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Article

Chemical Constituents from *Himatanthus articulata*

***Alaide de Sá Barreto*[a], *Mário Geraldo de Carvalho*[a]*, *Ivanilton de Almeida Nery*[a], *Luiz Gonzaga*[b] and *Maria Auxiliadora Coelho Kaplan*[b]**

[a]*Departamento de Química, Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, 23851-970 Seropédica - RJ, Brazil*

[b]*Núcleo de Pesquisa de Produtos Naturais, Universidade Federal do Rio de Janeiro, 21991-590 Rio de Janeiro - RJ, Brazil*

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O estudo fitoquímico de *Himatanthus articulata* (Vahl) Woodson permitiu o isolamento e identificação de estigmasterol, sitosterol, cicloartenol, 3β-cinamato de α-amirina + 3β-cinamato de β-amirina, 3β-acetato de α-amirina, 3β-acetato de β-amirina, 3β-cinamato de lupeol, 3β-acetato de lupeol, ácido ursólico, metilmioinositol, ácido 1β-O-β-D-glucopiranosilplumérico, 1β-O-β-D-glucopiranosilplumerídio, plumericina e isoplumericina. Essas substâncias e alguns derivados foram identificados com base na análise dos espectros de IV, EMIE e RMN de ^{1}H e ^{13}C.

Chemical investigation of *Himatanthus articulata* (Vahl) Woodson led to the isolation of stigmasterol, sitosterol, cycloartenol, α-amyrin-3β-O-cinnamoyl, β-amyrin-3β-O-cinnamoyl, lupeol-3β-O-cinnamoyl, α-amirin-3β-O-acetyl, β-amirin-3β-O-acetyl, lupeol-3β-O-acetyl, ursolic acid, methylmyoinositol, 1β-O-β-D-glucopyranosylplumeric acid, plumeride-1β-O-β-D-glucopyranosyl, plumericin and isoplumericin. Spectroscopic analysis (IR, ^{1}H, ^{13}C-NMR and MS) were used for the identification of these compounds and some derivatives.

Keywords: Himatanthus articulata, *Apocynaceae, steroids, triterpenes, iridoid glucosides*

Introduction

Himatanthus articulata (Vahl) Woodson, (Apocynaceae) is a tree occurring in the Amazon region. The local population uses its bark and latex as a tonic and as a antisyphilitic[1]. Species belonging to the genus *Himatanthus* have been scarcely mentioned in the chemical literature. Earlier studies of *Himatanthus articulata* recorded the isolation of the acetate and cinnamate of α-amyrin and of β-amyrin[2-4]. From *H. phageadaenica* were isolated and identified an acetylated mixture of the triterpenes α-amyrin and lupeol, in addition to sitosterol and the iridoid lactones: plumericin, allamandin and isoplumericin, as well as a mixture of plumieride glucoside and sucrose[5]. A glycosylplumieride has been also isolated from *H. lancifolius*[6,7], formerly known as *Plumeria lancifolia*[8].

Results and Discussion

Latex of *Himatanthus articulata* collected near Macapá-AP, Brazil, was extracted with hexane and methanol. The hexane extract yielded, after several chromatograpic steps, a mixture of the cinnamate of α-amyrin and β-amyrin (**6** and **7**) along with the acetate of lupeol (**4**), cinnamate of lupeol (**5**) and cycloartenol (**3**). Leaves and bark of this plant were extracted successively with hexane and methanol. The methanolic extract of leaves consisted almost exclusively of ursolic acid (90%, **8**). The hexane extract of bark yielded, besides the terpenoids **4** and **5**, stigmasterol (**9**) and sitosterol (**10**). The methanolic extract of bark yielded the spirolactone iridoids (**1** and **2**), plumericin (**12**), isoplumericin (**13**) and methylmyoinositol (**11**). Compounds **1**, **3**, **5**, **8**, **9**, **10** and **11** have been isolated for the first time from the genus *Himatanthus*.

The fractions obtained by chromatographic fractionation of the acetylated methanolic extract yielded the iridoid derivatives **1a** and **2a**. The ^{13}C-NMR (HBBD and DEPT) spectra of **1a** showed five signals for δ_{CH} and one δ_{CH2} of the sugar unit. Seven δ_H signals in the ^{1}H-NMR spectrum have been assigned to the same sugar moiety by the ho-

monuclear ^1H, ^1H-COSY and also by comparison with literature data[5,9]. The peaks at *m/z* 332 (2.0%, **1f**) and 33l (20.0%, **1g**) observed in the EIMS spectra are compatible with the 2,3,4,6-tetra-O-acetyl-1-O-β-D-glucopyranosyl group. The cross peaks observed in the 2D ^1H, ^{13}C-COSY-$^1J_{CH}$ allowed to correlation of the signals at δ_H l.48 (d, 6.6 Hz), 5.60 (q, 6,6 Hz), 5.10 (br) in the ^1H-NMR spectrum, respectively, with a methyl group and two hydrogen atoms attached to oxygenated carbons that are connected with carbons at δ_C 19.40, 66.18 and 93.33 ppm. The same spectrum showed four proton signals at 5.38 (br, 6.8 Hz), 6.96 (br), 6.43 (m) and 7.41 (br) connected to the sp^2 carbons at δ_C 144,50, 128,66, 148,50 and 151,75 ppm. Comparison of these data and the remaining ^1H and ^{13}C chemical shift of the acetyl derivative **1a** (see Experimental) with those reported for plumeride[5,10] allowed to identification of the aglycone of **1**. Peaks in the EIMS spectrum corresponding to fragments **1b-1e** are in agreement with the structure of **1**. To establish the β-D-glucopyranosyl moiety at the β-position of the carbon C-l, the δ_{C-1} (93,33 ppm) and δ_{H-1} (5, 10; br) were compared with the models 1β-O-acetyl (**2b**)[9] and 1β-O-glucopyranosyl (**2c**)[9], and with those of the penta-O-acetylplumeride glucoside (**2a**), previously isolated *from H. phageadaenica*.[5] The presence of a carboxylic acid group in **1** was confirmed by the signals at δH 3.93(s), δC 51.50(CH_3) and 170.50 (C) in the ^1H- and ^{13}C-NMR spectra of the methyl ester obtained after treatment of **la** with diazomethane.

The structures of plumeride glucoside (**2),** plumericin (**12**) and isoplumericin **(13)** were determined by analysis of ^1H- and ^{13}C-NMR spectra and comparison with literature data[5,11]. These iridoids have been commonly reported in the *Plumeria* genus[10,11].

Identification of compounds **3-10** was achieved by analysis of IR, NMR and EIMS spectra and comparison with literature data. The ^1H-NMR spectra allowed the identification of the respective series of **3** (cycloartene), **4-8** (pentacyclic triterpenes) and **9-10** (steroids). Analysis of ^{13}C-NMR data and the use of the Olea *et al*[12] methodology led to the confirmation of the triterpene series as cycloartene (**3**)[13], lupene (**4**, **5**), ursene (**6**, **8**) and oleanene (**7**).[14-16] The main peaks observed in the mass spectra are compatible with those fragment ions expected for triterpene units.

The acetate unit in **4** was identified by the $\delta_{C=O}$ (171.30 ppm) and δ_{CH3} (21.30 ppm) in the ^{13}C-NMR spectrum as well as the δ_H (2.05 ppm) in the ^1H-NMR spectrum.

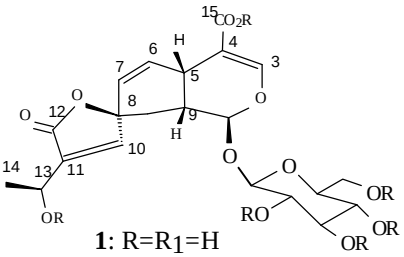
The *trans* cinnamate units of **5-7** were identified by analysis of IR data, showing signals at 1725 cm^{-1} ($\nu_{C=O}$, conjugated ester), 1600, 1500 cm^{-1} ($\nu_{C=C}$, aromatic) and ν_{C-O} at 1250 cm^{-1}. The ^1H-NMR spectrum showed two doublets at δ_H 7.60-7.68 (16.0 Hz, H-α) and 6.45-6.48 (16.0 Hz, H-β) and two signals for five aromatic protons [7.59 (m; H-2',6') and 7.37 (m; H-3',4',5')]. ^{13}C-NMR spectrum showed δ_C 166,20-166,80 (C=O), 134,50-134,70 (C-1'), δ_{CH}:129.00-129.20; 128.00-128.40; 130.00-130.50 (C-2'-6') and 118.30-118.70 ppm (C-α) which are similar to those found in the literature[16].

The chemical shifts of H-3 [δ_H 4.45 (dd, J = 10,0 and 4,0 Hz)] in **4** and **5** and [δ_H 4.72 (dd, 11,0 and 7,0 Hz)] in **6** and **7** as well as the carbon chemical shifts of C-3 [δ_C 80.90 (**4**, **5**, **6** and **7**)], C-2 [δ_C 23.70 (**4** and **5**), 23.50 (**6**), 23.70 (**7**)] and C-4 [δ_C 37.70 (**4**, **5**), 37.60 (**6**, **7**)] were compared with those of 3β-O-acetyl and 3β-O-cinnamoyl triterpene derivatives in the literature[15,16] to establish the β-position of O-acetyl and O-cinnamoyl moieties at C-3. A literature search revealed the absence of NMR spectral data for **1a** and ^{13}C-NMR data for **5** and **6**[14,17]. Therefore, these assignments are described in the experimental part.

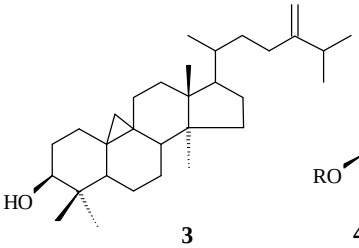
The structure of compound **8** was established as following: the IR signals at 3450 cm^{-1} (ν_{O-H}), 1620 cm^{-1} ($\nu_{C=C}$) and 1080 cm^{-1} (ν_{C-O}, secondary alcohol), the ^1H-NMR spectrum showed signals at δ_H 5,25 (m, H-12), 3,15 (m, H-3), 2,2 (d, 14.0 Hz, H-18) and signals relative to seven methyl groups at δ_H 0.75, 0.84, 0.96, 0.96, 1,11(s); 0.89 and 0.95 (d, 6.0 Hz). These data are in agreement with a pentacyclic acid triterpene of the ursane seires. The peaks at *m/z* 456 (M^+, 11%), 207 (47%), 208 (11%), 248 (100%), 189 (17%) observed in the mass spectrum, along with analysis of 1D and 2D NMR spectra of the acetyl derivative **8a** and comparison with those of the literature[18-20], allowed identification of the structure of the known triterpene **8**. The derivatives **8b** and **8c** showed δ_C: 171.0, 21.08 (H_3CCO), 51.41 (H_3C-O) in the ^{13}C-NMR spectrum and δ_H 2,04 (s, H_3CCO), 3,60 (s, H_3C-O) in the ^1H-NMR spectrum which were used to confirm the structure of **8** as urs-3β-hydroxy-12-en-28-oic acid (ursolic acid).

The mixture of sterols **9** and **10** was identified by the signals at δ_H 0.62 (s), 1.05 (s), 0.74-0.98 (m) in the ^1H-NMR spectrum corresponding to the absorptions of the methyl groups, the δ_H 3.49 (H-3), besides the signals at δ_H 5.10 (m, H-22 and H-23, **9**), δ_H 5.50 (d br, H-6, **9** and **10**) of the olefinic protons. These data along with the ^{13}C-NMR and EIMS spectral analysis of that mixture, and comparison with literature data[21], led us to identify **9** as stigmasterol and **10** as sitosterol.

The structure of the carbohydrate was established as methylmioinositol (**11**) by comparative analysis of chemical shifts of the monoprotoned carbon atoms observed in the ^{13}C-NMR (HBBD and DEPT) spectra with values described in the literature[22]. The spectral analysis of the derivative **11a** including ^1H-NMR, 1D and 2D (^1H,^1H-COSY) and ^1H,^{13}C-COSY, $^nJ_{CH}$, n = 1, 2 and 3) confirmed structure **11**[23].



1: R=R$_1$=H
1a: R=Ac, R$_1$=H
2: R=H, R$_1$= Me
2a: R=Ac, R$_1$= Me



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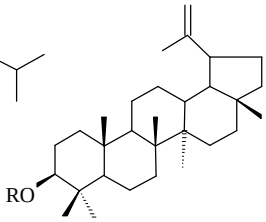
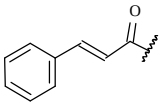
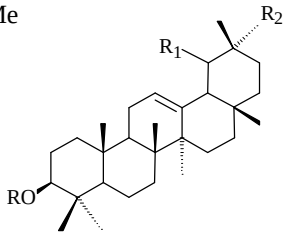


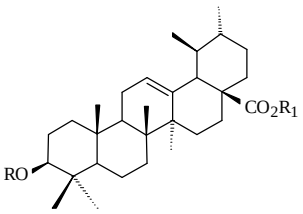
4 : R= Acetyl
5: R= Cinnamoyl



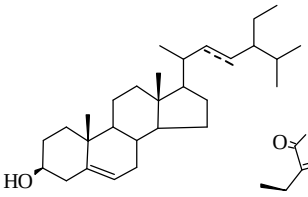
Cinnamoyl



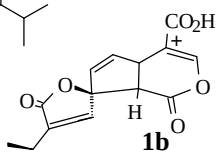
6: R$_1$ = CH$_3$, R$_2$: H, R= Cinnamoyl
7: R$_1$=H, R$_2$ = CH$_3$, R= Cinnamoyl



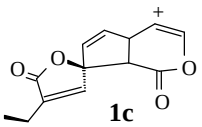
8 : R = H, R$_1$ = H
8a: R = Ac, R$_1$ = H
8b: R = Ac, R$_1$ = Me
8c: R = H, R$_1$ = Me



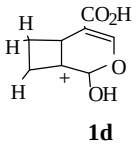
9: Δ ^{22,23}
10: 22,23-dihydro



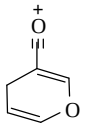
1b
m/z: 273(33.0%)



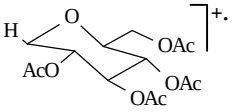
1c
m/z: 229(3.0%)



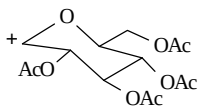
1d
m/z: 169(22.0%)



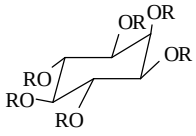
1e
m/z: 109(24)



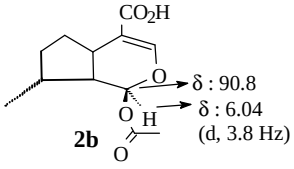
1f
m/z: 332(2.0%)



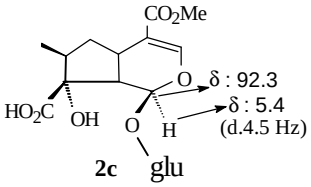
1g
m/z: 331(20.0%)



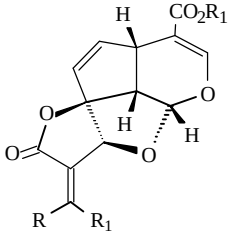
11: R= H
11a: R = Ac



2b
δ : 90.8
δ : 6.04
(d, 3.8 Hz)



2c glu
δ : 92.3
δ : 5.4
(d.4.5 Hz)



12: R=H, R$_1$=Me
13: R=Me, R$_1$=H

Experimental

General procedure

Melting points were determined using a Kofler hot stage instrument and are uncorrected. The NMR spectra were recorded in the Fourier transform mode on a Bruker AC-200 (^{1}H: 200 MHz, ^{13}C: 50.3 MHz) spectrometer. The solvents used were $CDCl_3$ and Methanol-d_6 with TMS as the internal standard. Mass spectra were obtained with GC-MS HP5988A at the Instituto de Química of the Uni-

versidade de São Paulo and with the Micro Mass-12 of the NPPN-Laboratório de Tecnologia Farmacêutica-Universidade Federal da Paraiba. Infrared spectra were recorded as KBr discs on a Perkin Elmer 1420 spectrophotometer. Column chromatography was run using silica gel S (Riedel 0.032-0.063 nm) for separation by gravity and with Merck 230/400 Mesh 60A for flash column chromatography. TLC analysis was done with silica gel G (Merck or Aldrich) and the spots were visualized by UV (254 nm) irradiation, reaction with an alcoholic solution of phosphomolybdic acid followed by heat, or by exposure to iodine vapor. Liquid-liquid partition chromatography was performed using the CCC Ito apparatus with a coil #10 (2.60 mm, 400 mL vol. approx., PTFE tubing). The preparative centrifugal chromatography was run with a Chromatotron from Harrison Research.

Plant material

Bark, leaves and latex of *H. articulata* (Vahl) Woodson were collected by botanist Benedito Vitor Rabello in Amapá state, Brazil. Authentication was performed by comparing it with a voucher specimen (Nº 0522) preserved at the Herbário Amapaense (HAMAB) of the IEPA, Macapá - AP, Brazil.

Extraction and isolation

The pulverized air-dried bark material (1.7 kg) and leaves (1.4 kg) were extracted by maceration at room temperature successively with hexane and methanol. The solvents were removed under vacuum to yield 10.8 g of hexanic extract and 30.0 g of methanolic extract from the bark and 73.6 g of hexanic extract and 50.0 g of methanolic extract from the leaves. The latex dissolved in $CHCl_3$ was filtered under vacuum and removal of the solvent gave 21.5 g of extract. The residue (5.0 g) of the latex was chromatographed on a nylon dried column of silica gel and eluted with CH_2Cl_2 and 15 fractions were collected. These fractions were analysed by TLC and submitted to centrifugal preparative chromatography (Chromatotron) with hexane/dichloromethane as eluents. From the fractions 1-4 was isolated the mixture of **6** and **7** (m.p.: 85-90°, 70.0 mg); fractions 5-15 were fractioned by flash chromatography on a silica gel column to yield **3** (m.p.: 167-169°, 170.0 mg), **9** and **10** (m.p.: 130-132°, 172.0 mg). and a mixture of these compounds along with aliphatic acids. The hexanic extract from bark (5.0 g) was fractioned on silica gel column using CH_2Cl_2/ethyl acetate as eluents in increasing polarities and 80 fractions were collected. Removal of the solvent give **5** (amorphous material, 60.0 mg) and **4** and **5** (100.0 mg) along with a mixture of these compounds and a mixture of aliphatic acids. The methanolic extract (30.0 g) from bark was submitted to acid-base extraction. The solution was concentrated and lyophylised to yield the HABM fraction which was dried in an Abderhalden apparatus. IR analysis of the fraction confirmed the absence of an ester carbonyl. The HABM was acetylated with acetic anhydride and pyridine to obtain HABM-Ac. Part of this product (4.0 g) was fractionated in a column of silica gel using chloroform as eluent yielding 17 fractions. Hexane was added to the these fractions yielding a solid **11a** (MP: 215-217°, 45 mg) and a solution with a mixture of iridoids, carbohydrates and other compounds. This mixture was partitionated by CCC (Ito) with $CHCl_3$:MeOH:H_2O (35:40:25) using $CHCl_3$ as the mobile phase. Aliphatic acids were found in the mobile phase. The remaining phase was fractionated by preparative centrifugal chromatography (Chromatotron) using hexane/ethyl acetate/methanol in increasing polarities to yield **11a** (370 mg), **1a** (amorphous material, 40 mg) and **2a** (amorphous material, 15 mg). NMR spectrum and TLC analysis of the hexanic extract from leaves revealed the presence of the same compounds found in the hexanic extract from bark. The portion of methanolic extract that was soluble in methanol gave **8** (m.p.: 226-228°, 25.0 g) after addition of ethyl acetate.

Acetylation of the fraction HABM and **8**

The fraction HABM (H*imatanthus* a*rticulata* Bark Methanol) and **8** were, separately, dissolved in a mixture of pyridine and Ac_2O (1:1) and the solution was allowed to stand for 24 h at room temperature. The usual work up yielded HABM-Ac (amorphous solid, 4.0 g) and **8a** (m.p.: 221-223°, 1.8 g).

Methylation of **8**, **8a** *and* **1a**

The ethereal solution of diazomethane previously prepared from Diazald was added in excess to solutions of **8**, **8a** and **1a** in methanol to yield **8c** (m.p.: 189-91 °C, 60.0 mg), **8b** (m.p.: 111-113 °C, 1.8 g) and **2a** (m.p.: 119-121 °C, 15.0 mg), respectively. The presence of these products was revealed by spectral analysis and comparison with the data of the corresponding natural compounds.

Penta-O-acetylplumeride glucoside acid (**1a**)

Gum, IR ν^{film}_{max} (cm^{-1}): 1740, 1660, 1620, 1370, 1270-1150; ^{1}H-NMR ($MeOD_4$,TMS, δ): 7.41(sb, H-10), 6.96 (br s, H-3); 6.43 (dd, 5.8 Hz; 1.5 Hz; H-6), 5.60 (qd, 6.6 Hz; 1.3 Hz; H-13), 5.38 (br d, 5.7 Hz; H-7), 5.16 (t, 8.0 Hz; H-3'), 5.10 (br s, H-1), 5.03 (t, 8.0 Hz; H-4'); 4.96 (t, 8.0 Hz; H-2'), 4.82 (d, 8.0 Hz; H-1'), 4.30 (dd; 12.6 Hz; 4.4 Hz; H-6'a), 4.10 (dd, 12.6 Hz; 2.0 Hz; H-6'b), 3.74 (m, H-5,5'), 3.50 (br d, 6.8 Hz; H-3'), 2.12, 2.06, 2.04, 1.98, 1.96 (s, H_3C-CO), 1.48 (d, 6.6 Hz, H-14). ^{13}C-NMR (HBBD, DEPT: θ = 90 and θ = 135) ($MeOD_4$, δ): 174.50 (C-15), 172.40-171.30 (O-C=O); 171.34 (C-12), 151.75 (C-10), 148.50 (C-3), 144.50 (C-7), 134.51 (C-11), 128.66 (C-6), 116.50 (C-4), 98.18 (C-1'), 97.33 (C-8), 93.33 (C-1), 73.81 (C-3'), 73.17 (C-5'), 72,16 (C-2'), 69.61 (C-4'), 66.18 (C-13), 62.86 (C-6'), 50.88 (C-9), 40.90 (C-5), 19.40

(C-14), 21.70 x 5 ($H_3\underline{C}CO$); EIMS, *m/z* (rel. int.): 332 (2, **1f**), 331 (20, **1g**), 289 (2), 273 (33, **1b**), 259 (3), 229 (3, **1c**), 169 (22, **1d**), 109 (24, **1e**), 80 (10), 43 (100).

*Lupeoyl 3*β*-O-cinnamate* (**5**): amorphous material

^{13}C-NMR (HBBD and DEPT: θ = 90 and θ = 135) ($CDCl_3$, TMS, δ): 166.00 (C-9'), 151.91 (C-20), 144.51 (C-7'), 134.50 (C-1'), 130.50 (C-4'), 129.05 (C-3',5'), 128.05 (C-2',6'), 118.77 (C-8'), 109.26 (C-29), 80.87 (C-3), 55.35 (C-5), 50.32 (C-9), 48.21 (C-18), 48.01 (C-19), 42.87 (C-17), 42.81 (C-14), 40.80 (C-8), 39.90 (C-22), 38.80 (C-13), 38.37 (C-1), 37.70 (C-4), 37.07 (C-10), 35.55 (C-16), 34.18 (C-7), 29.82 (C-21), 27.94 (C-23 and C-15), 25.09 (C-12), 23.69 (C-2), 20.87 (C-11), 19.17 (C-30), 18.20 (C-6), 17.98 (C-28), 16.48 (C-25), 16.18 (C-26), 15.89 (C-24), 14.51 (C-27).

*Urs-3*β*-O-cinnamoyl-12-en* (β-amyrin cinnamate)

^{13}C-NMR (PND, DEPT: θ = 90 and θ = 135) ($CDCl_3$, TMS, δ): 166.75 (C-9'), 144.22 (C-7'), 139.47 (C-13), 134.49 (C1'), 130.07 (C-4'), 128.78 (C-3',5'), 127.99 (C-2',6'), 124.27 (C-12), 118.77 (C-8), 80.94 (C-3), 58.88 (C-18), 55.22 (C-5), 47.49 (C-9), 41.59 (C-14), 41.49 (C-22), 39.97 (C-8), 39.76 (C-20), 39.55 (C-19), 38.43 (C-1), 37.91 (C-4), 36.76 (C-10), 33.69 (C-17), 32.54 (C-7), 31.20 (C-21), 28.34 (C-15), 28.06 (C-23 and C-28), 26.55 (C-2 and C-16), 23.50 (C-11), 23.34 (C-27), 23.21 (C-29), 21.30 (C-30), 18.61 (C-6), 16.85 (C-26), 15.72 (C-24 and C-25.

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