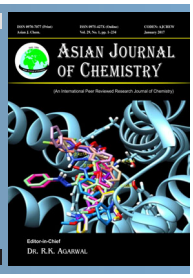
Asian Journal of Chemistry; Vol. 29, No. 3 (2017), 485-488

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20201



Isolation of Two New Cheilanthane-Type Tricarbocyclic Sesterterpenoids from Leaves of *Caesalpinia crista* Linn.: A Traditionally Used Antimalarial Plant of Assam, India

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Received: 20 July 2016; *Accepted*: 10 August 2016; *Published online*: 30 December 2016; AJC-18186

Caesalpinia crista L. (family Caesalpiniaceae) is a large scandent prickly evergreen shrub widely distributed in south-eastern Asia, Nigeria and Pacific region. The leaves are useful to cure skin infections, sore throat, intestinal worms, hepatic disorders, malaria and leprosy. Phytochemical investigation of a methanolic extract of the leaves of *C. crista* afforded two new cheilanthane-type tricarbocyclic sesterterpenoids characterized as 4α,4β,8β,13β-tetramethyl-14-(17-methyl-pent-14-enyl)-perhydrophenanthrene-11α-ol-22-oic acid (**1**, cristasesterterpenoic acid) and 4α,4β,8β,10β,13β-pentamethyl-14-(-17-methylpent-14-enyl)-perhydrophenanthrene-3β-olyl-O-β-D-glucopyranoside (**2**, cristasesterterpinol glucoside). The structures of these compounds were elucidated on the basis of spectral data analysis and chemical reactions.

Keywords: *Caesalpinia crista*, Leaves, Cristasesterterpenoic acid, Cristasesterterpenol glucoside.

INTRODUCTION

Caesalpinia crista L., syn. *C. bonduc* (L.) Roxb; *C. bonducella* (L.) Fleming, (family Febaceae/Caesalpiniaceae), known as kantikaranja or fever nut. is a large scandent prickly evergreen shrub widely distributed in south eastern Asia especially in India, Sri Lanka, Tibet, Indonesia, Thailand, Philippines, Vietnam, Queensland and New Caledonia, in Nigeria and Pacific region. Its leaves are bipinnately compound, alternate, leaflets elliptic-oblong, membranous, apex mucronate, margins curved, upper surface shiny, lower dull and petioles prickly [1]. The leaves and seeds are traditionally used in Assam (India) to treat malarial fever. The premature leaves are applied to affected areas to treat infections; a leaf decoction is used as a gargle for sore throat. Young leaves are used in intermittent fever and for expelling intestinal worms. The leaves are useful to cure hepatic disorders, malaria and leprosy. The leaves and bark are regarded as febrifuge, emmenagogue and anthelmintic. Leaf powder is given as postpartum remedy. A leaf decoction is used to prevent abortion and as a uterine tonic immediately after delivery. The leaves are antiperiodic, febrifuge, tonic and used to treat asthma and snake bite [2-4]. Its seeds and leaves contained cassane-and norcassane-type diterpenes, pulcherrimin and 6-methoxy-pulcherrimin, 8-methoxy-bonducellin, bonducellin, 2,6-dimethoxy-benzoquinone, 2',4',4-trihydroxychalcone and 2',4-dihydroxy-4'-methoxy-chalcone [5-15]. Caesalpinins C-G and norcaesalpinins A-E showed significant inhibitory effects on *Plasmodium falciparum* [11]. Some of the constituents of this species possessed anti-tumor, antimicrobial and antimalarial properties [12,16,17]. The diterpene, neocaesalpin P and other diterpenoids exhibited modest antibacterial activities [14]. This paper describes the isolation and characterization of two cheilanthane-type tricarbocyclic sesterterpenoids from the leaves of *C. crista*.

EXPERIMENTAL

Melting points were determined on a Perfit apparatus without correction. The IR spectra were measured in KBr pellet on a Bio-Red FT-IR spectrometer. Ultraviolet (UV) spectra were obtained in methanol with a Lambda Bio 20 spectrometer. ^{1}H (400 MHz), ^{13}C (100 MHz), COSY and HMBC NMR spectra were recorded on Bruker spectrospin spectrometer. $CDCl_3$ (Sigma-Aldrich, Bangalore, India) was used as solvent and TMS as an internal standard. ESI MS analyses were performed on a JEOL SX 102/Da-600 instrument equipped with direct inlet probe system. Column chromatography separations were carried out on silica gel (Merck, 60-120 mesh, Mumbai, India). Precoated silica gel plates (Merck, Silica gel 60 F254) were used for analytical thin layer chromatography visualized by exposure to iodine and UV radiations.

The leaves of *C. crista* were collected from Charaideu area of Sivsagar district of Assam, India, during the period of

April-May and taxonomically authenticated by Dr. L.R. Bhuyan, Systemic Botanist, State Forest Research Institute (SFRI), Itanagar. A voucher specimen has been preserved in the Department of Pharmaceutical Sciences, Dibrugarh University (No.- DU/PS/HRB-03/2005).

Extraction and isolation: The air dried leaves (1.2 kg) of *C. crista* were coarsely powdered and extracted with methanol (7.5 L) using a Soxhlet apparatus. The methanolic extract was concentrated to 500 mL under reduced pressure, mixed with distilled water (20 %) and extracted with dichloromethane (3 × 500 mL). The combined aqueous methanolic extract (chlorophyll free) was evaporated to dryness (72 g), dissolved in minimum amount of methanol and adsorbed on silica gel (60-120 mesh) to form a slurry. It was dried in the air, pulverized to get a uniform particle size and chromatographed over silica gel (60-120 mesh) column packed in petroleum ether (b.p. 60-80 °C). The column (1.6 m × 16 mm × 2 mm) was eluted successively with petroleum ether, mixture of petroleum ether and chloroform (9:1, 3:1, 1:1 and 1:3, v/v), chloroform and finally the mixture of chloroform and methanol (99:1, 97:3, 19:1, 23:2, 9:1, 3:1, 1:1, 1:3, 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. The isolated compounds were recrystallized to get pure compounds. The following compounds were isolated:

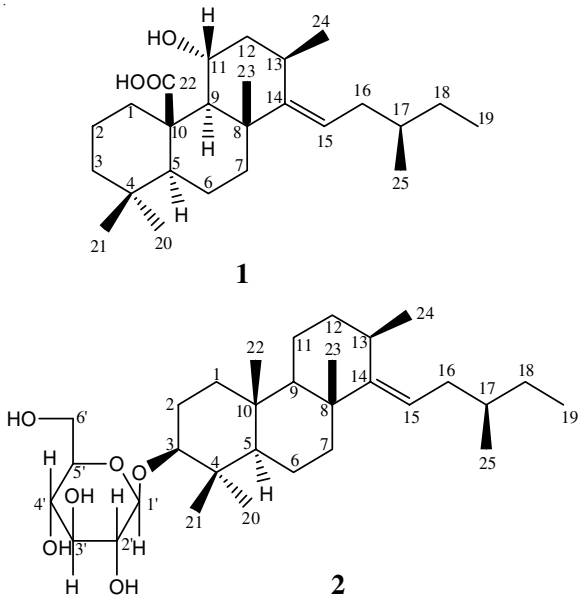
Cristasesterterpenoic acid (1): Elution of the column with chloroform-methanol (9:1) afforded colourless crystals of compound **1**, recrystallized from methanol, 33 mg (0.0027 % yield). m.p.: 183-185 °C; R_f 0.63 (chloroform-methanol-glacial acetic acid- water; 16:8:3:2). IR (KBr, ν_{max}, cm^{-1}): 3401, 3250, 2927, 2852, 2340, 1708, 1608, 1597, 1378, 1247, 1122, 1033, 770. +ve ion FAB MS *m/z* (rel. int.): 390 $[M]^+$ ($C_{25}H_{42}O_3$) (10.5), 372 (9.8), 344 (13.1), 326 (10.3), 311 (9.0), 296 (13.8), 281 (12.6), 266 (58.7), 252 (17.1), 248 (9.2), 236 (11.2), 234 (11.3), 222 (18.3), 221 (10.2), 208 (56.5), 207 (34.2), 204 (13.0), 182 (17.6), 177 (14.1), 168 (24.8), 165 (30.6), 164 (22.5), 157 (21.4), 154 (48.6), 151 (26.2), 150 (61.2), 145 (23.0), 142 (23.1), 138 (36.5), 137 (64.6), 136 (100), 124 (23.9), 123 (25.1), 109 (25.1), 106 (83.4). ^{1}H NMR ($CDCl_3$): δ 5.41 (1H, m, H-15), 3.71 (1H, brm, $w_{1/2}$ = 9.1 Hz, H-11β), 2.73 (1H, d, *J* = 5.5 Hz, H-9α), 2.47 (1H, dd, *J* = 5.5, 1.2 Hz, H_2-12α), 2.16 (1H, m, H-13), 2.05 (1H, m, H_2-16α), 2.03 (1H, dd, *J* = 5.7, 8.5 Hz, H_2-12β), 2.01 (1H, m, H_2-16β), 1.62 (1H, dd, *J* = 5.1, 1.2 Hz, H-5α), 1.89 to 1.30 (12H, m, 6 × CH_2), 1.28 (3H, brs, Me-20), 1.25 (1H, d, *J* = 6.8 Hz, Me-25), 1.21 (3H, brs, Me-20), 1.16 (3H, brs, Me-21), 0.84 (3H, d, *J* = 6.5 Hz, Me-24), 0.78 (3H, t, *J* = 6.1 Hz, Me-19); ^{13}C NMR ($CDCl_3$): δ 36.76 (C-1), 33.02 (C-2), 24.21 (C-3), 38.82 (C-4), 52.72 (C-5), 18.33 (C-6), 28.34 (C-7), 42.01 (C-8), 56.23 (C-9), 36.91 (C-10), 78.32 (C-11), 30.69 (C-12), 47.45 (C-13), 138.33 (C-14), 125.20 (C-15), 27.08 (C-16), 38.75 (C-17), 27.24 (C-18), 15.49 (C-19), 17.13 (C-20), 21.30 (C-21), 179.64 (C-22), 23.22 (C-23), 23.56 (C-24), 15.97 (C-25); HR-MS: 391.6166 $[M + H]^+$ (Calcd. for $C_{25}H_{43}O_2$, 691.6173).

Cristasesterterpinol glucoside (2): Elution of the column with chloroform-methanol (7:3) furnished colourless crystals **2**, recrystallized from methanol, 26 mg (0.0021 % yield). m.p.: 250-251 °C, R_f 0.49 (chloroform-methanol-water; 100:13.5:10). IR (KBr, ν_{max}, cm^{-1}): 3421, 3019, 2401, 1603, 1522, 1423, 1209, 1053, 770. +ve ion FAB MS *m/z*: (rel. int): 523 $[M+H]^+$ ($C_{31}H_{55}O_6$) (3.1), 359 (3.3), 342 (3.5), 260 (20.8), 192 (100), 167 (16.9) 153 (78.0), 152 (26.7), 150 (12.3), 139 (31.5), 138 (48.6), 136 (89.2), 124 (23.8), 122 (20.6), 107 (68.1). ^{1}H NMR (DMSO-d_6): δ 5.23 (1H, m, H-15), 4.98 (1H, d, *J* = 7.1 Hz, H-1'), 4.51 (1H, m, H-5'), 3.83 (1H, m, H-2'), 3.56 (1H, m, H-3'), 3.47 (1H, m, H-4'), 3.35 (1H, dd, *J* = 8.5, 5.1 Hz, H-3α), 3.21 (2H, brs, H_2-6'), 1.25 (3H, d, *J* = 7.1 Hz, Me-25), 1.22 (3H, brs, Me-23), 1.20 (3H, brs, Me-20), 1.12 (3H, brs, Me-21), 1.11 (3H, brs, Me-22), 0.81 (3H, d, *J* = 6.3 Hz, Me-24), 0.79 (3H, t, *J* = 6.5 Hz, Me-19); ^{13}C NMR (DMSO-d_6): δ 36.01 (C-1), 33.82 (C-2), 73.77 (C-3), 42.26 (C-4), 56.88 (C-5), 18.86 (C-6), 29.68 (C-7), 45.46 (C-8), 56.63 (C-9), 36.66 (C-10), 31.68 (C-11), 31.87 (C-12), 50.04 (C-13), 140.43 (C-14), 121.79 (C-15), 29.05 (C-16), 37.25 (C-17), 26.20 (C-18), 19.95 (C-19), 19.43 (C-20), 21.01 (C-21), 22.09 (C-22), 24.27 (C-23), 25.90 (C-24), 19.19 (C-25), 101.26 (C-1'), 76.45 (C-2'), 70.63 (C-3'), 67.61 (C-4'), 77.71 (C-5'), 61.97 (C-6'); HR-MS: 523.7769 $[M+H]^+$ (calcd. for $C_{13}H_{55}O_6$, 523.7765).

RESULTS AND DISCUSSION

Compound **1**, designated as cristasesterterpenoic acid, was obtained as a colourless crystalline mass from chloroform-methanol (9:1) eluents. It produced effervescences with sodium bicarbonate solution indicating the presence of carboxylic acid group in the molecule. Its IR spectrum showed characteristic absorption bands for hydroxyl group (3401 cm^{-1}), carboxylic function (3250, 1708 cm^{-1}) and unsaturation (1608 cm^{-1}). On the basis of FAB mass, HR-MS and ^{13}C NMR spectra, its molecular weight was established at *m/z*: 390, consistent with the molecular formula of a perhydrophenanthrene type sesterterpenoic acid, $C_{25}H_{42}O_3$. It indicated five double bond equivalents; three of them were adjusted in the tricyclic carbon framework of the sesterterpene and one each in the vinylic linkage and carboxylic function. The ion fragments arising at *m/z*: 372 $[M-H_2O]^+$, 344 $[M-HCOOH]^+$, 326 $[344-H_2O]^+$, 311 $[326-Me]^+$, 296 $[311-Me]^+$ and 281 $[296-Me]^+$ suggested the presence of the hydroxyl and carboxylic functions in the molecule. The ion peaks generating at *m/z*: 154, 236 [$C_{5,6}$ - $C_{9,10}$ fission]$^+$, 109 [154 - COOH]$^+$, 165 [236 - C_5H_{11}]$^+$, 168, 122 [$C_{6,7}$ - $C_{9,10}$ fission]$^+$, 123 [168 - COOH]$^+$, 151 [222 - C_5H_{11}]$^+$, 182, 208 [$C_{7,8}$ - $C_{9,10}$ fission]$^+$ and 137 [208 - C_5H_{11}]$^+$ supported the location of the carboxylic group in ring A/B, saturated nature of the rings A and B and C_5 side chain in the molecule. The ion peaks forming at *m/z*: 222, 168 [$C_{8,14}$ - $C_{9,11}$ fission]$^+$, 177 [222 - COOH]$^+$, 153 [168 - Me]$^+$, 252,138 [$C_{8,14}$ - $C_{11,12}$ fission]$^+$, 207 [252 - COOH]$^+$, 123 [138 - Me]$^+$, 266, 124 [$C_{8,14}$ - $C_{11,12}$ fission]$^+$, 248 [266-H_2O]$^+$, 221 [266 - COOH]$^+$ and 106 [124 - Me]$^+$ also supported the existence of the hydroxyl group at C-11, saturated nature of the ring *C* and C_5 side chain attached to the vinylic carbon. The ^{1}H NMR spectrum of **1** exhibited a one-proton multiplet at δ 5.41 assigned to vinylic H-15 proton. A one-proton broad multiplet at δ 3.71 with half width of 9.1 Hz was attributed to β-oriented H-11 carbinol proton. Two three-proton doublets at δ 0.84 (*J* = 6.5 Hz) and 1.25 (*J* = 6.8 Hz) were ascribed to secondary C-24 and C-25 methyl protons, respectively. Three broad singlets at δ 1.21, 1.16 and 1.28, integrated for three

protons each, were associated correspondingly with C-20, C-21 and C-23 tertiary methyl protons. A three-proton triplet at δ 0.78 (J = 6.1 Hz) was accounted to C-19 primary methyl protons. The remaining methylene and methine protons appeared from δ 2.73 to 1.30. The presence of all methyl signals between δ 1.28 - 0.78 indicated that these functionalities were located on the saturated carbons. The ^{13}C NMR spectrum of **1** displayed signals for carboxylic carbon at δ 179.64 (C-22), vinylic carbons at δ 138.33 (C-14) and 125.20 (C-15), carbinol carbon at δ 78.32 (C-11), methyl carbons at δ 15.49 (C-19), 17.13 (C-20), 21.30 (C-21), 23.22 (C-23), 23.56 (C-24) and 15.97 (C-25). The remaining methine and methylene carbons resonated between δ 56.23-18.33. The ^{1}H- ^{1}H COSY spectrum of **1** showed correlations of H-15 with H_2-16 and H-13; H-11 with H-9 and H_2-12; and H_3-20 with H_3-21, H_2-3 and H-5. The HMBC of **1** exhibited interactions of H_2-1 and H-9 with C-22; H-9 and H_2-12 with C-11; and H-13, H_3-24, H_3-23 and H-15 with C-14. The ^{1}H and ^{13}C NMR spectral values of **1** were compared with cheilanthane-type tricarbocyclic sesterterpenoids [18-20]. On the basis of the foregoing account the structure of **1** has been elucidated as 4α,4β,8β,13β-tetramethyl-14-(17-methyl-pent-14-enyl)perhydrophenanthrene-11α-ol-22-oic acid. This is a new tricyclic sesterterpenoid isolated from a plant sources for the first time.



Structures of compunds **1** and **2**

Compound **2**, named cristasesterterpinol glucoside, was obtained as a colourless crystalline mass from chloroform-methanol (7:3) eluents. It gave positive tests for glycosides. Its IR spectrum showed characteristic absorption bands for hydroxyl groups (3421 cm^{-1}) and unsaturation (1603 cm^{-1}). On the basis of FAB mass, HR-MS and ^{13}C NMR spectra, the molecular weight of **2** was established at m/z 523 $[M+H]^+$ consistent with the molecular formula of a perhydroxyphenanthrene type sesterterpenoid glycoside, $C_{31}H_{55}O_6$. It indicated five double bond equivalents; three of them were adjusted in the tricyclic carbon framework of the sesterterpenoid and one each in the vinylic linkage and glycoside. The ion peaks arising at m/z 359 $[M - C_6H_{11}O_5]^+$, 139 [$C_{5,6}$ - $C_{9,10}$ fission, $C_9H_{15}O]^+$, 153 [$C_{6,7}$ - $C_{9,10}$ fission $C_{10}H_{17}O]^+$, 167 [$C_{7,8}$ - $C_{9,10}$ fission, $C_{11}H_{19}O]^+$ and 192 [359 - 167]$^+$ suggested saturated nature of the ring A and B and the presence of carbinol proton in ring A. The ion fragments generating at m/z 342 $[M- C_6H_{12}O_6]^+$, 260 [$C_{4,5}$ - $C_{1,10}$ fission]$^+$, 122 [139-OH]$^+$, 136 [153- OH]$^+$ and 150 [167- OH]$^+$ also suggested the saturated nature of the ring B. The ion peaks formed at m/z 192 [342 - 150]$^+$, 152 [$C_{8,14}$ - $C_{9,11}$ fission, $C_{11}H_{20}]^+$, 138 [$C_{8,14}$- $C_{11,12}$ fission] and 124 [$C_{8,14}$- $C_{11,12}$ fission]$^+$ supported the saturated nature of the ring C and the existence of the vinylic linkage in the side chain. The ^{1}H NMR spectrum of **2** exhibited a one-proton multiplet at δ 5.23 assigned to vinylic H-15 proton. A one-proton doublet at δ 4.98 with coupling interaction of 7.1 Hz was ascribed to anomeric H-1′ proton. Four one-proton multiplet at δ 4.51, 3.83, 3.56 and 3.47 and a two-proton broad singlet at δ 3.21 were attributed to sugar H-5′, H-2′, H-3′, H-4′ and H_2-6′ protons, respectively. A one-proton double doublet at δ 3.35 (J = 8.5, 5.1 Hz) was accounted to α-oriented H-3 carbinol proton. Two three-proton doublets at δ 1.25 (J = 7.1 Hz) and 0.81 (J = 6.3 Hz) were ascribed to C-25 and C-24 secondary methyl protons, respectively. Four three-proton broad singlets at δ 1.22, 1.20, 1.12 and 1.11 were associated correspondingly with tertiary C-23, C-20, C-21 and C-22 methyl protons. A three-proton triplet at δ 0.79 (J = 6.5 Hz) was attributed to C-19 primary methyl protons. The presence of the methyl signals in the range from δ 1.25 to 0.79 suggested that these functionalities were located on the saturated carbons. The ^{13}C NMR spectrum of **2** showed signals for vinylic carbons at δ 140.43 (C-14) and 121.79 (C-15), oxymethine carbon at δ 73.77 (C-3), anomeric carbon at δ 101.26 (C-1'), other sugar carbons between δ 77.71 to 61.92, methyl carbons from δ 25.90 to 19.19 and methine and methylene carbons from δ 56.88 to 26.20. The ^{1}H-^{1}H COSY spectrum of **2** showed correlation of H-3 with H_2-2, H_3-21 and H-1′; H-15 with H-13 and H_2-16; H_3-20 with H-5 and H_3-21; and H-5′ with H-1′, H-4′ and H_2-6′. The HMBC spectrum of **2** exhibited correlation of H_2-2, H_3-21 and H-1′ with C-3; H-13, H_3-24 and H-15 with C-14; and H-1′, H-4′ and H_2-6′ with C-5′. The ^{1}H and ^{13}C NMR spectral values of **2** were compared with cheilanthane-type tricarbocyclic sesterterpenoids [18-20]. Acid hydrolysis of compound **2** yielded D-glucose (co-TLC comparable). On the basis of spectral data analysis and chemical reactions, the structure of **2** has been established as 4α,4β,8β,10β,13β-pentamethyl-14-(-17- methylpent-14-enyl)-perhydrophenanthrene-3β-olyl-O-β-D-glucopyranoside. To best of our knowledge, this is a new sesterterpenoid glucoside isolated from a plant sources for the first time.

ACKNOWLEDGEMENTS

The authors are grateful to University Grant Commission (UGC) for financial grant and also to Central Drug Research Institute (CDRI), Lucknow, India for recording the spectral data. Thanks are also due to Dr. M. Islam, Botanist, Department of Life Sciences, Dibrugarh University and Dr. L.R. Bhuyan, Systemic Botanist, State Forest Research Institute (SFRI), Itanagar, India for the authentication of plant material.

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