ejpmr, 2020,7(9), 386-394

SJIF Impact Factor 6.222

EUROPEAN JOURNAL OF PHARMACEUTICAL AND MEDICAL RESEARCH

www.ejpmr.com

Research Article

ISSN 2394-3211

EJPMR

CHEMICAL CONSTITUENTS FROM THE FRUITS OF *GARCINIA COWA*, AND LEAVES OF *PAEDERIA FOETIDA* AND *TETRASTIGMA ANGUSTIFOLIA*

Aparoop Das[1], Kamaruz Zaman[1], Dipak Chetia[1], Mohammed Ali[2*] and Showkat Rassol Mir[2]

[1]Department of Pharmaceutical Sciences, Dibrugarh University, Dibrugarh -786004, Assam, India.
[2]Phytopharmaceuticals Research Laboratory, School of Pharmaceutical Education and Research, Jamia Hamdard, P.O. Hamdard Nagar, New Delhi – 110062, India.

***Corresponding Author: Mohammed Ali**
Phytopharmaceuticals Research Laboratory, School of Pharmaceutical Education and Research, Jamia Hamdard, P.O. Hamdard Nagar, New Delhi – 110062, India.

Article Received on 06/07/2020 **Article Revised on 27/07/2020** **Article Accepted on 16/08/2020**

ABSTRACT

Garcinia cowa Roxb. Ex Choisy (family Clusiaceae) is an evergreen, deciduous trees. Its fruits are edible, expectorant and used to treat blood circulation, coughs, dysentery and indigestion. *Paederia foetida* L. (family Rubiaceae) is a perennial, climbing vine. Its leaves are effective against herpes infection, dysentery, dysuria, dyspepsia, enteritis, gastritis, rheumatism and urinary lithiasis. *Tetrastigma angustifolium* (Roxb.) Planch. (family Vitaceae) is a herbaceous, wiry climbers. The whole plant is edible and taken to control diabetes. Phytochemical investigation of the fruits of *Garcinia cowa* gave a new triterpenyl anthracenediol isopenanoate characterized as 3′-oxo- 4′, 4′,6′-trimethyl-5′-(10′,14′,18′,22′-tetramethyl hept-9′,13′,17′,22′-tetraene-8′-oxoyl)-cyclohexyl-(1→6′)]-oxy-4-isopentanoyloxy-9,11-dihydroxy-anthracene (**1**) and an unknown ditriterpenyl anthracene identified as 3′-oxo- 4′, 4′,6′-trimethyl-5′-(10′,14′,18′,22′-tetramethyl hept-9′,13′,17′,22′-tetraene-8′-oxoyl)-cyclohexyl-(1→6′)]- 3″-oxo- 4″, 4″,6″-trimethyl-5″-(10″,14″,18″,22″-tetramethyl hept-9″,13″,17″,21″-tetraene-8″-oxoyl)cyclohexyl--(4→6″)]- 1,4-anthracene (**2**). The leaves of *Paederia foetida* afforded two known monosaccharides characterized as β-D-galacturonic acid (**3**) and β-D-glucuronic acid (**4**) and an essential oil composed of high percentage of 1,8-cineole (56.21%), γ-terpinene (25.16%), 3-carene (10.07%), and n-dec-3-ene (5.14%). The leaves of *Tetrastigma angustifolia* furnished 8-hydroxy apigenin 7-O-β-D-glucopyranoside (**5**), a rare apigenin glucoside and α-L-xylose **(6)**.

KEYWORDS: *Garcinia cowa* fruits, *Paederia foetida* leaves, *Tetrastigma angustifolia* leaves, phytoconstituents, essential oil, isolation, characterization.

INTRODUCTION

Garcinia cowa Roxb. Ex Choisy, syn. *G. roxburghii* Wight, *G. umbellifera* Roxb., *G. wallichii* Choisy, *Oxycarpus gangetica* Buch.-Ham. (family Clusiaceae), known as kattaphal, kau-thekera, cowa moagosteen, brindal berry, is found in southwest China, India, Bangladesh, Myanmar, Malaysia, Thailand, Vietnam, Laos and Cambodia. It is an evergreen, deciduous trees, up to 16 m high; bark smooth, greyish-brown; exudation yellow, sticky, scanty; leaves simple, opposite, decussate, elliptic-oblong, base acute, attenuate or cuneate, apex acute or obtuse, margin entire, glabrous, thickly coriaceous; petiole stout, glabrous; flowers dioecious, small, yellow; fruit a fleshy berry, depressed, globose, with 4-8 vertical grooves, smooth, yellow or red, beaked; seeds 4-8, oblong-ovoid with a soft aril.[1] Young leaves and shoots are eaten cooked. A leaf infusion is drunk to cure diarrhoea. Fruits are acidic and edible; fruit powder is ingested to relieve dysentery. The fruits and leaves are taken as an expectorant and to improve indigestion and blood circulation. The pericarp is febrifuge and refrigerant; a fruit pericarp paste along with the fruits of *Solanum indicum* is taken against stomachache. A seed paste together with the seeds of *Spondias pinnata* is applied on the blister spots, itches and rashes. The bark, latex and root have been used as an antifever agent. The tree yields an inferior gum-resin, resembling gamboge.[2-4] The twigs contained acylphloroglucinol derivatives, cowadepsidone and phloroglucinols.[3, 5,6] The stem and branches yielded flavonoids, friedelin, phytosterols, cambogin, guttiferone K, xanthones and organic acids.[7-13] The fruits and twigs furnished flavones and fukugiside, cambogin and guttiferone K, daucosterol, beta-sitosterol, amentoflavone and morelloflavone, xanthone derivatives, cirsiumaldehyde and p-coumaric acid, and organic acids.[14-18] The leaves yielded chamuangone, citric and, isovanillic acids, xanthones, isojacareubin, cambogin, garcimultiflorones E and F, oblongifolin C, guttiferone F, garciniagifolone A, garcicowins C and D, symphonone H and jacareubin.[19-21]. The latex gave cowagarcinone A- E, cowanol, cowanin , fuscaxanthone

A and other xanthones.[22, 23] The bark afforded xanthones and citric and isovanillic acids.[18, 23]. The inflorescences possessed cowanone, mangostins and other xanthones.[24] The roots produced xanthones, named kaennacowanols A-C, anthraquinones, flavonoids and terpenes.[25,26]

Paederia foetida L., syn. *Apocynum foetidum* Burm.f., *Gentiana scandens* Lour., *Hondbesseion foetidum* (L.) Kuntze, *Paederia amboinensis* Miq., *P. barbulata* Miq., *P. chinensis* Hance (family Rubiaceae), known as gandhali, bakuchi, skunkvine, stinkvine, and Chinese fever vine, is a native to temperate and tropical Asia, and distributed in the Mascarenes, Melanesia, Polynesia, Hawaiian Islands, North America and in the Himalayas from Dehra Dun eastwards to north-eastern India. It is a perennial, climbing or trailing vine, up to 9.1 m long; leaves ovate to lanceolate, thin, entire, with long petioles and unpleasant odor; flowers small, pink or lilac, in leaf axils; fruits round, shiny, brown, berry; seeds compressed, smooth, enlarged, with membranous ring. Its leaves are antidysenteric, laxative and tonic, used against herpes infection, bacillary dysentery, dysuria, dyspepsia, enteritis, gastritis, rheumatism and urinary lithiasis. The roots are carminative and utilized to relieve colic, pain in the chest or liver, gout, rheumatism, spleen inflammation and as an emetic. The whole plant has antiphlogistic, aphrodisiac, astringent, tonic and laxative properties, useful to treat abscesses, colic, diarrhoea, dysentery, fever, flatulence, infertility, inflammations, pains, piles, fever, night blindness, paralysis, and rheumatic affections. The seeds are recommended to cure piles and leucoderma. The bark, root and leaves are useful in relieving maggots, urethral calculi, asthma, constipation and expulsion of the placenta caused after miscarriage. The fruits are effective to ameliorate tooth pain and for whitening blackened teeth.[27-30] The plant essential oil was consisted mainly of methanethiol, dimethyl disulfide, linalool, α-terpineol and geraniol.[31] The plant contained friedelan-3-one, β-sitosterol, epifriedelinol and p-methoxy-trans-cinnamate. The leaves and stem yielded iridoid glycosides – asperuloside, paederoside and scandoside; beta-sitosterol, stigmasterol, campesterol, ursolic acid, hentriacontane, hentriacontanol, ceryl alcohol, palmitic acid, vitamin C, phenols, methyl mercaptan and galacturonic acid.[29, 30, 32-37]

Tetrastigma angustifolium (Roxb.) Planch., syn. *Cissus angustifolia* Roxb., *Tetrastigma thomsonianum* Planch. *ex* Balakr. , *Vitis angustifolia* (Roxb.) Wall. (family Vitaceae), known as Nol Tenga, Naltanga, Nekung, Dousrem, and Demshri, is indigenous to Sumatra, Myanmar, north-eastern India and Bangladesh. In India it is found in Assam, Meghalaya, Nagaland, Kerala, and Odisha. It is a herbaceous, wiry climbers; stem dark, flattened, rooting at nodes; leaves 3-5 foliolate, leaflets lanceolate, serrate, acuminate, attenuate at base, glabrous, margin crenate-serrate, petiolate; tendril leaf opposed, slender, simple, branched near apex; flowers 4-merous, dioecious, green in axillary cymes, pitcher shaped, glabrous; fruit globose berry; 2-4 seeded, brown, ellipsoid, wrinkled. The whole plant is used as a green vegetable. Tender shoots and leaves are eaten which are acidic.[38] The plant is taken to control diabetes.[39] The leaves contained high amount of ascorbic acid.[40] The leaf extracts showed the presence of flavonoids, glycosides, alkaloids, proteins and phenolic compounds.[39] A related species *Tetrastigma hemsleyanum* yielded 6'-O-benzoyldaucosterol, daucosterol and beta-sitosterol.[41] Quercetin 3-O-rutinoside and kaempferol 3-O-glycosides were reported from the leaves of *Cissus ibuensis*.[42] *Tetrastigma obtectum* afforded C-glycosidic flavonoids, named tetrastigma A–D, and flavones.[43] *Tetrastigma planicaule* furnished gheddic acid, tricosanol, beta-sitosterol, palmitic acid, ethyl gallate and vanillin.[44] The flavonoids rutin, isoquercitrin, kaempferol-3-O-rutinoside and astragalin were isolated from the root of *Tetrastigma hemsleyanum*.[45] A hydro-ethanolic (3:7) leaf extract of *Tetrastigma angustifolia* showed significant anti-hyperglycemic activities.[46] Keeping in view the various therapeutic values of the plants and the development of ecofriendly, biodegradable and safer herbal preparations the fruits of *Garcinia cowa* and leaves of *Paederia foetida* and *Tetrastigma angustifolia* were screened for the isolation and characterization of their chemical constituents.

MATERIALS AND METHODS

The protocols of all methodologies (procedures, experimental designs and analysis assays) were adopted from the earlier published work.[47,48]

Plant Materials

The fruits of *Garcinia cowa* and leaves of *Paederia foetida* and *Tetrastigma angustifolia* were collected from their natural habitat of Dibrugarh, Assam. The fruits of *G. cowa* were authenticated by Dr. S. Chandra, Scientist, Department of Botany, Forest Research Institute, Dehradun, Uttarakhand. The leaves of *P. foetida* and *T. angustifolia* were identified and authenticated by Botanical Survey of India, Eastern Regional Centre, Shillong, India. The voucher specimens of the plant materials were deposited in the Department of Pharmaceutical Sciences, Dibrugarh University, Assam for future reference.

Extraction and isolation

The air-dried matured fruit powder of *G. cowa* and leaves of *P. foetida* and *T. angustifolia* (1.0 kg each) were defatted with n-hexane and extracted exhaustively with methanol in a Soxhlet apparatus. The methanolic extracts were concentrated under reduced pressure to yield dark brown viscous masses (242 g, 351 g, and 273 g, respectively). The dried residue (200 g each) was dissolved in minimum amount of methanol and adsorbed on silica gel column grade (60-120 mesh) separately to obtain slurries. Each slurry was air-dried and chromatographed over silica gel columns loaded in

petroleum ether (b. p. 60 – 80 °C) individually. Each column was eluted with petroleum ether, petroleum ether - chloroform (9:1, 3:1, 1:1, 1:3, *v/v*), chloroform and chloroform - methanol (99:1, 49:1, 19:5, 9:1, *v/v*). Various fractions were collected separately and matched by TLC to check homogeneity. Similar fractions having the same R_f values were combined and crystallized with solvents. The isolated compounds were recrystallized to get pure compounds.

Isolation of phytoconstituents from the fruits of *Garcinia cowa*

1-Triterpenolyl 4-(3′′-Methylbutanoyl) anthracene 9,11-diol (1)

Elution of the column with chloroform: methanol (19:1) eluants afforded a yellow colored amorphous powder of **1**, yield 189 mg; m. p. 228 - 229 °C; UV λmax (MeOH): 253, 357, 372, 395 nm (log ε 5.2. 1.1, 1.3. 1.5); IR υ_{max} (KBr): 3467, 3365, 2976, 2916, 1721, 1701, 1677, 1603, 1518, 1448, 1362, 1294, 1181, 1105, 954, 893, 821, 776 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.24 (1H, d, J = 2.0 Hz, H-10), 7.06 (1H, s, H-6), 7.02 (1H, d, J = 2.0 Hz, H-8), 6.87 (1H, s, H-13), 6.74 (1H, d, J = 8.4 Hz, H-2), 6.71 (1H, d, J = 8.4 Hz, H-3), 5.20 (1H, s, H-9′), 4.90 (1H, m, H-13′), 4.86 (1H, m, H-17′), 4.82 (1H, s, H-21′), 2.78 (2H, m, H_2-7′), 2.66 (1H, d, J = 6.0 Hz, H_2-2′a), 2.61 (2H, d, J = 5.5 Hz, H_2-2′b), 2.26 (2H, m, H_2-11′), 2.08 (2H, m, H_2-16′), 2.05 (2H, m, H_2-12′), 2.03 (2H, m, H_2-15′), 2.01 (2H, m, H_2-19′), 1.92 (2H, m, H_2-20′), 1.86 (1H, m, H-5′), 1.69 (3H, s, Me-27′), 1.67 (3H, s, Me-28′), 1.65 (3H, s, Me-29′), 1.59 (3H, s, Me-23′), 1.57 (3H, s, Me-30′), 1.36 (2H, m, H_2-1′), 1.25 (3H, s, Me-26′), 1.15 (3H, s, Me-24′), 0.90 (3H, s, Me-25′), 2.45 (2H, m, H_2-2′′), 1.71 (1H, m, H-3′′), 0.99 (3H, d, J = 5.6 Hz, Me-4′′), 0.97 (3H, d, J = 5.9 Hz, Me-5′′), ^{13}C NMR ($CDCl_3$): δ 146.55 (C-1), 122.91 (C-2), 121.16 (C-3), 145.95 (C-4), 135.41 (C-5), 126.33 (C-6), 134.62 (C-7), 122.91 (C-8), 152.55 (C-9), 121.16 (C-10), 152.53 (C-11), 133.97 (C-12), 115.63 (C-13), 130.83 (C-14), 28.86 (C-1′), 48.57 (C-2′), 207.94 (C-3′), 56.38 (C-4′), 30.55 (C-5′), 69.44 (C-6′), 48.57 (C-7′), 196.26 (C-8′), 121.16 (C-9′), 145.57 (C-10′), 49.21 (C-11′), 40.23 (C-12′), 115.64 (C-13′), 134.62 (C-14′), 39.52 (C-15′), 30.54 (C-16′), 116.50 (C-17′), 133.97 (C-18′), 30.52 (C-19′), 46.16 (C-20′), 111.84 (C-21′), 130.33 (C-22′), 20.96 (C-23′), 20.15 (C-24′), 21.83 (C-25′), 26.12 (C-26′), 26.50 (C-27′), 27.06 (C-28′), 26.48 (C-29′), 20.96 (C-30′), 173.74 (C-1′′), 49.01 (C-2′′), 39.83 (C-3′′), 18.64 (C-4′′), 18.62 (C-5′′), +ve ESI MS *m/z* (rel. int.) : 764 $[M]^+$ ($C_{49}H_{64}O_7$) (1.6), 679 (8.7), 439 (17.28), 240 (14.6), 179 (11.2), 151 (8.4).

1,4-Ditriterpenolyl anthracene (2)

Elution of the column with chloroform: methanol (9:1) eluants gave a yellow coloured amorphous powder of **2**, yield 189 mg; m. p. 152-153 °C; UV λmax (MeOH): UV λmax (MeOH): 251, 359, 373, 397 nm (log ε 5.6, 1.2, 1.4. 1.8); IR υ_{max} (KBr): 2966, 2916, 1708, 1691, 1614, 1521, 1440, 1375, 1290, 1215, 1195, 1116, 941, 893, 829, 790 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.16 (1H, d, J = 9.1 Hz, H-2), 7.03 (1H, s, H-6), 6.98 (1H, d, J = 9.1 Hz, H-3), 6.84 (1H, s, H-13), 6.80 (1H, m, H-9), 6.78 (1H, d, J = 9.3 Hz, H-11), 6.61 (1H, d, J = 9.3 Hz, H-8), 6.20 (1H, m, H-10), 5.16 (1H, s, H-9′), 5.04 (1H, t, J = 6.5 Hz, H-13′), 4.88 (1H, m, H-17′), 4.52 (1H, s, H_2-23′a), 4.50 (1H, s, H_2-23′b), 2.79 (2H, d, J = 5.2 Hz, H_2-7′), 2.75 (2H, m, H_2-2′), 2.60 (2H, m, H_2-12′), 2.21 (2H, m, H_2-11′), 2.16 (2H, m, H_2-15′), 2.10 (2H, m, H_2-16′), 2.08 (2H, m, H_2-19′), 1.90 (2H, m, H_2-21′), 1.88 (1H, m, H-5′), 1.80 (3H, s, Me-27′), 1.74 (3H, s, Me-28′), 1.64 (2H, m, H_2-1′), 1.62 (3H, s, Me-29′), 1.58 (3H, s, Me-30′), 1.40 (3H, s, Me-26′), 1.36 (2H, m, H_2-20′), 1.14 (3H, s, Me-24′), 1.04 (3H, s, Me-25′), 5.13 (1H, s, H-9′′), 4.90 (1H, t, J = 6.3 Hz, H-13′′), 4.86 (1H, m, H-17′′), 4.80 (1H, m, H-21′′), 2.77 (2H, d, J = 5.6 Hz, H_2-7′′), 2.72 (2H, m, H_2-2′′), 2.47 (2H, m, H_2-12′′), 2.19 (2H, m, H_2-11′′), 2.14 (2H, m, H_2-15′′), 2.18 (2H, m, H_2-16′′), 2.06 (2H, m, H_2-18′′), 1.98 (2H, m, H_2-19′′), 1.93 (2H, m, H_2-20′′), 1.86 (2H, m, H_2-5′′), 1.76 (3H, s, Me-27′′), 1.66 (3H, s, Me-28′′), 1.60 (6H, s, Me-23′′, Me-30′′), 1.53 (3H, s, Me-29′′), 1.47 (2H, m, H_2-1′′), 1.31 (3H, s, Me-26′′), 1.12 (3H, s, Me-24′′), 1.01 (3H, s, Me-25′′);

^{13}C NMR ($CDCl_3$): δ 148.76 (C-1), 123.62 (C-2), 124.08 (C-3), 148.75 (C-4), 136.15 (C-5), 129.37 (C-6), 131.80 (C-7), 121.51 (C-8), 118.43 (C-9), 118.66 (C-10), 119.15 (C-11), 129.96 (C-12), 138.94 (C-13), 136.09 (C-14), 24.82 (C-1′), 49.88 (C-2′), 199.23 (C-3′), 56.92 (C-4′), 33.16 (C-5′), 69.50 (C-6′), 46.35 (C-7′), 192.18 (C-8′), 123.47 (C-9′), 147.50 (C-10′), 43.46 (C-11′), 42.36 (C-12′), 115.43 (C-13′), 138.51 (C-14′), 35.17 (C-15′), 31.45 (C-16′), 116.03 (C-17′), 138.05 (C-18′), 38.18 (C-19′), 26.50 (C-20′), 27.89 (C-21′), 130.96 (C-22′), 108.13 (C-23′), 17.64 (C-24′), 18.53 (C-25′), 18.61 (C-26′), 25.70 (C-27′), 24.66 (C-28′), 23.48 (C-29′), 22.83 (C-30′), 24.55 (C-1′′), 49.86 (C-2′′), 209.45 (C-3′′), 58.03 (C-4′′), 33.07 (C-5′′), 65.60 (C-6′′), 46.33 (C- 7′′), 191.87 (C-8′′), 122.93 (C-9′′), 145.89 (C-10′′), 43.44 (C-11′′), 42.36 (C-12′′), 116.54 (C-13′′), 141.08 (C-14′′), 35.15 (C-15′′), 32.75 (C-16′′), 116.28 (C-17′′), 137.92 (C-18′′), 37.69 (C-19′′), 38.08 (C-20′′), 112.31 (C-21′′), 127.81 (C-22′′), 22.75 (C-23′′), 17.73 (C-24′′), 17.16 (C-25′′), 17.72 (C-26′′), 25.81 (C-27′′), 25.78 (C-28′′), 25.41 (C-29′′), 25.39 (C-30′′); +ve ESI MS *m/z* (rel. int.) : 1086 $[M]^+$ ($C_{74}H_{102}O_6$) (2.1), 439 (28.6), 208 (12.3), 179 (8.9), 151 (16.7).

Isolation of phytoconstituents from the leaves of *Paederia foetida*

D-Galacturonic acid (3)

Elution of the column with chloroform-methanol (1:1) furnished a colourless mass of **3**, recrystallized from methanol, yield 197 mg, R_f: 0.30 (ethyl acetate – acetic acid - water, 3 : 1 : 3), UV λmax (methanol): 208 nm, m. p. 158 -159 ºC; $[\alpha]^D_{24}$ + 98º (conc 4, H_2O); IR υ_{max} (KBr): 3392, 3230, 2921, 1670, 1445, 1417, 1370, 1317, 1247, 1195, 1147, 1113, 1049, 1003, 894 cm^{-1}; ^1H NMR (D_2O): δ 5.28 (1H, d, J = 7.1 Hz, H-5), 4.39 (1H, J = 7.2 Hz, H-1), 4.26 (1H, dd, J = 7.2, 5.9 Hz, H-2), 3.90 (1H, m, H-3), 3.82 (1H, m, H-4); ^{13}C NMR (D_2O): δ 98.69 (C-1), 75.59 (C-2), 74.21 (C-3), 73.51 (C-4), 78.49 (C-5),

178.76 (C-6); +ve ESI MS *m/z* (rel. int.): 194 $[M]^+$ ($C_6H_{10}O_7$) (11.3).

β-D-Glucuronic acid (4)

Further elution of the column with chloroform-methanol (1:1) yielded a colourless mass of **4**, recrystallized from methanol, yield 218 mg, R_f: 0.17 (ethyl acetate – acetic acid - water, 3 : 1 : 3), UV λmax (methanol): 209 nm, m. p. 164 -165 ºC; $[\alpha]^D_{24}$ + 36.5º (conc 1, H_2O); IR υ_{max} (KBr): 3421, 3390, 2924, 1653, 1447, 1384, 1243, 1189, 1051 891 cm^{-1}; ^1H NMR (D_2O): δ 4.89 (1H, d, J = 7.1 Hz, H-5), 4.02 (1H, d, J = 7.3, Hz, H-1), 3.81 (1H, m, H-2), 3.75 (1H, m, H-3), 3.56 (1H, m, H-4); ^{13}C NMR (D_2O): δ 98.63 (C-1), 76.84 (C-2), 75.38 (C-3), 74.61 (C-4), 78.84 (C-5), 179.49 (C-6); +ve ESI MS *m/z* (rel. int.): 194 $[M]^+$ ($C_6H_{10}O_7$) (11.3).

Isolation of the essential oil

The fresh leaves (1 kg) of *P. foetida* were hydrodistilled in a Clevenger type glass apparatus for 4 h. The essential oil was collected, measured, dried over anhydrous sodium sulphate and stored at 4 ^{0}C in the dark for GC and GC-MS analysis. The yield of essential oil obtained from the leaves was 1.07 %. The GC analysis and GC-MS analysis of the essential oil were carried out as reported earlier.[49, 50]

Isolation of phytoconstituents from the leaves of *Tetrastigma angustifolia*

8-Hydroxyapigenin-7-O-β-D-glucopyranoside (5)

Elution of the column with chloroform – methanol (9:1) gave a yellow amorphous powder of **5**, recrystallized from acetone – methanol (4:1), yield 211 mg, m. p. 250 - 251 °C; UV λmax (MeOH): 272, 304, 340 nm (log ε 5.6, 1.1, 0.9); IR υ_{max} (KBr): 3465, 3372, 3315, 3241, 2943, 2833, 1685, 1648, 1562, 1422, 1221, 1093, 876 cm^{-1}; ^1H NMR (DMSO-d_6): δ 8.02 (1H, d, J = 8.1 Hz, H-2′), 7.95 (1H, d, J = 8.4 Hz, H-6′), 6.94 (1H, d, J = 8.4 Hz, H-5′), 6.89 (1H, d, J = 8.1 Hz, H-3′), 6.71 (1H, s, H-6), 6.28 (1H, s, H-3), 5.01 (1H, d, J = 7.1 Hz, H-1″), 4.68 (1H, m, H-5″), 4.50 (1H, m, H-2″), 3.81 (1H, m, H-3″), 3.54 (1H, m, H-4″), 3.18 (2H, d, J = 4.8 Hz, H_2-6″); ^{13}C-NMR (DMSO-d_6): δ 163.01 (C-2), 102.92 (C-3), 182.55 (C-4), 161.59 (C-5), 98.61 (C-6), 164.43 (C-7), 146.24 (C-8), 156.46 (C-9), 104.51 (C-10), 122.08 (C-1′), 128.93 (C-2′), 116.28 (C-3′), 160.86 (C-4′), 114.27 (C-5′), 129.41 (C-6′), 105.76 (C-1″), 79.15 (C-2″), 73.85 (C-3″), 71.05 (C-4″), 82.28 (C-5″), 61.78 (C-6″); ESI MS *m/z* (rel. int.): 448 $[M]^+$ ($C_{21}H_{20}O_{11}$) (59.2), 431 (66.3), 330 (11.2), 302 (61.9), 285 (9.1), 163 (14.7).

α-L-xylose (6)

Elution of the column with chloroform-methanol (4:1) produced colourless needles of **6**, recrystallized from methanol, yield 253 mg, R_f: 0.15 (toluene -ethyl acetate-formic acid, 5:4:1.8), UV λmax (methanol): 210 nm, m. p. 149 -151 ºC; $[\alpha]^D_{24}$ -18.7º (conc 4, H_2O); IR υ_{max} (KBr): 3368, 3224, 2932, 2843, 1623, 1459, 1369, 1288, 1139, 1041, 985 cm^{-1}; ^1H NMR (D_2O): δ 4.69 (1H, d, J = 2.1 Hz, H-1), 3.92 (1H, m, H-2), 3.49 (1H, m, H-3), 3.41 (1H, m, H-4), 3.38 (2H, d, J = 5.6 Hz, H_2-5); ^{13}C NMR (DMSO-d_6): δ 99.23 (C-1), 73.50 (C-2), 72.32 (C-3), 72.11 (C-4), 71.04 (C-5); +ve ESI MS m/z (rel. int.): 150 $[M]^+$ ($C_5H_{10}O_5$) (6.8).

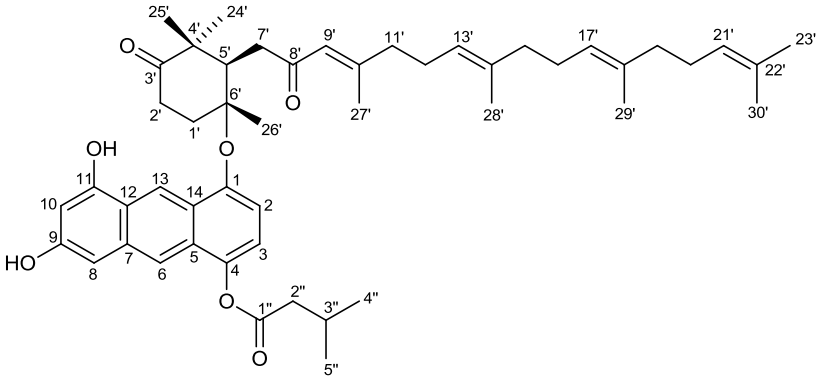
RESULTS AND DISCUSSION

Compound **1**, designated as 1-triterpenolyl 4-(3″-methylbutanoyl) anthracene 9,11-diol, gave positive tests for phenols, exhibited UV absorption maxima for anthracene (253, 357, 372, 395 nm) and distinctive IR absorption bands for hydroxyl groups (3467, 3365 cm^{-1}), ester group (1721 cm^{-1}), carbonyl functions (1701, 1677 cm^{-1}), unsaturation and aromatic rings (1603, 1518 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, the molecular ion peak of **1** was determined at *m/z* 764 consistent to a molecular formula of prenylated triterpenic anthracenol, $C_{49}H_{64}O_7$. The mass ion peaks produced at *m/z* 679 [O – $C_{1''}$ fission, M – $(CH_3)_2$-CH_2-CO]$^+$ and 240 [M – 439, $C_{14}H_8O_4]^+$ suggested that one monocyclic triterpenoid and a C_5 units were linked to an anthracene tetraol moiety. The ion fragments arising at *m/z* 439 [O – $C_{6'}$ fission, $C_{30}H_{47}O_2]^+$, 151 [$C_{7'}$ - $C_{8'}$ fission]$^+$ and 179 [C 8′ - C 9′ fission]$^+$ indicated the presence of one of the carbonyl function at C-8′ position. The ^1H NMR spectrum of **1** showed aromatic proton signals as two one -proton doublets at δ 7.24 (J = 2.0 Hz) and 7.02 (J = 2.0 Hz) assigned to meta-coupled H-10 and H-8 protons, as one- proton singlets at δ 7.06 and 6.87 due to H-6 and H-13 protons, and as one-proton doublets δ 6.74 (J = 8.4 Hz) and 6.71 (J = 8.4 Hz) ascribed to ortho-coupled H-2 and H-3 protons, respectively. Four one proton multiplets at δ 5.20, 4.90, 4.86 and 4.82 were attributed correspondingly to vinylic H-9′, H-13′ , H-17′ and H-21′ protons. Eight three-proton singlets at δ 1.69, 1.67, 1.65, 1.59, 1.57, 1.25, 1.15 and 0.90 and two three-proton doublets at δ 0.99 (J = 5.6 Hz) and 0.97 (J = 5.9 Hz) were associated with the tertiary C-27′, C-28′, C-29′, C-23′, C-30′, C-26′, C-24′ and C-25′ and secondary C-4″ and C-5″ methyl protons, respectively. The remaining methine and methylene protons resonated as multiplets between δ 2.78 - 1.36. The ^{13}C NMR spectrum of **1** displayed signals for an ester carbon at δ 173.74 (C-1″), carbonyl carbons at δ 207.94 (C-3′) and 196.26 (C-8′), aromatic and vinylic carbons between δ 152.55 -111.84, methylene carbons from δ 49.21 to 28.86, oxygenated carbon at δ 69.44 (C-6′), and methyl carbons in the range of δ 27.06 to 18.62. The ^1H-^1H COSY spectrum of **1** exhibited interactions of H-2 with H-3; H-6 and H-10 with H-8 ; H_2-2′ with H_2-1′; Me-24′, H_2-7′ and Me-26′ with H-5′ ; H_2-19′, H_2-20′, Me-23′ and Me- 30′ with H-21′; and H_2-2″, Me-4″ and Me-5″ with H-3″. On the basis of these evidences the structure of **1** has been elucidated as 3′-oxo- 4′, 4′,6′-trimethyl-5′-(10′,14′,18′,22′-tetramethyl hept-9′,13′,17′,22′-tetraene-8′-oxoyl)-cyclohexyl-(1→6′)]-oxy-–4-isopentanoyloxy-9,11-dihydroxyanthracene, a new triterpenyl anthracenediol isopenanoate (Fig. 1).

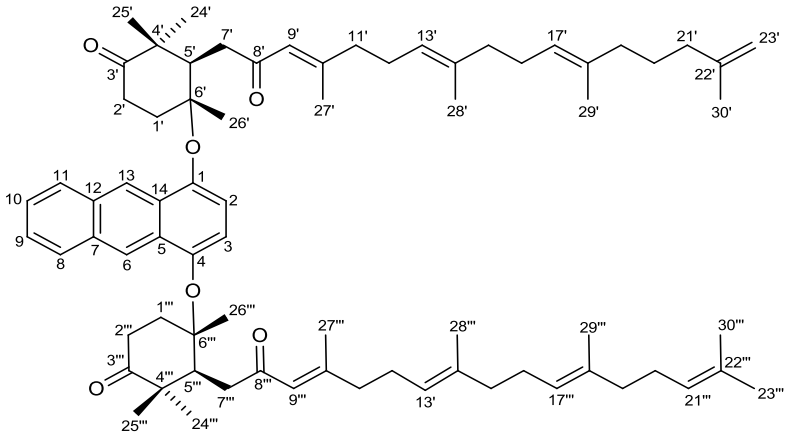
Compound **2**, named 1,4-ditriterpenolyl anthracene, $[M]^+$ at *m/z* 1086 ($C_{74}H_{102}O_6$), showed UV absorption maxima

for anthracene (251, 359, 373, 397 nm), IR absorption bands for carbonyl functions (1708, 1691 cm^{-1}), unsaturation and aromatic rings (1614, 1521 cm^{-1}). The mass ion peaks generated at *m/z* 208 [O – $C_{6'/6''}$ fission, $C_{14}H_8O_2$]$^+$ and 439 [M – 208, $C_{30}H_{47}O_2$]$^+$ suggested that two monocyclic triterpenoid units were linked to an anthracene diol moiety. The ion fragments produced at 151 [C 7′/7″ - C 8′/8″ fission]$^+$ and 179 [C 8′/8″ - C 9′/9″ fission]$^+$ indicated the existence of one of the carbonyl function at C-3′/C-3″ carbons and another carbonyl group at C-8′/C-8″ positions. The ^{1}H NMR spectrum of **2** displayed aromatic proton signals as four two-proton doublets at δ 7.16 (J = 9.1 Hz), 6.98 (J = 9.1 Hz), 6.78 (J = 9.3 Hz) and 6.61 (J = 9.3 Hz) assigned to ortho-coupled H-2, H-3, H-11 and H-8 protons, as one- proton singlets at δ 7.03 and 6.84 due to H-6 and H-13 protons, and as one-proton multiplets at δ 6.80 and 6.20 accounted to H-9 and H-10 protons, respectively. The vinylic protons appeared as one-proton singlets at δ 5.16 and 5.13 attributed to H-9′ and H-9″ adjacent to the carbonyl groups, as one-proton triplets at δ 5.04 (J = 6.5 Hz, H-13′) and 4.90 (J = 6.3 Hz, H-13″), as one-proton multiplets at δ 4.88 (H-17′), 4.86 (H-17″) and 4.80 (H-21″) and vinylic methylene protons as one-proton singlets at δ 4.52 (H_2-23′a), 4.50 (H_2-23′b). The methine and methylene protons appeared from δ 2.79 to 1.88 and at δ 1.64 (H_2-1′), 1.47 (H_2-1″) and 1.36 (H_2-20′). The nine methyl protons linked to the vinylic carbons resonated between δ 1.86 – 1.53. Two three – proton singlets at δ 1.40 and 1.31 were accounted to tertiary methyl Me-26′ and Me-26″ ptotons, respectively, located on oxygenated carbons. Four three-proton broad singlets at δ 1.14, 1.04, 1.12 and 1.01 were associated correspondingly with the tertiary methyl Me-24′, Me-25′ , Me-24″ and Me-25″ protons.

The ^{13}C NMR spectrum of **2** displayed signals for carbonyl carbons at δ 199.23 (C-3′), 192.18 (C-8′), 209.45 (C-3″) and 191.87 (C-8″), aromatic and vinylic carbons between δ 148.76 -108.13, methylene carbons from δ 49.88 – 24.55, oxygenated carbons at δ 69.50 (C-6′) and 65.60 (C-6″), and methyl carbons in the range of δ 25.81 to 17.16. The ^{1}H-^{1}H COSY spectrum of **2** exhibited interactions of H-2 with H-3; H-8, H-10 and H-11 with H-9; H_2-2′ with H_2-1′; Me-24′, H_2-7′ and Me-26′ with H-5′ ; H_2-19′, H_2-20′, H_2-23′ and Me- 30′ with H_2-21′; Me-24″, Me-26″ and H_2-7″ with H-5″; and H_2-19″, H_2-20″, Me-23″ and Me-30″ with H-21″. On the basis of spectral data analysis the structure of **2** has been established as 3′-oxo- 4′, 4′,6′-trimethyl-5′-(10′,14′,18′,22′-tetramethyl hept-9′,13′,17′,22′-tetraene-8′-oxoyl)-cyclohexyl-(1→6′)]- 3″-oxo- 4″, 4″,6″-trimethyl-5″-(10″,14″,18″,22″-tetramethyl hept-9″,13″,17″,21″-tetraene-8″-oxoyl)-cyclohexyl -(4→6″)]-1,4-anthracene, a new ditriterpenyl anthracene (Fig. 1).



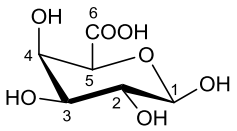
1-Triterpenolyl 4-(3″-methyl butanoyl) anthracene-9,11-diol **(1)**



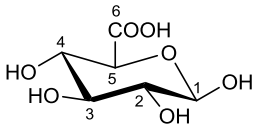
1,4-Diterpenolyl anthracene **(2)**

Fig 1: Structural formulae of the chemical constituents 1 and 2 isolated from the fruits of *Garcinia cowa*.

Compounds **3** and **4** were the known monosaccharides characterized as β-D-galacturonic acid and β-D-glucuronic acid, respectively (Fig. 2).



β-D-Galacturonic acid (3)



β-D-Glucuronic acid (4)

Fig 2: Structural formulae of the chemical constituents 3 and 4 isolated from the leaves of *Paederia foetida.*

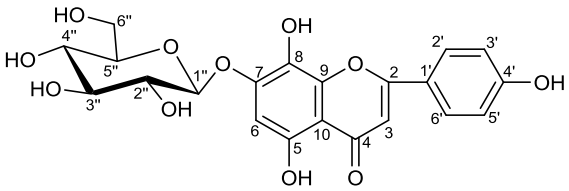
Table 1. Chemical composition of the essential oil of the fresh leaves of *Paederia foetida*

S.No	Components	Kowat index	Percentage Area
1	Furfural	830	0.19
2	n-Dec-3-ene	961	5.14
3	3-Carene	1001	10.07
4	1,8-Cineole	1017	56.21
5	γ-Terpinene	1053	25.16
6	S-Methyl thioacetate	1056	0.09
7	Dimethyl disulphide	1079	0.16
8	2-Methoxyphenol	1086	0.27
9	Linalool	1098	0.15
10	2-Phenyl ethanol	1110	0.07
11	α-Terpineol	1189	1.18
12	Methyl salicylate	1206	0.09
13	Nerol	1228	0.43
14	Geraniol	1255	0.28
15	1-Hexanol	1354	0.16
16	Benzaldehyde	1528	0.11

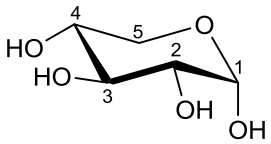
The chemical constituents of the essential oil of the leaves of *Paederia foetida* were identified by analysis of GC and GC-MS and are tabulated in Table 1 with their Kovat's indices and respective percentage. The essential oil was characterized by high percentage of 1,8-cineole (56.21%), γ-terpinene (25.16%), 3-carene (10.07%) and n-dec-3-ene (5.14%). There were seven monoterpenes (93.53 %) occurring from 56.21 to 0.15 % amounts, two sulphur compounds present in trace amounts (0.25 %), four aromatic compounds (0.54 %) from 0.27 to 0.07 % amounts, two aliphatic components (5.30 %), viz. *n*-dec-3-ene (5.14 %) and 1-hexanol (0.16%) and one heterocyclic constituent characterized as furfural (0.19%). The leaf essential oil was devoid of sesquiterpenes.

Compound **5,** a flavonoid glycoside, gave positive tests for glycosides, exhibited UV absorption maxima at 272, 304 and 340 nm for flavones and IR absorption bands for hydroxyl groups (3465, 3372, 3315, 3241 cm^{-1}), carbonyl group (1685 cm^{-1}), unsaturation (1648 cm^{-1}) and aromaticity (1562, 1093 cm^{-1}). There was a shift of band I with sodium methoxide suggesting the presence of free phenolic groups, absence of shift of bands with sodium acetate solution indicating bound nature of 7-hydroxyl group and a shift of band I with aluminum chloride suggesting the presence of free 5-hydroxyl group. There was no shift of band I with aluminum chloride and hydrochloric acid excluding the existence of B-ring *o*-dihydroxy functions.[51, 52] On the basis of mass and ^{13}C NMR spectra, the molecular ion peak of **5** was established at *m/z* 448 consistent with a molecular formula of flavone glycoside, $C_{21}H_{20}O_{11}$. The ion fragments arising at *m/z* 163 [$C_{1''}$ - O fission, $C_6H_{11}O_5]^+$, 431 [M - OH]$^+$, 285 [M – 163]$^+$, 302 [$C_{4,10}$ – $C_{2,\ O}$ fission, $C_{12}H_{14}O_9]^+$ and 330 [$C_{3,4}$ – $C_{2,O}$ fission, $C_{13}H_{14}O_{10}]^+$ suggested that a hexoside unit and two hydroxy groups were linked in the ring A and one hydroxy group was present in ring B of the flavone. The ^1H NMR spectrum of **5** displayed four one-proton doublets at δ δ 8.02 (J = 8.1 Hz), 7.95 (J = 8.4 Hz), 6.94 (J = 8.4 Hz) and 6.89 (J = 8.1 Hz) assigned to B-ring H-2′, H-6′, H-5′ and H-3′ protons, and two one-proton singlets at δ 6.71 and 6.28 due to H-6 and H-3 protons, respectively. A one-proton doublet at δ 5.01 (J = 7.1 Hz) was accounted to anomeric H-1″ proton. The other sugar protons appeared as one-proton multiplets from δ 4.68 to 3.18 and a two-proton doublet at δ 3.18 (J = 4.8 Hz, H_2-6″). The ^{13}C NMR spectrum of **5** exhibited signals for carbonyl carbon δ at 182.55 (C-4) and vinylic methine carbon at δ 102.92 (C-3) supporting the flavone-type carbon framework of the molecule, other flavone carbons between *δ* 162.87 – 98.61, anomeric carbons at δ 105.76 (C-1″) and remaining sugar carbons between δ 79.15 – 61.78. Acid hydrolysis of **5** yielded D-glucose, R_f 0.39 (water saturated phenol). On the basis of above mentioned discussion, the structure of compound **5** has been characterized as 8-hydroxy apigenin 7-O-β-D-glucopyranoside, a rare apigenin glucoside (Fig. 3).

Compound **6** was a known monosaccharide characterized as α-L-Xylose (Fig 3).



8-Hydroxy apigenin-7-*O*-β-D-glucopyranoside (5)



α-L-Xylose (6)

Fig 3: Structural formulae of the chemical constituents 5 and 6 isolated from the leaves of *Tetrastigma angustifolia.*

CONCLUSION

Phytochemical investigation of the fruits of *Garcinia cowa* gave a new triterpenyl anthracenediol isopenanoate (**1**) and an unknown ditriterpenyl anthracene (**2**). The leaves of *Paederia foetida* afforded β-D-galacturonic acid (**3**) and β-D-glucuronic acid (**4**) and an essential oil composed of high percentage of 1,8-cineole (56.21%), γ-terpinene (25.16%), 3-carene (10.07%), and *n*-dec-3-ene (5.14%). The leaves of *Tetrastigma angustifolia* furnished 8-hydroxy apigenin 7-O-β-D-glucopyranoside (**5**) and α-L-xylose **(6)**. This work has enhanced understanding about the phytoconstituents of these plants. These secondary metabolites can be used as analytical markers for quality control of these herbal drugs and their traditional formulations.

ACKNOWLEDGEMENT

The authors are thankful to the Head, Sophisticated Analytical Instrumentation Facility, Central Drug Research Institute (CSIR), Lucknow (U.P.) for recording spectral data of the compounds.

REFERENCES

1 Rajbhandari KR, Bhatt GD. Garcinia cowa (Clusiaceae), a new record from Nepal. The Journal of Japanese Botany, 2018; 93(1): 65–67.
2 Quattrocchi U., 2012. CRC World Dictionary of Medicinal and Poisonous Plants: Common Names, Scientific Names, Eponyms, Synonyms, and Etymology. CRC Press, Raton, Florida, 2012; 1801.
3 Ritthiwigrom T, Laphookhieo S, Pyne SG. Chemical constituents and biological activities of *Garcinia cowa* Roxb. Maejo International Journal of Science and Technology, 2013; 7(2): 212-231.
4 .Mongkontanawat N, Phuangborisut S. Product development of *Garcinia cowa* Roxb. tea mixed with high β-glucan content from edible mushroom. International Journal of Agricultural Technology, 2016; 12(7.1): 1247-1258.
5 Xu G, Kan WLT, Zhou Y, Song J-Z, Han Q-B, Qiao C-F, Cho C-H, Rudd J A, Lin G, Xu H-X. Cytotoxic acylphloroglucinol derivatives from the twigs of *Garcinia cowa*. Journal of Natural Products, 2010; 73: 104-108.
6 Cheenpracha S, Phakhodee W, Ritthiwigrom T, Prawat U, Laphookhieo S. A new depsidone from the twigs of *Garcinia cowa*. Heterocycles, 2011; 83: 1139-1144.
7 Shen J, Tian Z, Yang J-S. The constituents from the stems of *Garcinia cowa* Roxb. and their cytotoxic activities. Pharmazie, 2007; 62: 549-551.
8 Shen J, Yang J. Chemical constituents of branch of *Garcinia cowa* Roxb., Zhongcaoyao, 2007; 38: 993-994.
9 Shen J, Yang J-S. A novel benzophenone from *Garcinia cowa*. Acta Chim. Sinica, 2007b; 65: 1675-1678.
10 Lihitwitayawuid K, Phadungcharoen T, Mahidol C, Ruchirawat S. 7-O-Methylgarcinone E from *Garcinia cowa*. Phytochemistry, 1997; 45: 1299-1301.
11 Lee H-H, Chan H-K. 1,3,6-Trihydroxy-7-methoxy-8-(3,7-dimethyl-2,6-octadienyl) xanthone from *Garcinia cowa*. Phytochemistry, 1977; 16: 2038-2040.
12 Wahyuni FS, Byrne LT, Dachriyanus, Dianita R, Jubahar J, Lajis NH, Sargent MV. A new ring-reduced tetraprenyltoluquinone and a prenylated xanthone from *Garcinia cowa*. Australian Journal of Chemistry, 2004; 57: 223-226.
13 Shen J, Yang J-S. Two new xanthones from the stems of *Garcinia cowa*. Chemical and Pharmaceutical Bulletin, 2006; 54 (1): 126-128; doi: 10.1248/cpb.54.126.
14 Shen J, Yang J-S. Chemical constituents from fruit of *Garcinia cowa*. Chinese Pharmaceutical Journal, 2006; 5: 660 – 661.
15 Panthong K, Hutadilok-Towatana N, Panthong A. Cowaxanthone F, a new tetraoxygenated xanthone, and other anti-inflammatory and antioxidant compounds from *Garcinia cowa*. Canadian Journal of Chemistry, 2009; 87: 1636-1640.
16 Jayaprakasha GK, Jena BS, Rao LJM, Varadaraj MC. A process for the isolation of cambogin from *Garcinia cowa*. Indian Patent, 2010; No. 242799.
17 Panthong K, Pongcharoen W, Phongpaichit S, Taylor WC. Tetraoxygenated xanthones from the fruits of *Garcinia cowa*. Phytochemistry, 2006; 67: 999-1004.
18 Jena BS, Jayaprakasha GK, Sakariah KK. Organic acids from leaves, fruits, and rinds of *Garcinia cowa*. Journal of Agricultural and Food Chemistry, 2002; 50 (12): 3431-3434; Doi: https://doi.org/10.1021/jf011627j.
19 Sakunpak A, Panichayupakaranant P. Antibacterial activity of Thai edible plants against gastrointestinal pathogenic bacteria and isolation of a new broad spectrum antibacterial polyisoprenylated

benzophenone, chamuangone. Food Chemistry, 2012; 130: 826-831.
20 Xia Z, Zhang H, Xu D, Lao Y, Fu W, Tan H, Cao P, Yang L, Xu H. Xanthones from the leaves of *Garcinia cowa* induce cell cycle arrest, apoptosis, and autophagy in cancer cells. Molecules. 2015; 20(6): 11387–11399; doi: 10.3390/molecules200611387.
21 Mahabusarakam W, Chairerk P, Taylor WC. Xanthones from *Garcinia cowa* Roxb. latex. Phytochemistry, 2005; 66(10):1148-1153; DOI: 10.1016/j.phytochem.2005.02.025.
22 Pattalung PN, Thongtheeraparp W, Wiriyachitra P, Taylor WC. Xanthones of *Garcinia Cowa*. Planta Medica, 1994; 60: 365-368.
23 Likhitwitayawuid K, Phadungcharoen T, Krungkrai J. Antimalarial xanthones from *Garcinia cowa*. Planta Medica, 1998; 64: 70-72.
24 Trisuwan K, Ritthiwigrom T. Benzophenone and xanthone derivatives from the inflorescences of *Garcinia cowa*. Archives of Pharmacal Research, 2012; 35: 1733-1738; https://doi.org/10.1007/s12272-012-1004-z.
25 Kaennakam S, Siripong P, Tip-Pyang S. Kaennacowanols A-C, three new xanthones and their cytotoxicity from the roots of *Garcinia cowa*. Fitoterapia, 2015; 102: 171-176; DOI:10.1016/j.fitote.2015.03.008 .
26 Tayana N, Suteerapataranon S, Deachathai S. Phytochemistry and bioactive compounds from *Garcinia cowa* Roxb. Asia-Pacific Journal of Science and Technology, 2017; 22(3): 1-8. https://doi.org/10.14456/apst.2017.37.22 .
27 Macwan C. *Paederia foetida* Linn. as a potential medicinal plant : a review. Journal of Pharmacy Research, 2010; 3(12): 3135-3137.
28 Chanda S, Sarethy IP, De B, Singh K. *Paederia foetida* - a promising ethno- medicinal tribal plant of northeastern India. Journal of Forestry Research, 2013; 24 (4): 801-808; DOI:10.1007/s11676-013-0369-2.
29 Ojha S, Raj A, Roy A, Roy S. Extraction of total phenolics, flavonoids and tannins from *Paederia foetida* L. leaves and their relation with antioxidant activity. Pharmacognosy Journal, 2018; 10(3): 541-547.
30 Wang L, Jiang Y, Han T, Zheng C, Qin L. A phytochemical, pharmacological and clinical profile of *Paederia foetida* and *P. scandens*. Natural Product Communications, 2014; 9(6): 879-886.
31 Wong KC, Tan GL. Steam volatile constituents of the aerial parts of *Paederia foetida* L. Flavour and Fragrance Journal, 1994; 9(1): 25-28; https://doi.org/10.1002/ffj.2730090106.
32 Shukla YN, Lloyd HA, Morton JF, Kapadia GJ. Iridoid glycosides and other constituents of *Paederia foetida*. Phytochemistry, 1976; 15(12): 1989-1990.
33 Osman H, Rahim AA, Isa NM, Bakhir NM. Antioxidant Activity and phenolic content of *Paederia foetida* and *Syzygium aqueum*, Molecules, 2009; 14(3): 970-978; https://doi.org/10.3390/molecules14030970.
34 Kumar V, Yadav Pankajkumar S, Singh UP, Bhatt HR, Zaman K, Ali M. Isolation of new racemic sugar (D/L galacturonic acid) from leaves of *Paederia foetida* Linn. Nature Precedings, 2011, DOI: http://dx.doi.org/10.1038/npre.2011.5752.1.
35 Rosli NHM, Tajuddin NA, Shafi S. Preliminary study: vitamin C in *Paederia foetida* leaves. The Open Conference Proceedings Journal, 2013; 4 (Suppl-2, M3): 9-11.
36 Uddin N, Hossain MK, Haque MR, Hasa CM. Cheimcal investigation of *Paederia foetida* (Rubiaceae). Asian Journal of Chemistry, 2013; 25(2): 1163.
37 Dwivedi J, Gupta A, Verma S, Dwivedi M, Paliwal S, Rawat AKS. Validated high- performance thin-layer chromatographic analysis of ursolic acid and β-sitosterol in the methanolic fraction of *Paederia foetida* L. leaves. JPC - Journal of Planar Chromatography -Modern TLC, 2018; 31(5): 377 – 381; DOI 10.1556/1006.2018.31.5.5.
38 Begum SS, Gogoi R. Herbal recipe prepared during Bohag or Rongali Bihu in Assam. Indian Journal of Traditional Knowledge, 2007; 6: 417-422.
39 Junejo JA, Singh KH, Islam J, Mondal P, Zaman K. Phytochemical analysis and in vivo toxicity evaluation of green vegetable *Tetrastigma angustifolia* (Roxb.) leaves. Asian Journal of Biological and Life Science, 2016; 5 (2): 105 – 111.
40 Narzary H, Swargiary A, Basumatary S. Proximate and vitamin C analysis of wild edible plants consumed by Bodos of Assam, India. Journal of Molecular Pathophysiology, 2015; 4(4): 128-133; doi: 10.5455/jmp.20151111030040.
41 Yang D, Liu H, Li X, Huang X, Qin J. Chemical constituents of *Tetrastigma hemsleyanum* Diels. et Gilg. Zhongguo Zhong Yao Za Zhi, 1998; 23(7): 41921, 4478.
42 Ahmadu AA, Onanuga A, Aquino R. Flavonoid glycosides from the leaves of *Cissus ibuensis* Hook (Vitaceae). African Journal of Traditional, Complementary and Alternative Medicine, 2010; 7(3): 225–230.
43 Jina M-N, Shia G-R, Tanga S-A, Wei Qiaoa N-Q, Duana H-Q. Flavonoids from *Tetrastigma obtectum* enhancing glucose consumption in insulin-resistance HepG2 cells via activating AMPK. Fitoterapia, 2013; 90: 240–246.
44 Li B, Liao GF, Huang YL, Chen JH. Chemical constituents of ethyl acetate fraction of *Tetrastigma planicaule*. Zhong Yao Cai, 2014; 37(4): 610-611.
45 Fan SM, Huang ZH, Lin J, Huang XC, Xu YF, Xu W. Separation and quantitative determination of four flavonoids in *Tetrastigma hemsleyanum*. Zhong Yao Cai, 2014; 37(12): 2226-2230.
46 Junejo JA, Mondal P, Verma VK, Rudrapal M, Zaman MK. Anti-diabetic assessment of the hydro-alcoholic leaf extracts of the plant *Tetrastigma angustifolia* (Roxb.), a traditionally used North-

Eastern Indian vegetable. Biomedical and Pharmacology Journal, 2014; 7(2): 635–644.
47 Mir SR, Ali M, Waris M, Sultana S. Chemical constituents from the fruits of *Withania coagulans* (Stocks) Dunal. Trends in Phytochemistry Research, 2020; 4(2): 45-58.
48 Sultana S, Ali M, Mir SR. Chemical constituents from the leaves of *Callistemon lanceolatus* (Sm.) Sweet. European Journal of Pharmaceutical and Medical Research, 2020; 7(6): 692-701.
49 Ali M, Sultana S. Composition of essential oils of *Cuminum cyminum* unripe fruits, *Piper betle* variety *Bangla* leaves and *Vitex negundo* leaves, flowers and fruits. European Journal of Pharmaceutical and Medical Research, 2019; 6(12): 394-401.
50 Ali M, Jameel M, Mir SR, Ahmad ZZ, Patel KA. Chemical composition of essential oils of the flowers of *Clerodendrum phlomidis* L. f. and *Plumeria alba* L. European Journal of Pharmaceutical and Medical Research, 2020; 7(6): 738-742.
51 Mabry TJ, Markham KR, Thomas MB. The systemic identification of flavonoids, New York, Springer- Verlag, 1970; 41-64.
52 Harborne JB, Williams CA. Flavone and flavonol glycosides, In: The Flavonoids, Harborne JB, Mabry TJ, Mabry H. London, Chapman and Hall, 1975.