ISSN : 0974 - 7508 Volume 7 Issue 6

Trade Science Inc.

Natural Products

An Indian Journal

Full Paper

NPAIJ, 7(6), 2011 [320-324]

Terpenoid constituents from the stem bark of *Mangifera indica* variety '*Langra*'

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Received: 3rd October, 2011 ; Accepted: 3rd November, 2011

ABSTRACT

Phytochemical investigation of the chloroform extract of the stem bark of *Mangifera indica* variety "*Langra*" yielded four new phytoconstituents characterized as 3,7,11-trimethyl dodec-7-ene-12-ol-5,10-dione (farnesenedione) **(1)**, 3,7,11,15-tetramethyl hexadecane-12-one-1-yl-3'¦,7'¦-dimethyl oct-2'¦-en-1'¦-oate **(2)**, *n*-dodecanyl-*n*-eicos-2-en-16-oxo-1-oate **(3)** and *n*-hexacosan-17-one-1-yl acetate **(4)** along with the known fatty acid ester dodecanyl palmitate **(5)**. The structures of these phytoconstituents have been elucidated on the basis of spectral data analysis and chemical reactions.

KEYWORDS

Mangifera indica var. *Langra*;
Stem bark;
Farnesenedione;
Oxophytyl geranate;
Aliphatic esters.

INTRODUCTION

Mangifera indica L. (Anacardiaceae), commonly known as Am or mango, is a large evergreen tree with a heavy dome shaped crown and straight, stout bole. It occurs throughout India, other parts of temperate Asia, southern Europe and America[1]. It is the prominent fruit crop and over 1,000 mango types are grown in various parts of India, each having its own peculiar taste, flavour and consistency of pulp. The mango stem bark is astringent, anthelmintic and used to treat haemoptysis, haemorrhage, nasal catarrh, diarrhoea, ulcers, diphtheria, rheumatism and for lumbrici[2]. The stem bark stops vomiting[3]. Aliphatic constituents, coumarin, mangiferine[4-6], sequiterpinenoids[6,7], triterpinoids[8,9] and phenolics[10] have been reported from the stem barks of different cultivars of *M. indica*. This paper describes the isolation and characterization of phytoconstituents from the bark of *Mangifera indica* var. *Langra*.

EXPERIMENTAL

The melting points were determined on a Perfit apparatus and are uncorrected. The IR spectra were recorded in KBr pellet on Win IR FTS 135 instrument (Biorad, USA). ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded by Bruker spectrospin NMR instrument in $CDCl_3$ using TMS as internal standard. EIMS were scanned at 70 eV on a Jeol D-300 instrument (Jeol, USA). Column chromatography was performed on silica gel (Merck, 60-120 mesh) and thin layer chromatography on silica gel G-coated TLC plates (Merck).

Plant material

Stem bark of *Mangifera indica* variety "*Langra*" was collected from Laharpur, Sitapur (U.P.) and identified by Prof. M. P. Sharma, Taxonomist, Department of Botany, Faculty of Science, Jamia Hamdard

Full Paper

(Hamdard University). A voucher specimen No. PRL/JH/08/44 was deposited in the herbarium of the Faculty of Pharmacy, Jamia Hamdard (Hamdard University), New Delhi, India.

Extraction and isolation of compounds

The dried and powdered stem bark (4.0 kg) was extracted with chloroform in a Soxhlet apparatus. The extracts were combined and the solvent evaporated under reduced pressure to obtain a dark brown viscous mass (480 g). The dried alcoholic extract was dissolved in minimum amount of methanol and adsorbed on silica gel to form slurry. The slurry was air-dried and chromatographed over silica gel column prepared in petroleum ether. The column was eluted with petroleum ether, chloroform and methanol to isolate the following compounds:

Farnesenedione (1)

Elution of the column with petroleum ether furnished colourless crystals of **(1)**, 3.2 g (0.08% yield), R_f = 0.96 (petroleum ether), m.p. 40-41º, $[\alpha]_D^{25}$ = +2.2 (C 1.3250, MeOH); UV γ_{max} ($CHCl_3$): 236 nm (log ε 3.5); IR λ_{max} (KBr): 3445, 2905, 2855, 1710, 1690, 1635, 1465, 1385, 1170, 1110, 725 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.30 (H, d, *J*=5.0 Hz, H-8), 3.25 (1H, d, *J*=5.0 Hz, H_2-12a), 3.20 (1H, d, *J*=7.3 Hz, H_2-12b), 2.35 (2H, m, H_2-6), 2.20 (2H, m, H_2-9), 2.11 (2H, m, H_2-4), 2.00 (1H, brs, H-11), 1.90 (1H, m, H-3), 1.85 (3H,brs, H_3-14), 1.25 (4H, brs, 2 × CH_2), 0.98 (3H, d, *J*=6.3 Hz, Me-13) 0.90 (3H, d, *J*=6.0 Hz, Me-15), 0.77 (3H, t, *J*=6.1 Hz, Me-1); ^{13}C NMR ($CDCl_3$): δ 14.31 (C-1), 22.25 (C-2), 32.60 (C-3), 38.07 (C-4), 205.83 (C-5), 43.12 (C-6), 139.83 (C-7), 121.33 (C-8), 52.81 (C-9), 201.52 (C-10), 28.56 (C-11), 62.83 (C-12), 17.45 (C-13), 19.51 (C-14), 21.68 (C-15); EIMS m/z (*rel. int.*): 254 $[M]^+$ ($C_{15}H_{26}O_3$) (6.1), 195 (11.5), 155 (19.2), 141 (12.6), 113 (11.5), 99 (10.2), 71 (22.3), 59 (21.3).

Oxophytyl geranate (2)

Further elution of the column with petroleum ether furnished colourless crystalline product **(2)**, recrystalized from $CHCl_3$-MeOH (1:1), 12.0 g (0.30% yield), R_f=0.28, (petroleum ether), m.p. 59-60º, $[\alpha]_D^{25}$ = + 13.22 (C, MeOH); UV γ_{max} (MeOH): 227 nm (log ε 6.1); IR λ_{max} (KBr): 2920, 2850, 1735, 1710, 1640, 1465, 1415, 1375, 1260, 1205, 1185, 1115, 725 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.42 (1H, brs, H-3'), 4.10 (2H, t, *J*=9.1 Hz, H_2-1), 2.30 (2H, m, H_2-4'), 2.24 (1H, m, H-11), 2.03 (2H, m, H_2-13), 1.90 (1H, m, H-3), 1.60 (3H, brs, Me-10'), 1.52 (1H, m, H-7), 1.39 (1H, m, H-15), 1.29 (10 H, brs, 5 × CH_2), 1.25 (4H, m, 2 × CH_2), 1.22 (4H, m, 2 × CH_2), 1.19 (2H, m, CH_2), 1.12 (3H, d, *J*=6.5 Hz, Me-19), 1.07 (3H, d, *J*=6.1Hz, Me-18); 1.03 (6 H, d, *J*=6.5 Hz, Me-8', Me-9'), 0.96 (3H, d, *J*=6.0 Hz, Me-17), 0.90 (3H, d, *J*=6.6 Hz, Me-20), 0.83 (3H, d, *J*=6.1 Hz, Me-16); ^{13}C NMR ($CDCl_3$): δ 62.75 (C-1), 35.81 (C-2), 37.63 (C-3), 29.66 (C-4), 29.51 (C-5), 29.80 (C-6), 36.89 (C-7), 29.45 (C-8), 29.15 (C-9), 28.43 (C-10), 45.87 (C-11), 203.77 (C-12), 46.25 (C-13), 24.39 (C-14), 31.76 (C-15), 18.32 (C-16), 19.83 (C-17), 21.76 (C-18), 20.68 (C-19), 18.41 (C-20), 173.14 (C-1'), 122.43 (C-2'), 139.58 (C-3'), 52.40 (C-4'), 28.13 (C-5'), 26.19 (C-6'), 35.94 (C-7'), 16.52 (C-8'), 15.85 (C-9'), 22.48 (C-10'); EIMS m/z (rel. int.): 464 $[M]^+$ ($C_{30}H_{56}O_3$) (2.3), 365 (21.5), 337 (25.3), 311 (18.2), 167 (56.0), 153 (20.4), 127 (12.3), 99 (44.3).

Dodecanyl oxoeicosenoate (3)

Compound **(3)** was obtained as colourless amorphous powder from petroleum ether eluants, recrystallized from $CHCl_3$-MeOH (1:1), 4.1g (0.103 % yield), R_f=0.29, (petroleum ether-benzene,1:1), m.p. 95-96º, UV λ_{max} : 222 nm (log ε 6.1); IR γ_{max} : 2920, 2850, 1721, 1705, 1619, 1465, 1420, 1315, 1260, 1185, 715 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.25 (1H, d, *J*=9.5 Hz, H-2), 5.87 (1H, m, H-3), 3.65 (2H, m, H_2-1'), 2.37 (2H, m, H_2-15), 2.26 (2H, m, H_2-17), 1.98 (2H, m, H_2-4), 1.56 (4H, m, 2 × CH_2), 1.23 (44H, brs, 22 × CH_2); 0.85 (3H, t, *J*=6.6 Hz, Me-20), 0.82 (3H, t, *J*=6.3 Hz, Me-12'), ^{13}C NMR ($CDCl_3$): δ 205.76 (C-16), 171.53 (C-1), 133.68 (C-2), 120.75 (C-3), 66.42 (C-1'), 54.23 (C-4), 35.85 (C-15), 33.54 (C-17), 29.70 (CH_2), 28.39 (18 × CH_2), 25.64 (CH_2), 24.21 (CH_2), 22.17 (CH_2), 14.86 (C-12'), 14.07 (C-20); EIMS m/z (rel. int.): 492 $[M]^+$ ($C_{32}H_{60}O_3$) (3.5), 477 (5.9), 435 (17.6), 407 (18.1), 323 (14.3), 307 (14.6), 253 (15.1), 239 (16.3), 185 (17.9), 169 (21.2), 155 (6.2), 141 (11.3), 113 (18.5), 85 (66.8), 71 (52.6), 57 (100).

Hexacosanyl acetate (4)

Elution of the column with petroleum ether-chloro-

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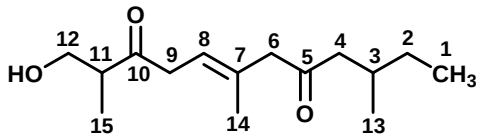
form (9:1) afforded colourless compound **(4)**, recrystallized from chloroform-methanol (1:1), 17.0 mg (0.42% yield), R_f=0.85 (petroleum ether–MeOH, 3:1), m.p. 102-104°, UV λ_{max} (MeOH): 210 nm (log ε 6.5); IR γ_{max} (KBr): 2900, 2810,1730,1700,1450, 1365, 1245, 1185, 1095, 720 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.01 (1H,brs, H_2-1a), 3.93 (1H, brs, H_2-1b), 2.40 (2H, m, H_2-16), 2.20 (2H, m, H_2,-18), 2.06 (3H, brs, $COCH_3$), 1.70 (4H, m, 2 × CH_2), 1.52 (4H, m, 2 ×CH_2), 1.26 (34H, brs, 17 × CH_2), 0.81 (3H, t, *J*=6.5 Hz, Me-1); ^{13}C NMR ($CDCl_3$): δ 206.81 (C-17), 170.62 (C-1'), 65.89 (C-1), 34.86 (CH_2), 32.57 (CH_2), 29.94 (CH_2), 29.72 (CH_2), 29.38 (CH_2), 29.06 (15 × CH_2), 28.67 (CH_2), 24.15 (CH_2), 22.83 (CH_2), 21.27 ($COCH_3$), 14.51 (Me-26); EIMS m/z (*rel. int.*): 438 $[M]^+$ ($C_{28}H_{54}O_3$) (2.0), 395 (24.3), 381 (11.6), 311 (10.1), 283 (13.2), 155 (28.6), 143 (7.8), 127 (21.6).

Dodecanyl palmitate (5)

Further elution of the column with petroleum ether-chloroform (9:1) furnished colourless amorphous mass of **(5)**, recrystallized from chloroform-methanol (3:1), 6.5 g (0.16% yield), R_f=0.55 (petroleum ether-$CHCl_3$, 1:1), m.p. 77-78°; IR γ_{max} (KBr): 1735, 725 cm^{-1}; EIMS m/z (*rel. int.*): 424 $[M]^+$ ($C_{28}H_{56}O_2$) (5.7).

RESULTS & DISCUSSION

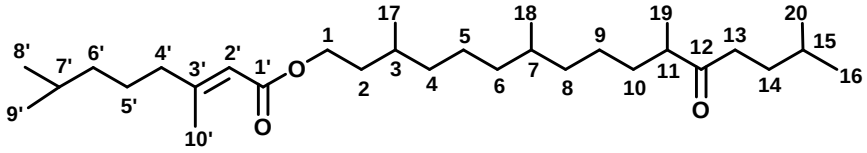
Compound **(1)**, named farnesenedione, was obtained as colourless crystals from petroleum ether eluants. Its IR spectrum displayed typical absorption bands for hydroxyl group (3445 cm^{-1}), carbonyl groups (1710, 1690 cm^{-1}) and unsaturation (1635 cm^{-1}). It had a molecular ion peak at m/z 254 corresponding to an unsaturated acyclic sesquiterpenic formula, $C_{15}H_{26}O_3$. The ion peaks arising at m/z 59, 195 [C_{10}-C_{11} fission]$^+$, 99, 155 [C_5-C_6 fission]$^+$ and 113, 141 [C_6-C_7 fission]$^+$ suggested the location of the carbonyl groups at C-5 and C-10, vinylic linkage at C-7 and hydroxyl function at C-12. The ^1H NMR spectrum of 1 exhibited a one–proton doublet at δ 5.30 (*J*=5.0 Hz) assigned to H-8 vinylic proton. Two one-proton doublets at δ 3.25 (*J*=5.01 Hz) and 3.20 (*J*=7.3 Hz) were ascribed to C-12 hydroxymethylene proton. A three-proton broad singlet at δ 1.85 was associated with C-14 methyl group attached to vinylic C-7 carbon. The methylene protons adjacent to C-4 and C-8 carbonyl groups appeared as multiplets at δ 2.35 (H_2-6) and 2.20 (H_2-9) and 2.11 (H_2-4). Two three-proton doublets at δ 0.98 (*J*= 6.3 Hz) and 0.90 (d, *J*=6.00 Hz) and a three proton triplet at δ 0.77 (*J*=6.1 Hz) were accounted correspondingly to secondary C-13 and C-15 and primary C-1 methyl protons. The remaining protons resonated at δ 2.00 (1H), 1.90 (1H) and 1.25 (4H). The ^{13}C NMR spectrum of **(1)** displayed signals for carbonyl carbons at δ 205.83 (C-5) and 201.52 (C-10), vinylic carbons at δ 139.83 (C-7) and 121.33 (C-8) and hydroxymethylene carbon at δ 62.83 (C-12). On the basis of these evidences, the structure of **(1)** has been elucidated as 3, 7, 11-trimethyl dodec-7-en-12-ol-5, 10-dione. This is a new sesquiterpene isolated for the first time a natural source.



(1)

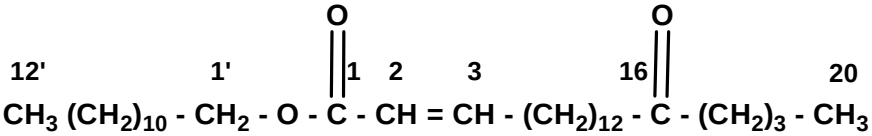
Compound **(2)**, named oxophytyl geranate, was obtained as colourless crystalline product from petroleum ester eluents. Its IR spectrum demonstrated the presence of characteristic absorptions for ester function at (1735 cm^{-1}), carbonyl group (1710 cm^{-1}) and unsaturation (1640 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, its molecular ion peak was determined at m/z 464 corresponding for a molecular formula $C_{30}H_{56}O_3$. The mass[11] spectrum showed a prominent ion peak at m/z 153 $[C_{10}H_{17}O]^+$ relating to geranyl group and an ion fragment at m/z 311 [CO-O fission]$^+$ due to an acyclic diterpenic chain containing a carbonyl group. The ion fragments generating at m/z 99 [C_{12}-C_{13} fission]$^+$, 365 [M-99]$^+$, 127 [C_{11}-C_{12} fission]$^+$ and 337 [M-127]$^+$ supported the presence of carbonyl group at C-12. The ^1H NMR spectrum of **(2)** displayed a one-proton broad signal at δ 6.42 and its existence in the deshielded region supported the presence of the vinylic linkage nearby the ester function identical to geraniol. A two-proton triplet at δ 4.10 (*J*=9.1 Hz) was ascribed to oxygenated methylene H_2-1 protons. A one-proton multiplet at δ 2.24 and two two-proton multiplets at δ 2.24 and 2.30 were attributed to methine H-11 and methylene H_2-13 nearby carbonyl function and methyl-

ene H_2-4' adjacent to the vinylic carbon, respectively. The other methine and methylene protons appeared between δ 2.03-1.19. A three-proton broad signal at δ 1.60 was due C-10' methyl protons located on the vinylic carbon. The other secondary methyl protons resonated as doublets from δ 1.12 to 0.83. The ^{13}C NMR spectrum o **(2)** exhibited important signals for carbonyl carbon at δ 203.77 (C-12), ester carbon at δ 173.14 (C-1'), vinylic carbons at δ 122.43 (C-2') and 139.59 (C-3') and oxygenated methylene carbon at δ 62.75 (C-1). The HMBC spectrum of **(2)** showed correlataions of C-1' with H-2' and H_2-1; C-3' with H-2', H_2-4' and H_3-10', and C-12 with H-11, H_2-10, H_2-13 and H_3-19. On the basis of above discussion the structure of 2 has been elucidated as 3,7,11,15-tetramethyl hexadecane-12-one-1-yl-3',7'-dimethyl oct-2'-en-1'-oate. This is a new phytyl geranate isolated from a herbal drug.



(2)

Compound **(3)**, named dodecanyl oxoeicosenoate, was obtained as colourless amorphous powder from petroleum ether eluants. Its IR spectrum exhibited characteristic absorption bands for ester group (1721 cm^{-1}) and carbonyl function (1705 cm^{-1}), unsaturation (1619 cm^{-1}) and long aliphatic chain (715 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, the molecular weight of **(3)** was determined at m/z 492 consistent to the molecular formula of a fatty acid ester, $C_{32}H_{60}O_3$. The prominent ion peaks arising at m/z 57, 437 $[C_{16}\text{-}C_{17}$ fission$]^+$ and 85, 407 $[C_{15}\text{-}C_{16}$ fission$]^+$ suggested the existence of the carbonyl function at C-16. The ion fragments generating at m/z 239, 253 $[C_3\text{-}C_4$ fission$]^+$ and 185, 307 [O-CO fission]$^+$ indicated eicosenoyl unit with vinylic linkage at C-2 position. Formation of the mass unit at m/z 169 $[CH_3(CH_2)_{10}CH_2]^+$ and 323 $[M\text{-}169]^+$ supported that decanyl alcohol was esterified with C_{20} fatty acids. The ^1H NMR spectrum of **(3)** established a one-proton doublet at δ 6.25 (J=9.5 Hz) and a one-proton multiplet at δ 5.87 assigned to *cis*-oriented vinylic H-2 and H-3, respectively and their presence in the deshielded field indicated the location of the vinylic linkage near ester function. A two-proton multiplet at δ 3.56 was ascribed to oxygenated methylene H_2-1' protons. Two multiplets at δ 2.37 and 2.26 integrating for two protons each were attributed to methylene H_2-15 and H_2-17, respectively, adjacent to the keto function. The other methylene protons resonated at δ 1.98 (2H), 1.56 (4H) and 1.23 (44H). Two three-protons triplets at δ 0.85 (J=6.0 Hz) and 0.82 (J=6.3 Hz) were accounted to terminal C-20 and C-12' primary methyl protons, respectively. The ^{13}C NMR spectrum displayed important signals for carbonyl carbon at δ 205.76 (C-16), ester carbon at δ 171.53 (C-1), vinylic carbons at δ 133.68 (C-2) and 120.75 (C-3), oxygenated methylene at δ 66.42 (C-1') and primary methyl carbons at δ 14.86 (C-12') and 14.07 (C-20). The HMBC of **(3)** showed correlations of C-16 with H_2-15, H_2-16 and H_2-17; and C-1 with H-2, H-3 and H_2-1'. On the basis of these evidences the structure of 3 has been formulated as *n*-dodecanyl *n*-eicos-2-en-16-oxo-1-oate. This is a new fatty acid ester isolated from a natural source.



(3)

Compound **(4)**, named hexacosanyl acetate, was obtained as colourless product from petroleum ether-chloroform (9:1) eluents. Its IR spectrum showed characteristic absorption bands for ester group (1730 cm^{-1}), carbonyl function (1700 cm^{-1}) and long aliphatic chain (720 cm^{-1}). On the basis of mass and ^{13}C NMR spec-

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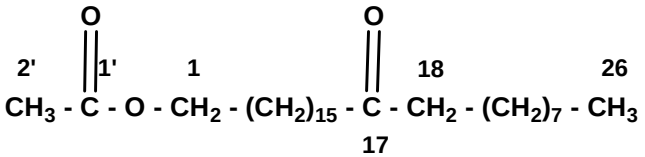
tra, the molecular ion peak of **(4)** was determined at m/z 438 consistent with the molecular formula of an oxofatty acid ester, $C_{28}H_{54}O_3$. Elimination of the acetyl group from the molecular ion peak generated a prominent ion peak at m/z 395 suggesting that C_{26} alcohol was esterified with acetyl group. The location of the carbonyl group at C-17 was inferred from the ion peaks appearing at m/z 155 $[CO(CH_2)_8CH_3]^+$ and 283 $[M-155]^+$ formed due to β-fission and at m/z 127 $[CH_3(CH_2)_8]^+$ and 311 $[M-127]^+$ arose due to α-fission of the carbonyl function. The ^1H NMR spectrum of **(4)** showed two one-proton each broad signals at δ 4.01 and 3.93 assigned to oxygenated methylene H_2-1 protons. Two multiplets at δ 2.40 and 2.20 integrating for two protons each were due to methylene H_2-16 and H_2-18 adjacent to the carbonyl group. A three-proton broad signal at δ 2.06 was attributed to acetyl protons. A three-proton triplet at δ 0.81 (J=6.5 Hz) was accounted to primary C-26 methyl protons. The remaining methylene protons resonated at δ 1.70 (4H), 1.52 (4H) and 1.26 (34H). The ^{13}C NMR spectrum of **(4)** displayed signals for carbonyl carbon at δ 206.81 (C-17), ester carbon at δ 170.62 (C-1'), oxygenated methylene carbon at δ 65.89 (C-1'), methylene carbon from δ 34.86 to 22.83, acetyl methyl at δ 21.27 ($COCH_3$) and methyl carbon at δ 14.51 (Me-26). The HMBC spectrum of **(4)** showed correlations of C-1' with H_3-2' and H_2-1; C-17 with H_2-16, H_2-18 and H_2-19; C-26 with H_2-25 and H_2-24. On the basis of above mentioned evidences, the structure of **(4)** was elucidated as *n*-hexacosan-17-one-1-yl acetate. This is a new aliphatic alcohol ester.



(4)

Compound **(5)**, was the known fatty acid ester characterized as dodecanyl palmitate.

CONCLUSION

The phytochemical investigation of the stem bark of *M.india* var. *langra* led to the isolation of four new chemical constituents which might be used as chromatographic markers for quality control of the drug.

ACKNOWLEDGEMENT

The authors are thankful to the Head, Sophisticated Analytical Instrumentation Facility (SAIF), Central Drug Research Institute, Lucknow, for recording mass spectrum of the compounds.

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