GLYCOSIDES FROM THE LEAVES OF ARTOCARPUS HETEROPHYLLUS LAM.

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ABSTRACT

Phytochemical investigation of the leaves of Artocarpus heterophyllus furnished six compounds from different combinations of petroleum ether, chloroform and methanol. Structures of these compounds were elucidated and established by standard spectroscopic methods. Isolated compounds are n-Octadec-9-enoyl-α-L-rhamnopyranoside (1), n-octadec-9,12-dienoyl-α-L-rhamnopyranoside (2), n-octadec-9,12-dienoyl-β-D-glucopyranoside (3), n-octadec-9-enoyl-β-D-glucopyranoside (4), n-octadec-9-enoyl-β-D-arabinopyranoside (5) and n-octadec-9-enoyl-α-D-xylopyranoside (6) respectively. The structures of all the phytoconstituents are elucidated on the basis of spectral data analyses and chemical reactions.

Keywords: Artocarpus heterophyllus, Leaves, Column chromatography, Phytoconstituents

INTRODUCTION

Artocarpus heterophyllus Lam (Moraceae) commonly known as jackfruit is native to western ghats of India, Malaysia and also found in central and eastern Africa, southeastern Asia, the Caribbean, Florida, Brazil, Australia, Puerto Rico and many Pacific islands. It is a large, evergreen tree, 10-15m in height, indigenous to the evergreen forests at altitude of 450 - 1200m throughout the hotter parts of India. Stem of this plant is straight, rough whereas bark is green or black. 1.25 cm thick exuding milky latex, leaves broad obovate. Jackfruit is essentially a carbohydrate food and therefore useful as a source of energy. They contain vitamin C, protein, fat, calcium, phosphorus and iron in quantities normally present in other fruits. 2. Jackfruit (Artocarpus heterophyllus Lam) produces heavier yield than any other tree species, and bear the largest known edible fruit (up to 35 kg).

The plants of Artocarpus species have been used by traditional folk medicine in Indonesia against inflammation, malarial fever, stomachache, ulcers, abscesses, dysentery, diarrhoea, defective urinary secretion, skin disease 3-5 and asthma. 6 The plant parts contain Flavonoids 6, Terpenic compounds 7, Sapogenins 8 and Carotenoids 9. The present paper describes the isolation and characterization of six compounds from the leaves of A. heterophyllus.

MATERIAL AND METHODS

Plant material

The leaves of Artocarpus heterophyllus were collected from Patna, Bihar and identified by Dr. H.B. Singh, Scientist and Head, Niscair, NewDelhi. A voucher specimen of the plant leaves (NISCAIR/RHMD/consult/-20-09-10/1322/124) was deposited in the herbarium of NISCAIR, India.

Extraction and isolation

Dried powder of Artocarpus heterophyllus leaves (1.7 kg) was extracted with methanol (4 L) at 50 °C for 1 day. Extract was concentrated to dryness under reduced pressure to obtain slurry (148 g). The slurry was dissolved in minimum amount of methanol and was adsorbed on silica gel (60-120 mesh). The slurry was chromatographed over silica gel column packed in petroleum ether. The column was eluted successively with petroleum ether/CHCl3/Methanol gradient system (1:0.0, 1:1.0, 1:3.0, 0.1:0.0, 0.0:1.0, 0.0:1.0, 0.0:1.0, 0.0:1.0, 0.87:13 and 0.17:3; 2.0 L for each gradient system). Six different compounds were isolated at different fractions. Compound 1 (110 mg) from CHCl3, compound 2 (90 mg) from CHCl3/Methanol (2:3), compound 3 (286 mg) from CHCl3/Methanol (19:1) were obtained as pale yellow crystals; compound 4 (100 mg) from CHCl3/Methanol (9:3) was obtained as colorless crystals, compound 5 (500 mg) from CHCl3/Methanol (9:1), compound 6 (90 mg) from CHCl3/Methanol (45:7) were obtained as pale yellow crystals.

RESULT AND DISCUSSION

Characterization of compound 1

It was obtained as a pale yellow crystalline mass from chloroform eluant.

M.P. 78 – 80°C

Ref: 0.57 (Petroleum ether/CHCl3; 1:1)

 UV λmax (MeOH): 275 nm (log ε 4.8)

 IR ymax (KBr): 3415, 3320, 2927, 2857, 1727, 1606, 1454, 1376, 1252, 1217, 1081, 971, 762 cm\(^{-1}\)

1H NMR (CDCl3): 8.5.38 (1H, m, H-9), 5.36 (1H, m, H-10), 5.10 (1H, d, J= 7.0 Hz, H-1’), 4.57 (1H, m, H-5), 4.23 (1H, m, H-2), 4.07 (1H, m, H-3’), 3.75 (1H, m, H-4’), 2.72 (1H, d, J= 6.6 Hz, H-2a), 2.67 (1H, d, J= 7.5 Hz, H-2b), 2.30 (2H, m, H-8), 2.04 (2H, m, H-11), 1.68 (2H, brs, CH2), 1.60 (2H, m, CH2), 1.41 (2H, brs, CH2), 1.33 (2H, brs, CH2), 1.29 (4H, brs, 2x CH2), 1.04 (3H, d, J= 6.6 Hz, Me-6), 0.80 (3H, t, J= 6.3 Hz, Me-18).

It gave positive tests for glycosides. Its IR spectrum displayed characteristic absorption bands for hydroxyl groups (3415, 3320 cm\(^{-1}\)), ester group (1727 cm\(^{-1}\)), unsaturation (1606 cm\(^{-1}\)) and long aliphatic chain (762 cm\(^{-1}\)). On the basis of Mass spectrum of the structure of compound 1, its molecular formula was determined as C\(_{16}\)H\(_{24}\)O\(_{6}\). It indicated three double bond equivalents which were adjusted one each in the vinyl linkage, ester group and sugar unit. The 1H-NMR spectrum of compound 1 showed two one proton- multiplets at 8 5.38 and 5.36 assigned to vinylic H-9 and H-10 respectively. A one proton doublet at 8 5.10 with coupling interaction of 7.0 Hz was ascribed to anemic H-1’ proton. Four one-proton multiplets at 8 4.57, 4.23, 4.07 and 3.75 were due to carbinol proton of the sugar unit. Two proton doublets at 8 2.72 (J=6.6 Hz) and 2.67 (J=5.5Hz) were attributed to methylene H-2 protons adjacent to the ester groups. The remaining methylene protons resonated as two proton multiplets at 8 2.30, 2.04 and 1.60 and as broad signals from 8 1.68 to 1.25. A three proton doublet at 8 1.04 (J=6.6 Hz) and a three proton triplet at 8 0.90 (J=6.3 Hz) were accounted to secondary methyl Me-6’ and primary methyl Me-18 protons.

Acid hydrolysis yielded Oleic acid and D-rhamnose (C\(_{6}\)H\(_{10}\)O\(_{5}\)). On the basis of spectral data analysis and chemical reactions, the structure of compound 1 is elucidated as n-octadec-9-enoyl α-L-rhamnopyranoside.
Characterization of compound 2

It was obtained as Pale yellow crystalline mass in chloroform: Methanol (23:2) eluants.

**M.P.** 75 – 76°C

**Rf:** 0.85 (CHCl₃/Methanol 19:1)

**UV λmax (MeOH):** 276 nm (log ε 2.1), 3393, 3335 cm⁻¹.

**IR γmax (KBr):** 763, 1978, 1024, 7576 cm⁻¹.

**Rf:** 0.85: 19:1 eluant.

**M.P.:** 1219, 1078, 768 cm⁻¹.

**Fig. 1: n-octadec-9-enoyl α-L-rhamnopyranoside**

It gave positive tests for glycosides. Its IR spectrum showed characteristic absorption bands for hydroxyl group at 3450, and 3393, ester group at 1721 cm⁻¹, unsaturation at 1657 cm⁻¹ and long aliphatic chain. On the basis of mass spectrum, the molecular formula of compound 2 was determined as C₂₀H₄₀O₆. The 1H-NMR spectrum showed four one-proton multiplets at δ 5.40, 5.35, 5.33 and 5.25 assigned to vinylic H-13, 12, 10 and H-9 protons, respectively. A one proton doublet at δ 65.10 (J=7.1 Hz) was due to anomeric H-1' proton. The other sugar protons appeared as multiplets between δ 4.66-3.77. A two proton multiplet at δ 2.76 was ascribed to methylene H-11 protons located between two vinylic carbons. Two one–proton doublets at δ 2.32 (J=7.2 Hz) and 2.27 (J=7.2 Hz) were accounted to methylene H-2 protons adjacent to the ester group. The other methylene proton appeared from δ 3.77 to 2.04. A three proton doublet at δ 1.04 (J=7.8 Hz) and a three proton triplet at δ 0.87 (J=6.6 Hz) were due to tertiary methyl protons. Acid hydrolysis yielded linoleic acid and L-rhamnose. On the basis of the above discussion, the structure of compound 2 has been characterized as n-octadec-9, 12-dienoyl-α-L-rhamnopyranoside.

**Characterization of compound 3**

It was obtained as Pale yellow crystals from chloroform: Methanol (19:1) eluants.

**M.P.:** 76 – 77°C

**Rf:** 0.87 (CHCl₃/Methanol 19:1)

**UV λmax (MeOH):** 271 nm (log ε 2.3), 3393, 3335 cm⁻¹.

**IR γmax (KBr):** 763, 1978, 1024, 7576 cm⁻¹.

**Characterization of compound 3**

It was obtained as Pale yellow crystals from chloroform: Methanol (19:1) eluants.

**M.P.:** 76 – 77°C

**Rf:** 0.87 (CHCl₃/Methanol 19:1)

**UV λmax (MeOH):** 271 nm (log ε 2.3), 3393, 3335 cm⁻¹.

**IR γmax (KBr):** 763, 1978, 1024, 7576 cm⁻¹.

**Characterization of compound 3**

It was obtained as Pale yellow crystals from chloroform: Methanol (19:1) eluants.

**M.P.:** 76 – 77°C

**Rf:** 0.87 (CHCl₃/Methanol 19:1)

**UV λmax (MeOH):** 271 nm (log ε 2.3), 3393, 3335 cm⁻¹.

**IR γmax (KBr):** 763, 1978, 1024, 7576 cm⁻¹.

**Characterization of compound 3**

It was obtained as Pale yellow crystals from chloroform: Methanol (19:1) eluants.

**M.P.:** 76 – 77°C

**Rf:** 0.87 (CHCl₃/Methanol 19:1)

**UV λmax (MeOH):** 271 nm (log ε 2.3), 3393, 3335 cm⁻¹.

**IR γmax (KBr):** 763, 1978, 1024, 7576 cm⁻¹.

**Characterization of compound 3**

It was obtained as Pale yellow crystals from chloroform: Methanol (19:1) eluants.

**M.P.:** 76 – 77°C

**Rf:** 0.87 (CHCl₃/Methanol 19:1)

**UV λmax (MeOH):** 271 nm (log ε 2.3), 3393, 3335 cm⁻¹.

**IR γmax (KBr):** 763, 1978, 1024, 7576 cm⁻¹.

**Characterization of compound 3**

It was obtained as Pale yellow crystals from chloroform: Methanol (19:1) eluants.

**M.P.:** 76 – 77°C

**Rf:** 0.87 (CHCl₃/Methanol 19:1)

**UV λmax (MeOH):** 271 nm (log ε 2.3), 3393, 3335 cm⁻¹.

**IR γmax (KBr):** 763, 1978, 1024, 7576 cm⁻¹.
Characterization of compound 4

It was obtained as colourless crystalline mass in chloroform: Methanol (93:7) eluants.

M.P.: 88–90°C

RF: 0.17 (CHCl3/MeOH, 19:1)

UV λmax (MeOH): 204 nm (log ε 2.6)

IRγmax (KBr): 3480, 3376, 3255, ester function (1722) cm⁻¹; and 3255, ester group at 1725 cm⁻¹, unsaturation at 1667 cm⁻¹ and long aliphatic chain at 769 cm⁻¹. On the basis of mass spectrum, the molecular formula of compound 4 was determined as C₇₇H₁₀₀O₄. It has three double bonds equivalents, each of them were adjusted in the vinylic linkage, ester group and glycosidic unit. The ¹H-NMR spectrum showed a two-proton multiplets at δ 5.36 assigned to vinylic H-9 and H-10. A one proton doublet at δ 85.03 (J=7.1 Hz) was due to anomeric H-1' proton. The other sugar protons appeared as multiplets between δ 4.87- 3.70 and one proton doublets at δ 3.41 (J=6.9 Hz) and 3.36 (J=7.2 Hz) due to hydroxymethylene H₂-6' protons.

Two one proton doublets at δ 2.41 (J=7.8 Hz) and 2.36 (J=8.4 Hz) were attributed to methylene H₂-2' protons adjacent to the ester function. Four two – proton multiplets between δ 2.20 - 1.58 and two broad signals at δ 1.31(4Hz) and 1.25 (14Hz) were associated with the other methylene protons. A three proton triplet at δ 0.82 (J=6.9 Hz) was due to terminal C-18 primary methyl protons. Acid hydrolysis of compound 4 yielded oleic acid and D-glucose. On the basis of above discussion, the structure of compound 4 has been characterized as n-octadec-9-enoyl-β-D-glucopyranoside.

Characterization of compound 5

It was obtained as Pale yellow crystalline mass in chloroform: Methanol (9:1) eluants.

M.P.: 93–95°C

RF: 0.25 (CHCl₃/MeOH, 19:1)

UV λmax (MeOH): 204 nm (log ε 2.6)

IRγmax (KBr): 3410, 3360, 2920, 2855, 1721, 1625, 1440, 1220, 1105, 770 cm⁻¹

¹H NMR (CDCl₃): δ 5.35 (2H, m, H-9, H-10), 4.94 (1H, d, J=10.8 Hz, H-1), 4.30 (1H, d, J=9.3, 10.8Hz,H-2'), 3.92 (1H, m, H-3'), 3.83 (1H, m, H-4'), 3.66 (1H, d, J=8.2Hz, H-5'a), 3.6 (1H,d, J=10.2 Hz, H-5'b), 2.30 (1H,d, J=9.6Hz,H-2'a), 2.27 (1H, d, J=9.5 Hz, H-2'b), 2.18 (2H, m, H-8), 2.05 (2H, m, H-11), 1.64 (2H, m, CH₂), 1.59 (2H, m, CH₂), 1.41 (2H, m, CH₂), 1.28 (6H, brs,2x CH₃), 1.25 (12H, brs,6x CH₃). 0.87 (3H, t, J=6.5 Hz, Me-18).

It responded positively to glycosidic units. Its IR spectrum showed characteristic absorption bands for hydroxyl groups at 3408, 3365 cm⁻¹, ester function (1722) cm⁻¹, unsaturation at 1603 cm⁻¹ and long aliphatic chain at 768 cm⁻¹. On the basis of mass spectrum, the molecular formula of compound 5 was determined as C₇₇H₁₀₀O₄. It has three double bonds equivalents, each of them were adjusted in the vinylic linkage, ester group and glycosidic unit. The ¹H-NMR spectrum of compound 5 showed a two-proton broad signal at δ 5.35 assigned to vinylic H-9 and H-10 protons. A one proton doublet at δ 84.94 (J=1.08 Hz) was due to anomeric H-1' proton. A one proton double doublet at δ 8.40 (J=9.3, 10.8Hz) and two one proton doublets at δ 3.92 and 3.83 and two one proton doublets at δ 3.66 (J=8.1Hz) and 3.60 (J=10.2Hz) were attributed to carbinol protons H-2', H-3' and H-4' and to oxygenated methylene H₂-5' protons, respectively.

Two one proton doublets at δ 2.30 (J=9.6Hz) and 2.27 (J=9.5Hz) were accounted to methylene H₂-2' protons adjacent to the ester group. The other methylene protons appeared between δ 2.18-1.25. A three proton triplet at δ 0.57 (J=6.5 Hz) was due to terminal C-18 primary methyl protons. Acid hydrolysis yielded oleic acid and arabinose. On the basis of the above discussion, the structure of compound 5 has been identified as n-octadec-9-enoyl-β-D-arabinopyranoside.
Characterization of compound 6

It was obtained as pale yellow crystalline mass in Chloroform: Methanol (43:7) eluants.

**M.P:** 83–85°C

**Rf 0.76 (CHCl₃:MeOH, 19:1)**

**UV λ max (MeOH):** 205 nm (log ε 2.6)

**IR  ymax (KBr):** 3410, 3360, 2920, 2855, 1721, 1625, 1440, 1220, 1105, 770 cm⁻¹

**1H-NMR(CDCl₃):** δ 5.35 (2H, brs, H-9, H-10), 5.01 (1H, d, J=7.5 Hz, H-1'), 4.32 (1H, m, H-4'), 3.81 (1H, m, H-4), 3.66 (1H, d, J=9.9 Hz, H-5'a), 3.64 (1H,d, J=9.9 Hz, H-5'b), 3.20 (1H,d, J=8.7 Hz, H-2a), 2.27 (1H, d, J=8.7 Hz, H-2b), 2.07 (2H, brs, H-8), 2.05 (2H, H-11), 1.61 (2H, m, CH₂), 1.50 (2H, m, CH₂), 1.41 (2H, brs, CH₂), 1.29 (6H, brs,3x CH₃), 1.25 (10H, brs,10x CH₃), 0.55 (3H, t, J=6.7 Hz, Me-18); **13C-NMR (CDCl₃):** δ 173.09 (C-1), 130.56 (C-9), 122.05 (C-10), 103.58 (C-18), 80.41 (C-2'), 78.36 (C-3'), 69.50 (C-4') 66.12 (C-5'), 33.25 (C-2'), 3.89 (C-3), 29.65 (6xCH₃), 29.47 (CH₃), 28.97 (CH₃), 28.61 (CH₃), 28.53(CH₃), 25.44(CH₃), 22.65(CH₃), 14.07 (Me-18).

It responded positively to glycoside tests. Its IR spectrum showed characteristic absorption bands for hydroxyl groups (3410, 3360 cm⁻¹), ester function (1721) cm⁻¹, unsaturation at 1625 cm⁻¹ and long aliphatic chain at 770 cm⁻¹. On the basis of mass spectrum, the molecular formula of compound 6 was determined as C₁₀H₂₀O₆. It has three degrees of unsaturation, each of them were adjusted in the vinylic linkage, ester group and glycosidic unit. The 1H-NMR spectrum of compound 6 showed a two-proton broad signal at δ 5.35 assigned to vinylic H-9 and H-10 protons. A one proton doublet at δ 5.01 (J=7.5 Hz) was due to anomic H-1' proton. Three one proton multiplets at δ 4.32, 4.10 and 3.81 and two one proton doublets at δ 3.66 (J=9.9Hz) and 3.64 (J=9.9Hz) were attributed to carbonyl protons H-2', H-3'and H-4' and to oxygenated methylene H-2' protons of the sugar unit, respectively. Two one proton doublets at δ 2.07 (J=8.7Hz) and 2.27 (J=8.7Hz) were accounted to methylene H-2 protons adjacent to the ester group. The other methylene protons appeared between δ 2.07-1.25. A three proton triplet at δ 0.57 (J=6.7 Hz) was due to terminal C-18 primary methyl protons. The 13 C NMR spectrum exhibited signals for ester carbon at δ 173.09 (C-1), vinyl carbons at δ 130.56 (C-9) and 122.05 (C-10), anomic carbon at δ 103.58 (C-18), other sugar carbons from δ 80.41 to δ 66.12, methylene carbon between δ 33.25-22.65 and methyl carbon at δ 14.07 (C-18). Acid hydrolysis yielded oleic acid and α-D-xylose. On the basis of the above discussion, the structure of compound 6 has been identified as n-octadec-9-enoyl-α-D-xylopyranoside.

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