eluants. It gave positive tests for glycosides and showed characteristic IR absorption bands for hydroxyl groups (3416, 3265 cm^{-1}) and lactone ring (1734 cm^{-1}). On the basis of mass and ^{13}C NMR spectral data the molecular ion peak of 3 was determined as *m*/*z* 386 corresponding to a molecular formula of a sesquiterpenic glycoside, $C_{20}H_{34}O_7$. The ^1H NMR of the 3 exhibited a one-proton triplet at δ 5.36 (*J* = 4.0 Hz) assigned to vinylic H-3 proton, a two-proton triplet at δ 3.69 (J = 5.5 Hz) ascribed to oxygenated methylene H_2-12 protons, two three-proton broad singlets at δ 1.65 and 1.63 due to C-1 and C-13 methyl protons located on the vinylic carbon C-2, two one-proton multiplets at δ 2.68 and 2.25 attributed to methine H-10 and H-6 protons, respectively, and other methylene protons between δ 2.39-1.49. The sugar protons appeared as a one-proton doublet at δ 4.22 (*J* = 7.1 Hz) accounted to anomeric H-1' protons, two one-proton multiplets at 3.92 and 3.76 due to hydroxymethine H-3' and H-4' protons and a two-proton broad singlet at δ 3.51 assigned to oxygenated methylene H_2-5' protons. The ^{13}C NMR spectrum of 3 displayed signals for γ lactone carbon at δ 174.41 (C-15), vinylic carbons at δ 130.15 (C-2) and 121.06 (C-3), oxygenated methylene carbons at δ 60.12 (C-12), 66.83 (C-14), anomeric carbon at δ 101.41 (C-1'), other sugar carbons between δ 72.61-67.17 and methyl carbons at δ 22.48 (C-1) and 23.86 (C-13). Acid hydrolysis of 3 yielded *D*-xylose. On the basis of these spectral data analysis and chemical reactions the structure of 3 was elucidated as 2-methyl-6-hydroxymethylenedodecan-10-oyl-12, 15-olide14-O-β-*D*-xylo- pyranoside. This is a new sesquiterpenic xyloside.

Compound 4, named parvisterol-3β-*D*-glucoside, was obtained as a colorless crystalline product from chloroform-methanol (93:7) eluants. It showed positive test for glycosides and IR absorption bands for hydroxyl groups (3415, 3165 cm^{-1}), ketonic group (1693 cm^{-1}), and unsaturation (1643 cm^{-1}). On the basis of mass and ^{13}C NMR spectra the molecular ion peak of 4 was determined at *m*/*z* 590 corresponding to the molecular formula of a keto steryl glycoside $C_{35}H_{58}O_7$. The ^1H NMR spectrum of 4 exhibited

a one-proton multiplet at δ 5.32 assigned to vinylic H-6 proton and a one-proton doublet δ 5.10 (*J* = 7.5 Hz) ascribed to anomeric H-1' proton, a one-proton double doublet at δ 3.81 (J = 5.1, 8.5 Hz) attributed to oxygenated methine H-3α proton, other sugar protons as one-proton multiplets at δ 4.73 (H-5'), 3.74 (H-2'), 3.53 (H-3') and 3.50 (H-4') and as a two-proton broad singlet at δ 3.22 (H_2-6'), methyl signals as three- proton broad singlets at δ 1.21 and 0.64 and doublets at δ 0.96 (*J* = 6.6 Hz), 0.87 (*J* = 6.3 Hz), 0.80 (*J* = 6.6 Hz), and 0.76 (*J* = 6.1 Hz) associated with tertiary C-19 and C-18, secondary C-21, C-26 and C-27 and primary C-29 primary methyl protons, respectively, all attached to saturated carbons. The ^{13}C NMR spectrum of 4 displayed signals for vinylic carbons at δ 140.17 (C-5) and 122.16 (C-6), oxygenated methine carbon at 73.48 (C-3), carbonyl carbon at δ 208.15 (C-4), anomeric carbon at δ 101.01 (C-1'), other sugar carbons from δ 79.14 to 61.87 and methyl carbons between δ 20.10 -11.25. The ^{1}H NMR and ^{13}C NMR spectral data of 4 were compared with the reported data of steroid.[14-16] On the basis of above evidences the structure of 4 has been established as 4-oxo-stigmast-5-en-3β-ol-*D*-gluc opyranoside. This is a new steroidal glycoside.

Compound 5**,** named salicylic acid-*O*-β-*D*-xyloside, was obtained as brown crystals from chloroform-methanol (9:1) eluants. Its IR spectrum showed absorption bands for hydroxyl groups (3515, 3445 cm^{-1}), aromatic ring (1635, 1545 cm^{-1}) and free carboxylic group (3205, 1692 cm^{-1}). It showed a molecular ion peak at *m/z* 270 consistent with the molecular formula of a phenolic acid glycoside ($C_{12}H_{14}O_7$). The ion peak generating at *m/z* 138 [HO-C_6H_4COOH]$^+$ suggested that hydroxy benzoic acid was linked to a C_5 sugar unit. The ^{1}H NMR spectrum of 5 exhibited a one-proton double doublet at δ 6.46 (*J* = 8.5 Hz, 3.0 Hz) assigned to ortho-, meta- coupled aromatic H-3 proton, three one-proton multiplets at δ 6.29, 6.22, and 6.19 ascribed to other aromatic H-6, H-4 and H-5 protons. A one-proton doublet at δ 4.94 (*J* = 7.5 Hz) ascribed to anomeric H-1' and the remaining sugar protons appeared as one-proton multiplets δ 4.24 (H-2'), 3.77 (H-3') and 3.54 (H-4'). A two-proton doublet δ 3.46 (*J* = 7.5 Hz) was accounted to H_2-5'. Acid hydrolysis of 5 yielded salicylic acid and β-*D*-xylose. On the basis of foregoing discussion the structure of 5 has been formulated as **s**alicylic acid-*O*-β-*D*-xylopyranoside. This is a new phenolic acid glycoside.

Compound 6, named as palmityl glucoside, was obtained as colorless needles from chloroform-methanol (9:1) eluants. It responded to general tests of glycosides and showed IR absorption bands for hydroxyl groups (3541, 3419, 3260 cm^{-1}), ester group (1721 cm^{-1}) and long aliphatic chain (722 cm^{-1}). On the basis of mass and ^{13}C NMR spectral data the molecular ion peak of 6 was determined at *m/z* 418 [M]$^+$ corresponding to a molecular formula of an acyl glycoside, $C_{22}H_{42}O_7$. The ion peaks arising at *m/z* 255 [$C_{16}H_{31}O_2$]$^+$ and *m/z* 163 [$C_6H_{11}O_5$]$^+$ suggested that the palmityl group was attached with a hexose moiety. The ^{1}H NMR spectrum of 6 displayed a one-proton doublet at δ 4.88 (J = 3.5 Hz) assigned to anomeric H-1' proton, other sugar protons as one-proton multiplets at δ 3.83, 3.76, 3.63 and 3.56 and as a two-proton doublet at δ 3.16 (*J* = 6.0 Hz) due to hydroxymethylene H_2-6' protons, a two-proton triplet at δ 2.30 (*J* = 7.5 Hz) ascribed to methylene H_2-2 adjacent to the ester function, other methylene protons between δ 2.08 -1.18 and a three-proton triplet at δ 0.84 (*J* = 6.5 Hz) accounted to terminal C-16 methyl protons. The ^{13}C NMR spectrum of 6 exhibited signals for ester carbon at δ 169.64 (C-1), anomeric carbon at δ 102.89 (C-1'), other sugar carbons from δ 75.58 to 61.02, methylene carbons between δ 54.08-23.06 and methyl carbon at δ 17.18 (C-16). Acid hydrolysis of 6 yielded palmitic acid and *D*-glucose. Based on these evidences the structure of 6 was characterized as α-*D*-glucopyranosyl hexadecanoate.

Compound 7, α-*D*-diglucoside, was obtained as a colorless crystalline mass from chloroform-methanol (17:3) eluants. It responded positively to general chemical tests of glycosides and showed IR absorption bands for hydroxyl groups (3455, 3350, 3261 cm^{-1}). On the basis of mass spectral data its molecular ion peak was determined at *m/z* 342 [M]$^+$ corresponding to a molecular formula of a disaccharide $C_{12}H_{22}O_{11}$. An ion peak arising at *m/z* 163 [$C_6H_{11}O_5$]$^+$ suggested that C_6 sugar units were linked in the molecule. The ^{1}H NMR signal of 7 displayed two one-proton doublets at δ 4.93 doublet (*J* = 4.0 Hz) and 4.86 (*J* = 5.1 Hz) assigned to anomeric H-1 and H-1' protons, respectively. The other sugar protons appeared as one-proton multiplets from δ 4.07 to 3.30 and two-proton doublets at δ 3.05 (*J* = 4.5 Hz) and 3.01 (*J* = 7.5 Hz) due to hydroxymethylene H_2-6 and H_2-6' protons, respectively. The presence of oxygenated methine H-2 proton in the deshielded region at δ 3.99 suggested (2 → 1') attachment of the sugar units. Acid hydrolysis of 7 yielded *D*-glucose. On the basis of these evidences the structure of 7 has been elucidated as α-*D*-glucopyranosyl-(2 → 1')-α-*D*-glucopyranoside.

CONCLUSION

The present work highlights isolation of several new plant secondary metabolites [Figure 1], which makes the study significant over the previous phytochemical investigations of *Fumaria parviflora* Lam. The isolated compounds are useful as they will provide essential data and information for the further researchers and development of effective analytical marker for identity, purity and quality control of this Traditional Unani medicinal plant.

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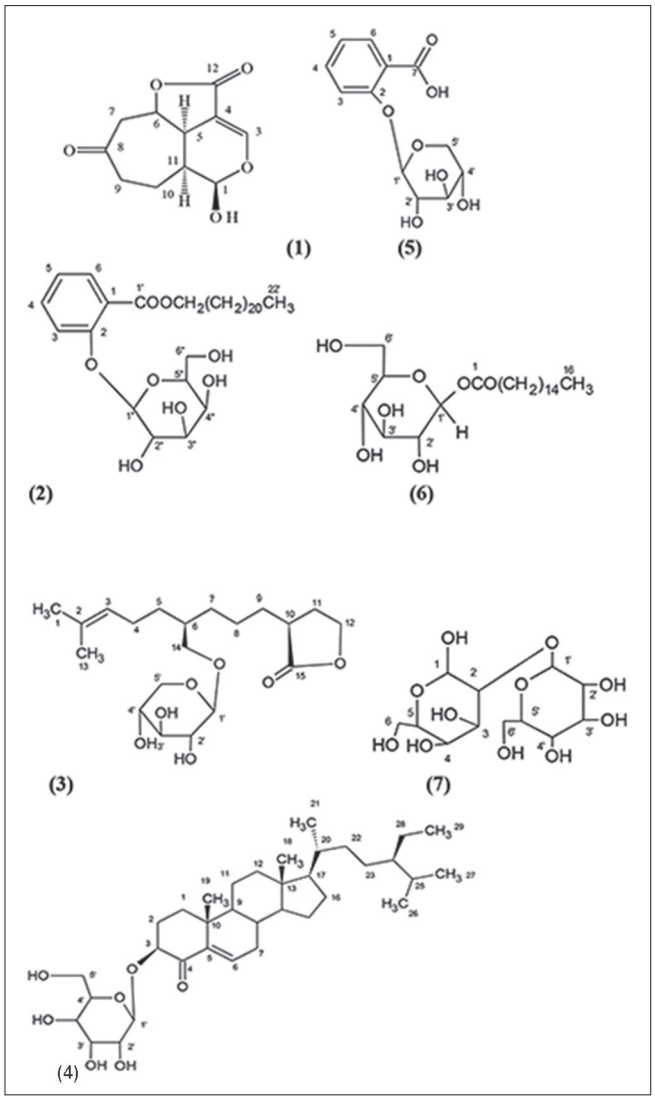

Figure 1: Structure of compounds 1-7 isolated from the methanolic extract of aerial parts of *F. parviflora*.

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