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CHEMICAL CONSTITUENTS FROM THE BARK OF *ALBIZIA LEBBECK* (L.) BENTH., AND WHOLE PLANTS OF *ANDROGRAPHIS PANICULATA* (BURM. F.) NEES AND *PARTHENIUM HYSTEROPHORUS* L.

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ABSTRACT

Albizia lebbeck (L.) Benth. (family Fabaceae) is a fast-growing, medium-sized deciduous tree. Its stem bark is used to treat allergic disorders, anxiety, depression, diarrhoea, dysentery, flu, eye, genital, liver, lung and skin diseases, gingivitis, gonorrhoea, helminth infection, leucorrhoea, paralysis, piles, spermatorrhoea, animals bites and stings and wounds. *Andrographis paniculata* (Burm.f.) Nees (family Acanthaceae) is an annual, branched, erect, herbaceous plant. The plant is used to treat allergies, respiratory, liver, skin and stomach diseases, cholera, diabetes, dysmenorrhoea, gonorrhoea, scalp hair loss, influenza, insect and snake bites, kidney problems, leucorrhoea, malaria, osteoarthritis, piles, rabies, sinusitis, sore throat, sprain, syphilis, tuberculosis, ulcers, worms and wounds. *Parthenium hysterophorus* L. (family Asteraceae) is the worst toxic weeds responsible for severe human and animal health disorders, such as dermatitis, asthma, bronchitis, skin lesions, watery eyes, swelling and itching of the membranes of the mouth and nose, coughing, continually running nose, sneezing, itching of the mouth and fatigue. Our study was planned to isolate chemical constituents from the methanolic extracts of these plants and to characterize their structures on the basis spectral data analysis. Phytochemical investigation of the stem bark of *Albizia lebbeck* led to isolate a di-β-D-glycoside identified as β-D-glucopyranosyl-(6→1′)-O-β-D-glucopyranoside (**1**). The methanolic extract of the whole plant of *Andrographis paniculata* afforded two aliphatic alcohols recognized as *n*-triacont-3,7,11,15,19,23-hexaene-1-ol (**2**), a new aliphatic unsaturated higher alcohol and heneitriacontan-1-ol (**3**), a rare aliphatic higher alcohol. The methanolic extract of the whole plant of *Parthenium hysterophorus* furnished a sesquiterpene lactone characterized as 1β-hydroxy-12,14-dihydroparthenin-15-olyl oleate (**4**), a new pseudoguainolide.

KEYWORDS: *Albizia lebbeck* stem bark, *Andrographis paniculata* plant, *Parthenium hysterophorus* plant, phytoconstituents, isolation, characterization.

INTRODUCTION

Albizia lebbeck (L.) Benth., syn. *Acacia lebbeck* (L.) Willd., *Acacia speciosa* (Jacq.) Willd. and *Mimosa lebbeck* L. (Fabaceae), known as shirish, Indian walnut and fry wood, is distributed in Indomalaya, India, Indonesia, Sri Lanka, Thailand, tropical Africa, and northern Australia. It is a fast-growing, medium-sized deciduous tree with bipinnate, alternate, stipulate leaves; flowers are white, bisexual, very fragrant; fruit is a 15–30 cm long, flat, oblong, compressed, reddish-brown pod; seeds 6 -12, ovate, brown, flattened.[1] Its fruits are toxic. Bark extract is used against conception in women. The stem bark, flowers and seeds are anti-asthmatic, antimicrobial, astringent, antiallergic, antiinflammatory, antianaphylactic, antispermatogenic, antiandrogenic, antitoxin, anti-tubercular, astringent, blood purifier, cardiotonic, digestive, hypocholesterolemic, psychoactive and tonic; used to treat allergic disorders, anxiety, asthma, boils, cough, depression, diarrhoea, dysentery, eczema, edema, eye problems, flu, genital diseases, gingivitis, gonorrhoea, helminth infection, high blood cholesterol, insect bites, jaundice, leprosy, leucoderma, leucorrhoea, liver and lung problems, paralysis, allergic rhinitis, pectoral problems, piles, ringworms, skin diseases, spermatorrhoea, stress, swellings, abdominal tumours, vagina infections, venomous animals bites and stings and wounds.[1-3] Its root bark is effective to cure bronchitis, blood and gum related diseases, inflammation, itching, leucoderma, piles and skin diseases.[4]

The *A. lebbeck* roots possessed lupeol, steroids, 4-hydroxy-3-methoxycinnamic acid, *p*-coumaric acid, echinocystic acid glycoside, fatty esters and acids, isotriacontanol, salicylic acid-2-O-β-D-glucofuranosyl-6′-octadec-9′′-enoate, lebbeksterone, *n*-tricontan-10α-ol,[5-7] and saponin.[8] The bark yielded albiziasaponins A, B, and C, flavonoids, lebbecacidin, friedelin, β-sitosterol, acacic acid lactone 3-O-glycoside, anthraquinone glycosides and betulinic acid derivatives.[9,10] The heartwood contained melanoxetin, d-pinitol, okanin, leucopelangonidin, melacacidins and lebbecacidin.[11] The leaves afforded flavonoids, N-benzoyl-L-phenylalaninol, friedelan-3-one, steroids, albigenin, albizziahexoside, cardiac glycosides, 4′-0-methyl rutin, triterpene saponins and β-sitosterol.[12] The seeds yielded budmunchiamine alkaloids.[13,14] The flowers gave flavonoids including quercetin.[15]

Andrographis paniculata (Burm.f.) Nees (family Acanthaceae), known as Kalmegh, Kirayat, and green chiretta, is distributed in south-eastern Asia including India, Java, Malaysia, Indonesia, the West Indies, Philippines and Thailand. It is an annual, branched, erect, 30-90 cm tall herbaceous plant , stem quadrangular; leaves opposite, sessile or subsessile, linear- lanceolate, acute, glabrous or minutely puberulous beneath, base cuneate, margin undulate; flowers pedicelled, bi-lipped, purple and solitary; fruit an oblong, glabrous capsule; seeds are subquadrate, yellow to brown and rugose. Andrographis is used as an analgesic, anodyne, antiandrogenic, antifertility, anti-HIV, antihypertensive, antiinflammatory, antileishmanial, antimicrobial, antispasmodic, astringent, blood purifier, cytotoxic, diuretic, expectorant, febrifuge, hepatoprotective, hypoglycemic, immunosoppressive, insecticide, bitter tonic, vermifuge and to treat allergies, asthma, boils, bronchitis, common cold, cholera, colic, constipation, coughs, cuts, diabetes, diarrhoea, dysentery, dysmenorrhoea, intestinal gas, gastroenteritis, gonorrhoea, scalp hair loss, influenza, insect and snake bites, itchiness, jaundice, kidney problems, leprosy, leucorrhoea, liver disorders, loss of appetite, malaria, Mediterranean fever, osteoarthritis, piles, pneumonia, rabies, sinusitis, skin diseases, sore throat, sprain, stomach pain, syphilis, throat infection, tonsillitis, tuberculosis, ulcerative colitis, ulcers, worms and wounds.[3,16] Leaf powder mixed with boiled rice and cow's milk is taken orally to control diabetes. Leaf juice is drunk during menstruation to prevent excessive bleeding. A leaf extract mixed with turmeric juice is ingested against intestinal worms. A leaf and turmeric paste is applied to eradicate skin lice and to cure skin ailments. A cake prepared from the Andrographis leaves and grains of *Eleusine coracana* is taken to overcome gastrointestinal disorders, inflammation and microbial infections. [3]A root decoction is given to calm down rheumatic pains. A decoction of the Andrographis roots with the leaves of *Tiliacora acuminata* is effective to relieve stomach-aches.[3] In Veterinary medicine, juice of the whole plant and leaves mixed with pepper and garlic is fed to cattle to cure epilepsy; a root paste is given to cure insect bite; leaves along with those of *Vitex negundo*, *Cardiospermum halicacabum* or roots of *Agave americana*, tubers of *Curculigo orchioides* and *Urginea indica* are pounded and extract is given to relieve ephemeral fever.[3]

The Andrographis plant contained neoandrogrpholide and andrographolide analogues[17-23], 7-*O*-methylwogonin, apigenin, onysilin and 3,4-dicaffeoylquinic acid, 5,7,2',3'-tetramethoxyflavanone, 5-hydroxy-7,2',3'-trimethoxyflavone, other flavonoids, 14-deoxy-15-isopropylidene-11,12-didehydro and-rographolide, [24-27] 19-*O*-β-D-glucopyranosyl-*ent*-labda-8(17),13-dien-15,16,19-triol. [28] The leaves contained andrographolides, β-sitosterol, stigmasterol, 14-deoxyandrographolide, 14-deoxy-12-hydroxyand-rographolide, chlorophyll a, neoandrographolide, 1,5-dimethyl-1,5-cyclooctadiene, 2-hydroxyethyl benzoate, α-amyrin acetate, triacylglycerols, lupeol, α-amyrin, β-amyrin and squalene,[29-31] 3, 13, 14, 19-tetrahydroxy-*ent*-labda-8 (17),11-dien-16, 15-olide, and 3, 19-isopropylidene-14-deoxy-*ent*-labda-8 (17), 13-dien-16, 15-olide.[32] The roots afforded andrographidine A and andrographidines B – F,[33] flavones,[34] flavanones, dihydroneobaicalein, andrographidine A-C, diterpenoids, trans-cinnamic acid, 4-hydroxy-2-methoxycinna-maldehyde, oleanolic acid, β-sitosterol and β-daucosterol,[35] skullcapflavone I, stigmasterol, trans-cinnamate esters, 5,2'-dihydroxy-7,8- dimethoxyflavone and β-sitosteryl fatty acid esters.[30,31] The roots gave andrographine, panicoline, apigenin – 7,4'-di-O-methyl ether, andrographolide, α-sitosterol, flavanone and flavone analogues. The pods furnished monogalactosyl diacylglycerols, lupeol, β-sitosterol and triacylglycerols.[30,31] The stem possessed flavones,[34] 14-deoxyandrographolide, neoandrographolide, squalene, polyprenol, lutein, chlorophyll a, β-sitosterol, stigmasterol and 1,5-dimethyl-1,5-cyclooctadiene.[30,31]

Parthenium hysterophorus L. (family Asteraceae), commonly known as Santa Maria feverfew, famine weed, carrot grass, congress grass, Parthenium weed, bitter weed, false camomile and ragweed, is a native to the American tropics and the West Indies. It is a common invasive species in India, Australia and parts of Africa.[36] It is an aggressive, ubiquitous, annual, ephemeral, much-branched, erect, up to 1.5 m tall herbaceous plant; leaves basal rosette, mature stems are greenish and longitudinally grooved, hirsute, alternate; flowers numerous, small flower-heads, white or cream, arranged in clusters at the tips of the branches. The herb is noxious growing vigorously especially in warmer climates. It is one of the worst toxic weed responsible for severe human and animal health issues, such as dermatitis, asthma, bronchitis, skin lesions, watery eyes, swelling and itching of the membranes of the mouth and nose, constant coughing especially at night, continually running nose and sneezing, itching of the roof of the mouth and fatigue. Allergy-prone people are particularly

susceptible to both the dermatitis and respiratory problems. If eaten, it causes mouth ulcers with excessive salivation. Significant amount (10–50%) of this weed in the diet can kill cattle. In addition, it causes anorexia, pruritus, alopecia, diarrhoea and eye irritation in dogs. It also causes acute illness, when bitter milk and tainted meat from buffaloes, cows and goats, are fed on grass mixed with parthenium. The parthenium extract results in significant reduction of rat WBC count which signifies its immune system weakening ability. The pollen grains, airborne dried plant parts and roots of parthenium cause various allergies like contact dermatitis, hay fever, asthma and allergic bronchitis in human beings. Contact of plant with the body causes dermatitis. The parthenium pollen grains inhibit fruit set in tomato, brinjal, beans and other crop plants.[37] It is a germination and radical growth inhibitor in a variety of dicot and monocot plants. The weed affects nodulation in legumes due to inhibition of activity of nitrogen fixing and nitrifying bacteria, namely, *Rhizobium, Actinomycetes, Azotobacter*, and *Azospirillum.* Parthenium produces enormous numbers of pollens which are carried away in clusters of 600–800 grains, and settles on the vegetative and floral parts inhibiting fruit setting in crops like tomato, brinjal, beans, capsicum and maize. In India, *P. hysterophorus* causes a yield decline of up to 40% in agricultural crops.[38.39] It can be used as green manure, compost, soil improver and as a bioherbicide. It is a remedy for skin inflammation, rheumatic pain, diarrhoea, urinary tract infections, dysentery, malaria and neuralgia. Other potential uses include removal of heavy metals, substrate for commercial enzyme production and additives in cattle manure for biogas production.[40]

P. hysterophorus contained a bitter glycoside parthenin, hysterin, ambrosin, hymenin, coronopilin, dihydroisoparthenin, hysterophorin and tetraneurin, fumaric acid;[39,40] *p*-hydroxy-benzoic, vanillic, caffeic, *p*-courmaric, p-anisic, chlorogenic, neochlorogenic, protocatechuic and ferulic acids, sitosterol and alcohols,[41-44] a sesquiterpenoid, charminarone,[45] flavonoids quercetagetin-3,7-dimethyl ether, apigenin, kaempferol-3-O-glucoside, quercetin-3-O-glucoside, kaempferol-3-O-glucoarabinoside, luteolin, lignin, jaceidin, syringaresinol, santin, chrysoeriol, kaempferolglucoside, centaureidin, 6-hydroxykaempferol-3,6-dimethyl ether, tanetin (6-hydroxykaempferol-3,6,4-trimethyl ether), quercetinglucoside, 6-hydroxykempferol-3,7-dimethylether and 6-hydroxy kaempferol 3-O-glucoarabinoside.[39,40,46-48] The major chemical constituents of the essential oils included geraniol, germacrene-D, myrcene, α-fernesene, β-caryophyllene, trans-β-ocimene, carotol, caryophyllene oxide, and 1-octen-3-ol are the major constituents.[49,50] The pollens furnished a hydroxyproline-rich glycoprotein as the major allergen.[51] The flowers of *P. hysterophorus* afforded acetylated pseudoguaianolides along with several known constituents, deacetyltetraneurin A, hysterone A-E parthenin, coronopilin, tetraneurin A, 8-*β*-hydroxycoronopilin, scopoletin, conchasin A, 10α-hydroxyparthenin, 2,3-dihydro-10α-hydroxyparthenin, 2β-hydroxycoronopilin, conchasin A, 15-deacetyl tetraneurin A and 3β-acetoxyneoambrosine.[52-54] The leaves possessed 11β*H*,13-dihydroparthenin, 13-methoxy- 11, 13-dihydroambrosin and 13-methoxy-11,13-dihydroparthenin.[55,56]

The presence of herbal chemical constituents vary due to many factors such as geographic regions, soils, seasonal changes, plant species and application of fertilizers. Keeping in views the various therapeutic values and variation aspects of chemical constituents of the plants and development of ecofriendly, biodegradable and safer herbal preparations, it has been aimed to establish chemical structures of phytoconstituents isolated from the bark of *Albizia lebbeck* and the whole plants of *Andrographis paniculata* and *Parthenium hysterophorus*.

MATERIALS AND METHODS

The protocols of all methodologies (procedures, experimental designs and spectral data analysis) were adopted from the earlier published work. [6, 10, 57]

Collection and authentication of plant materials

The bark of *Albizia lebbeck* and the whole plant of *Andrographis paniculata* were purchased from the local Khari Baoli market of Delhi. The whole plant of *Parthenium hysterophorus* was collected from a wild field of Delhi. The plant materials were identified and authenticated by Prof. M. P. Sharma, Taxonomist, Department of Botany, Jamia Hamdard, New Delhi. Voucher specimens of the plant materials were preserved in the herbarium of the Department of Pharmacognosy and Phytochemistry, Jamia Hamdard, New Delhi.

Extraction and isolation

The bark of *A. lebbeck* and the whole plants of *A. paniculata* and *P. hysterophorus* (1 kg each) were dried in air, coarsely powdered and extracted separately and exhaustively with methanol in a Soxhlet apparatus. The extracts were concentrated under reduced pressure to get dark brown masses, 121.7 g, 167.6 g and 158.3 g, respectively. Each dried residue (100 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, 19:1, 9:1, *v/v*) mixtures. 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 a phytoconstituent from the bark of *Albizia lebbeck*

β-D-Glucopyranosyl-(6→1′)-O- β-D-glucopyranoside (1)

Elution of the column with chloroform – methanol (9:1) afforded a colourless powder of **1**, recrystallized from ethanol, yield 193 mg, m. p. 160 - 162 °C; IR υ_{max} (KBr): 3518, 3278, 2921, 2883, 1442, 1375, 1327, 1138, 1045, 1003, 945, 838, 794 cm^{-1}; ^1H NMR (DMSO-d_6): δ 4.77 (1H, d, J = 7.2 Hz, H-1), 4.26 (1H, m, H-5), 3.96 (1H, m, H-2), 3.83 (1H, m, H-3), 3.74 (1H, m, H-4), 3.51 (1H, d, J = 9.1 Hz, H_2-6), 4.72 (1H, d, J = 7.1 Hz, H-1′), 4.18 (1H, m, H-5′), 3.89 (1H, m, H-2′), 3.77 (1H, m, H-3′), 3.71 (1H, m, H-4′), 3.12 (1H, d, J = 8.9 Hz, H_2-6′); ^{13}C NMR ($CDCl_3$): δ 100.18 (C-1), 74.98 (C-2), 71.37 (C-3), 68.39 (C-4), 76.63 (C-5), 61.12 (C-6), 98.77 (C-1′), 73.26 (C-2′), 69.91 (C-3′), 66.69 (C-4′), 75.14 (C-5′), 60.34 (C-6′); +ve ESI MS *m/z* (rel. int.): 342 $[M]^+$ ($C_{12}H_{22}O_{11}$) (9.1), 179 (22.8), 163 (15.4).

Isolation of phytoconstituents from the whole plant of *Andrographis paniculata*

***n*-Triacont-3,7,11,15,19,23- hexaene-1-ol (2)**

Elution of the column with petroleum ether - chloroform mixture (1: 3) produced a pale yellow semisolid mass of **2**, yield 157 mg; IR υ_{max} (KBr): 3364, 2928, 2849, 1649, 1404, 1385, 1272, 1091, 755 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.06 (2H, m, H-3, H-4), 5.03 (4H, m, H-7, H-8, H-11, H-12), 5.01 (4H, m, H-15, H-16, H-19, H-20), 4.99 (2H, m, H-23, H-24), 3.19 (2H, t, J = 5.8 Hz, H_2-1), 2.21 (4H, m, H_2-2, H_2-6), 2.19 (4H, m, H_2-9, H_2-14), 2.11 (2H, m, H_2-18), 2.08 (4H, m, H_2-21, H_2-22), 2.01 (2H, m, H_2-25), 1.85 (2H, m, H_2-26), 1.56 (2H, m, H_2-27), 1.32 (2H, m, H_2-28), 1.24 (2H, m, H_2-29), 0.85 (3H, t, J = 6.5 Hz, Me-30); ESI MS *m/z* (rel. int.): 426 $[M]^+$ ($C_{30}H_{50}O$) (46.2).

Heneitriacontan-1-ol (3)

Elution of the column with chloroform yielded a colourless amorphous powder of **3**, yield 119 mg, m. p. 88 - 89 °C; IR υ_{max} (KBr): 3326, 2923, 2842, 1654, 1441, 1328, 1259, 1171, 1074, 713 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.34 (2H, t, J = 6.5 Hz, H_2-1), 1.58 (4H, m, H_2-2, H_2-3), 1.42 (2H, m, H_2-4), 1.36 (2H, m, H_2-5), 1.31 (4H, m, H_2-6, H_2-7), 1.25 (46H, br s, 23 × CH_2), 0.83 (3H, t, J = 6.5 Hz, Me-31); ^{13}C NMR ($CDCl_3$): δ 66.01 (C-1), 52.30 (C-2), 34.21 (C-3), 32.18 (C-4), 30.13 (C-5), 29.75 (17 x CH_2), 29.53 (C-23), 29.46 (C-24), 29.30 (C-25), 29.16 (C-26), 29.02 (C-27), 27.51 (C-28), 26.28 (C-29), 22.68 (C-30), 14.61 (Me-31); ESI MS *m/z* (rel. int.): 452 $[M]^+$ ($C_{31}H_{64}O$) (46.2).

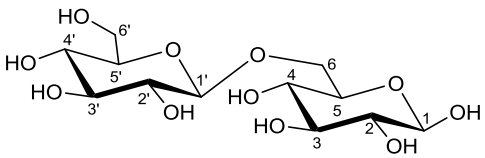
Isolation of a phytoconstituent from the whole plant of *Parthenium hysterophorus*

Hystereopholyl oleate (4)

Elution of the column with chloroform furnished a semisolid mass of **4**, yield 121 mg, IR υ_{max} (KBr): 3426, 3260, 2929, 2854, 1721, 1712, 1701, 1606, 1436, 1378, 1274, 1166, 1098, 1034, 748 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.92 (1H, d, J = 9.0 Hz, H-2), 6.90 (1H, d, J = 9.0 Hz, H-3), 4.15 (1H, d, J = 4.8 Hz, H-6α), 3.65 (1H, d, J = 6.6 Hz, H_2-15a), 3.61 (1H, d, J = 6.6 Hz, H_2-15b), 2.39 (1H, m, H-7α), 1.85 (1H, m, $w_{1/2}$ = 8.5 Hz, H-10α), 2.30 (1H, m, H-12β), 1.73 (2H, m, H_2-8), 1.69 (2H, m, H_2-9), 1.03 (3H, d, J = 7.8 Hz, Me-14), 1.01 (3H, brs, Me-11), 5.49 (1H, m, H-9′), 5.30 (1H, m, H-10′), 2.33 (2H, t, J = 7.5 Hz, H_2-2′), 2.12 (2H, m, H_2-8′), 2.08 (2H, m, H_2-11′), 1.77 (2H, m, H_2-3′), 1.59 (2H, m, H_2-7′), 1.51 (2H, m, H_2-12′), 1.24 (12H, brs, 6 x CH_2), 1.14 (8H, brs, 4 x CH_2), 0.84 (3H, t, J = 6.3 Hz, Me-18′); ^{13}C NMR ($CDCl_3$): δ 83.41 (C-1), 163.33 (C-2), 131.53 (C-3), 211.16 (C-4), 57.16 (C-5), 77.95 (C-6), 53.60 (C-7), 25.10 (C-8), 23.09 (C-9), 55.45 (C-10), 19.71 (C-11), 39.37 (C-12), 179.28 (C-13), 22.67 (C-14), 63.05 (C-15), 165.95 (C-1′), 37.39 (C-2′), 35.56 (C-3′), 34.41 (C-4′), 33.95 (C-5′), 30.84 (C-6′), 30.26 (C-7′), 36.02 (C-8′), 123.14 (C-9′), 114.04 (C-10′), 37.28 (C-11′), 29.67 (C-12′), 29.57 (C-13′), 29.33 (C-14′), 29.21 (C-15′), 29.06 (C-16′), 22.79 (C-17′), 14.07 (C-18′); ESI MS *m/z* (rel. int.) 544 $[M]^+$ ($C_{33}H_{52}O_6$) (1.2), 281 (22.3), 265 (11.7).

RESULTS AND DISCUSSION

Compound **1**, a di-β-D-glycoside, $[M]^+$ at *m/z* 342 ($C_{12}H_{22}O_{11}$), gave positive tests for glycosides and showed IR absorption bands for hydroxyl groups (3518, 3278 cm^{-1}). The ion peaks arising at *m/z* 179 [C_6 - $C_{1'}$ fission, $C_6H_{12}O_6]^+$ and 163 $[M - 179]^+$ indicated that two hexose units were linked to each other. The ^1H NMR spectrum of **1** exhibited two one-proton doublets at δ 4.77 (J = 7.2 Hz) and 4.72 (J = 7.1 Hz) assigned to anomeric H-1 and H-1′ protons, respectively, supported the existence of β-glycosidic linkage of the disaccharide unit. The other sugar protons resonated as one-proton multiplets between δ 4.26 - 3.71 and as two-proton doublets at δ 3.51 (J = 9.1 Hz) and 3.12 (J = 8.9 Hz) ascribed to oxymethylene H_2-6 and H_2-6' of the hexose units, respectively. The ^{13}C NMR spectrum of **1** displayed signals for anomeric carbons at δ 100.18 (C-1) and 98.77 (C-1′) and other sugar carbons from δ 76.63 to 60.34. The presence of the sugar methylene H_2-6 signal in the deshielded region as a two-proton doublet at δ 3.51 in the ^1H NMR spectrum and C-6 carbon signal at δ 61.12 in the ^{13}C NMR spectrum suggested (6→1′) linkage of the sugar units. Acid hydrolysis of **1** yielded D-glucose, R_f 0.26 (*n*-butanol- acetic acid – water, 4 : 1 : 5). On the basis of these evidences the structure of **1** has been formulated as β-D-glucopyranosyl-(6→1′)-O-β-D-glucopyranoside (Fig. 1).[57]



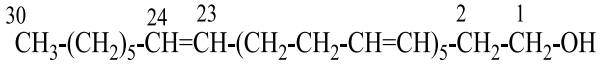
β-D-Glucopyranosyl-(6→1′)-O- β-D-glucopyranoside (1)

Fig. 1: Chemical constituent 1 isolated from the bark of *Albizia lebbeck*.

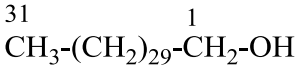
Compound **2**, $[M]^+$ at *m/z* 426 ($C_{30}H_{50}O$), exhibited IR absorption bands for a hydroxyl function (3364 cm^{-1}),

unsaturation (1654 cm^{-1}) and long aliphatic chain (755 cm^{-1}). The ^1H NMR spectrum of **2** showed four multiplets assigned to vinylic protons at δ 5.06 (H-3, H-4), 5.03 (H-7, H-8, H-11, H-12), 5.01 (H-15, H-16, H-19, H-20) and 4.99 (H-23, H-24). A two–proton triplet at δ 3.19 (J = 5.8 Hz) was ascribed to hydroxymethylene H_2-1 protons. The other methylene protons appeared as multiplets at δ 2.21 (4H), 2.19 (4H), 2.11 (2H), 2.08 (4H), 2.01 (2H), 1.85 (2H), 1.56 (2H), 1.32 (2H) and 1.24 (2H). A three-proton triplet at δ 0.85 (J = 6.5 Hz) was ascribed to primary C-30 methyl protons. On the basis of these spectral data analysis, the structure of **2** has been elucidated as *n*-triacont-3,7,11,15,19,23-hexaene-1-ol, a new aliphatic unsaturated higher alcohol (Fig. 2).

Compound **3** showed IR absorption bands for hydroxyl function (3326 cm^{-1}) and long aliphatic chain (713 cm^{-1}). Its mass spectrum had a molecular ion peak at *m/z* 452 consistent with the molecular formula of an aliphatic alcohol, $C_{31}H_{64}O$. The ^1H NMR spectrum of **3** displayed a two–proton triplet at δ 3.34 (J = 6.5 Hz) assigned to hydroxymethylene H_2-1 protons. The other methylene protons appeared as multiplets at δ 1.58 (4H), 1.42 (2H), 1.36 (2H) and 1.31 (4H) as a singlet at δ 1.25 (46H). A three-proton triplet at δ 0.83 (J = 6.5 Hz) was ascribed to primary C-31 methyl protons. The ^{13}C NMR spectrum of **3** displayed signals for the hydroxymethylene carbon at δ 66.01 (C-1), other methylene carbons in the range of δ 52.30 – 22.68 and methyl carbon at δ 14.61 (Me-31). The absence of any signal beyond δ 3.34 in the ^1H NMR spectrum and δ 66.01 in the ^{13}C NMR spectrum supported saturated nature of the molecule. On the basis of these spectral data analysis, the structure of **3** has been elucidated as heneitriacontan-1-ol, a rare aliphatic higher alcohol (Fig. 2).



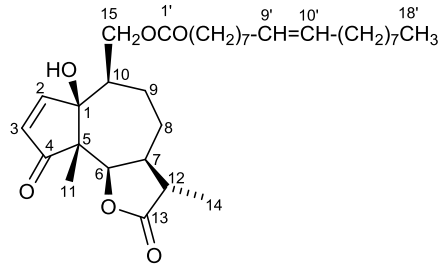
n-Triacont- 3, 7, 11, 15, 19, 23-heaxene-1-ol **(2)**



n-Heneitriacontanol **(3)**

Fig. 2: Chemical constituents 2 and 3 isolated from the whole plant of *Andrographis paniculata.*

Compound **4**, named hystereopholyl oleate, showed IR absorption bands for a hydroxyl group (3426 cm^{-1}), a lactone ring (1721 cm^{-1}), an ester function (1712 cm^{-1}), carbonyl group (1701 cm^{-1}), unsaturation (1606 cm^{-1}) and long aliphatic chain (748 cm^{-1}). On the basis of mass and ^{13}C NMR spectral data, the molecular ion peak of **4** was established at *m/z* 544 consistent with the molecular formula of a partheninolyl ester type sesquiterpenoid $C_{33}H_{52}O_6$. The ion peaks generating at *m/z* 265 [O – C_1 fission, $CH_3(CH_2)_7$-CH=CH$(CH_2)_7CO]^+$ and 281 [C_{15} – O fission, $CH_3(CH_2)_7$-CH=CH$(CH_2)_7COO]^+$ indicated that a dihydropartheninol was esterified with oleic acid. The ^1H NMR spectrum of **4** displayed two one – proton deshielded doublets at δ 7.92 (J = 9.0 Hz) and 6.90 (J = 9.0 Hz) assigned to cis-oriented vinylic H-2 and H-3 protons, respectively, and the existence of these protons in the deshielded region suggested their presence nearby the carbonyl function. Three one-proton doublets at δ 4.15 (J = 4.8 Hz), 3.65 (J = 6.6 Hz) and 3.61 (J = 6.6 Hz) were ascribed correspondingly to oxymethine H-6α and oxymethylene H_2-15 protons. Two three-proton signals as a doublet at δ 1.03 (J = 7.8 Hz) and as a singlet at δ 1.01 were attributed to secondary C-14 and tertiary C-11 methyl protons, respectively. The other sesquiterpenic protons appeared as one-proton multiplets at δ 2.39 (H-7α), 1.85 ($w_{1/2}$ = 8.5 Hz, H-10α) and 2.30 (12β) and as two-proton multiplets at δ 1.73 (H_2-8) and 1.69 (H_2-9). Two one – proton multiplets at δ 5.49 and 5.30 were due to vinylic protons H-9′ and H-10′, respectively, of the oleate unit. The other methylene protons appeared as a two-proton triplet at δ 2.33 (J = 7.5 Hz, H_2-2′) nearby the ester group, as two-proton multiplets between δ 2.12-1.59 and as broad singlets at δ 1.24 (12H) and 1.14 (8H). A three-proton triplet at δ 0.84 (J = 6.3 Hz) was accounted to primary C-18′ methyl protons. The ^{13}C NMR spectrum of **4** displayed signals for a lactone carbon at δ 179.28 (C-13), ester carbon at δ 165.95 (C-1′), vinylic carbons at δ 163.33 (C-2), 131.53 (C-3), 123.14 (C-9′) and 114.04 (C-10′), carbonyl carbon at δ 211.16 (C-4), carbinol carbon at δ 83.41 (C-1), oxymethylene carbon at δ 63.05 (C-15), oxymethine carbon at δ 77.95 (C-6) and methyl carbons at δ 19.71 (C-11), 22.67 (C-14) and 14.07 (C-18′). The DEPT spectrum of **4** showed the presence of three methyl, seventeen methylene, eight methine and five quaternary carbons. The ^1H-^1H COSY spectrum of **4** exhibited correlation of H-2 with H-3 and H-10; H-6 with H-7, H_2-8 and H_3-11; H-12 with H-7, H_2-8 and H_3-14; H_2-15 with H-10 and H_2-2′; and H-9′ with H_2-8′, H-10′ and H2-11′. The HMBC spectrum of **4** displayed interactions of H-2, H-3 and H_3-11 with C-4; H-6 and H-7 with C-5; H-7, H-12 and H_3-14 with C-13; H-2, H-10 and H_2-15 with C-1; H_2-15 and H_2-2′ with C-1′; and H_2-8′, H-9′, H_2-11′ with C-10′. The ^1H and ^{13}C NMR spectral values of **4** were compared with those of parthenin and related sesquiterpene lactones. [58-60] On the basis of these evidences, the structure of **4** has been elucidated as 1β-hydroxy-12,14-dihydroparthenin-15-olyl oleate, a new pseudoguainolide (Fig. 3).



Hysteropholyl oleate (4)

Fig. 2: Chemical constituent 4 isolated from the whole plant of *Parthenium hysterophorus.*

CONCLUSION

Phytochemical investigation of the stem bark of *Albizia lebbeck* led to isolate a di-β-D-glycoside identified as β-D-glucopyranosyl-(6→1′)-O-β-D- glucopyranoside (**1**). The methanolic extract of the whole plant of *Andrographis paniculata* afforded two aliphatic alcohols recognized as *n*-triacont-3,7,11,15,19,23-hexaene-1-ol (**2**) and heneitriacontan-1-ol (**3**). The methanolic extract of the whole plant of *Parthenium hysterophorus* furnished a new sesquiterpene lactones characterized as 1β-hydroxy-12,14-dihydroparthenin-15-olyl oleate (**4**). This work has enhanced understanding about the chemical constituents of the undertaken plants. Further research is recommended to screen bioactivities of the isolated phytoconstituents with a view for supplementing conventional drug development especially in developing countries.

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