Triterpene Esters Isolated from Leaves of *Maytenus salicifolia* REISSEK

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The triterpene ester (3β)-olean-18-en-3-yl stearate (**1**), together with (3β)-urs-12-en-3-yl stearate (**2**), and (3β)-lup-20(29)-en-3-yl stearate (**3**) were isolated from leaves of *Maytenus salicifolia* REISSEK (Celastraceae). The structure of **1**, a new compound, including its configuration, was established by ^{1}H, ^{13}C, and DEPT-135 NMR data, including 2D experiments (HSQC, HMBC, COSY, and NOESY). The molecular mass (692 Da) was confirmed by gas chromatography coupled with mass spectrometry (CG/MS).

Introduction. – Many species of the Celastraceae family have been studied by phytochemical methods because these plants present some special pharmacological activities. The studies that have been carried out on these plants during the last decades demonstrate that the principles of biological interest are mainly due to flavonoids, sesquiterpene alkaloids, steroids, and pentacyclic triterpenes (PCTTs) [1].

Pentacyclic triterpene esters are considered to be important anti-arthritic compounds [2]. Moreover, other pharmacological effects like anti-inflammatory [3], antidepressive [4], antitumor [5], and hepatic protection activities [6] are also cited in the literature. Because of this wide variety of pharmacological activities, the presence of this class of organic compounds in plants is very interesting.

Maytenus salicifolia REISSEK is a species of the Celastraceae family commonly found in the Brazilian state of Rio de Janeiro, São Paulo, and Minas Gerais. In many locations, it is popularly known as 'Cafezinho'. The tea from leaves is used in folk medicine for stomach's ulcers treatments, and all parts of the plant are used to alliviate itches and for the treatment of allergies [7].

During the study of the hexane extract obtained from *Maytenus salicifolia* leaves, three PCTT esters were isolated and chemically characterized, *i.e.*, (3β)-olean-18-en-3-yl stearate (**1**), a new compound, and (3β)-urs-12-en-3-yl stearate (**2**) and (3β)-lup-20(29)-en-3-yl stearate (**3**) (*Fig. 1*) previously isolated from *Koelpinia linearis* [8] which have already been reported [9][10]. The structure and configuration of these three compounds were elucidated on the basis of their ^{1}H- and ^{13}C-NMR data. The molecular formula $C_{48}H_{84}O_2$ attributed to these compounds was established by quantitative ^{13}C-NMR measurements, and the molecular mass of 692 Da attributed to **1** and **2** was confirmed by gas chromatography coupled with mass spectrometry (CG/MS).

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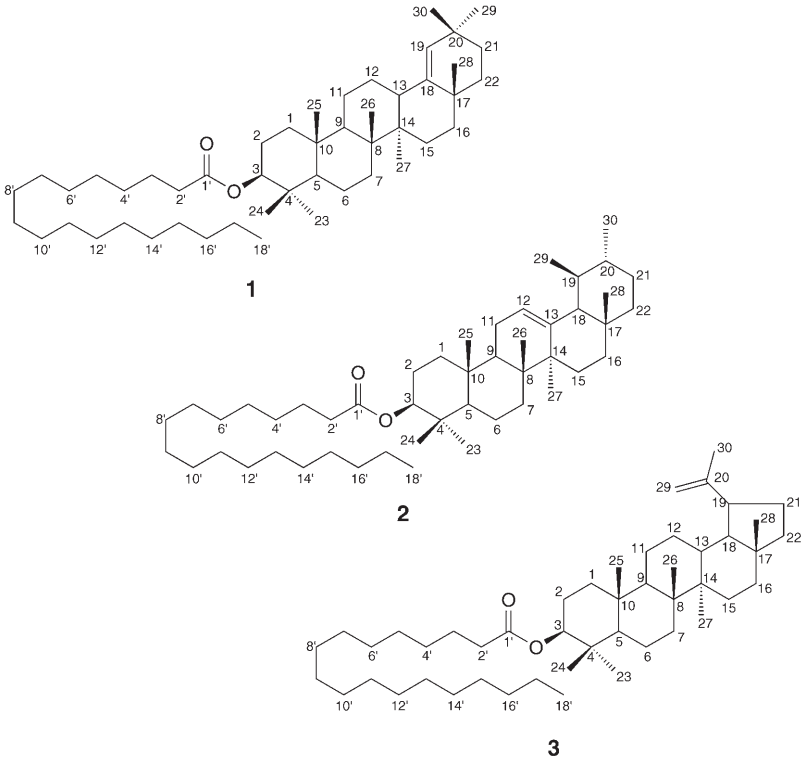

Fig. 1. *Triterpene esters isolated from* Maytenus salicifolia

Results and Discussion. – Compounds **1**–**3** showed positive results when submitted to the *Liebermann–Burchard* (*LB*) test [11], indicating that they were pentacyclic triterpenes.

The IR spectrum of compound **1** showed an absorption at 1724 cm^{-1} establishing the presence of a carbonyl group in the molecule. The MS of **1** presented a peak at *m*/*z* 204, suggesting a break of the C(11)–C(12) bond, the base peak at *m*/*z* 189, arising from the subsequent loss of a Me-group fragment, and a peak at *m*/*z* 177, arising from a *retro-Diels–Alder* fragmentation. These standard fragmentations are characteristic of the olean-18-ene PCTT series [12]. The MS data of compound **1**, together with signals observed in the ^{13}C-NMR spectrum (δ(C) 129.77 (CH) and 142.68 (C)) suggested that compound **1** belongs to the olean-18-ene series [12]. The ^{1}H- and ^{13}C-NMR chemical shifts (*Table*) of **1** and their comparison with the literature data of (3β)-olean-18-en-3-yl acetate [13] together with the data of a PCTT aliphatic stearate chain [9][14] confirmed the proposed structure. The data of (3β)-olean-18-en-3-yl stearate (**1**) contribute to the PCTT-ester NMR studies.

The signals at δ(C) 80.60 and δ(H) 4.48 suggested the presence of an ester group in **1**. Intense signals at δ(C) 29.69 and δ(H) 1.25 corresponding to CH_2 groups, together with signals at δ(C) 173.68 (CO) and

Table. *^1H-* (400 MHz) *and ^{13}C-NMR* (100 MHz) *Data of (3β)-Olean-18-en-3-yl Stearate* (**1**) *and Comparison with Literature Data of (3β)-olean-18-en-3-yl Acetate* [13] *and the Stearic Acid Ester Chain* [9][14]. δ in ppm, *J* in Hz; in $CDCl_3$.

	δ(C) (Acetate [13])	δ(C) (**1**)	δ(H) (**1**)	HMBC		δ(C) (Stearate [9])	δ(C) (**1**)	δ(H) (**1**)	HMBC
CH_2(1)	38.6	38.63	0.98 (H_{ax}), 1.69 (H_{eq})		C(1′)	173.54	173.68	–	
CH_2(2)	23.6	23.75	1.62–1.68 (*m*)	C(3)	CH_2(2′)	34.87	34.54	2.27 (*dd*, *J* = 7, 3)	C(1′), C(3′), C(4′)
H–C(3)	80.8	80.60	4.48 (*dd*, *J* = 10.4, 5.5)	C(1′), C(1), C(2), C(4), C(23), C(24)	CH_2(3′)	25.21	25.18	1.60	
C(4)	37.7	37.88	–		CH_2(4′)	29.21	29.18	1.25	
H–C(5)	55.5	55.60	0.82–0.85 (*m*)		CH_2(5′)	29.28	29.35	1.25	
CH_2(6)	18.0	18.16	1.48–1.50 (*m*, H_{eq}), 1.78–1.82 (*m*, H_{ax})		CH_2(6′)	29.37	29.35	1.25	
CH_2(7)	34.5	34.87	1.32–1.37 (*m*, H_{ax}), 1.44–1.49 (*m*, H_{eq})		CH_2(7′)	29.61	29.69	1.25	
C(8)	40.7	40.79	–		CH_2(8′)	29.68	29.69	1.25	
H–C(9)	51.0	51.14	1.28–1.32 (*m*)		CH_2(9′)	29.70	29.69	1.25	
C(10)	37.0	37.17	–		CH_2(10′)	29.72	29.69	1.25	
CH_2(11)	21.1	21.14	1.50–1.54 (*m*)		CH_2(11′)	29.72	29.69	1.25	
CH_2(12)	26.0	26.19	1.49–1.52 (*m*)		CH_2(12′)	29.72	29.69	1.25	
H–C(13)	38.3	38.41	2.24–2.26 (*m*)	C(11), C(12), C(19), C(27)	CH_2(13′)	29.72	29.69	1.25	
C(14)	43.2	43.35	–		CH_2(14′)	29.66	29.69	1.25	
CH_2(15)	27.4	27.53	1.07–1.10 (*m*, H_{eq}), 1.68–1.72 (*m*, H_{ax})		CH_2(15′)	29.49	29.69	1.25	
CH_2(16)	37.3	37.70	1.38–1.40 (*m*)		CH_2(16′)	31.95	31.92	1.25	
C(17)	34.2	34.35	–	C(19), C(28)	CH_2(17′)	22.70	22.68	1.25	
C(18)	142.5	142.68	–	C(12), C(19), C(22), C(28)	Me(18′)	14.09	14.09	0.88	C(17′), C(16′)
H–C(19)	129.6	129.77	4.86 (*s*)	C(13), C(17), C(21), C(29), C(30)					
C(20)	32.2	32.35	–						
CH_2(21)	33.3	33.36	1.30–1.36 (*m*, H_{eq}), 1.40–1.44 (*m*, H_{ax})						
CH_2(22)	37.6	37.39	1.33–1.36 (*m*)						
Me(23)	27.8	27.99	0.85 (*s*)	C(3), C(4), C(5), C(24)					
Me(24)	16.6	16.59	0.85 (*s*)	C(3), C(4), C(5), C(23)					
Me(25)	16.0	16.74	0.89 (*s*)	C(1), C(5), C(9), C(10)					
Me(26)	16.4	16.09	1.08 (*s*)	C(7), C(8), C(9), C(14)					
Me(27)	14.4	14.54	0.74 (*s*)	C(8), C(13), C(14), C(15)					
Me(28)	25.1	25.27	1.02 (*s*)	C(16), C(17), C(18), C(22)					
Me(29)	31.2	31.32	0.93 (*s*)	C(19), C(20), C(21), C(30)					
Me(30)	29.1	29.25	0.94 (*s*)	C(19), C(20), C(21), C(30)					

δ(H) 2.27 (CH_2) confirmed that compound **1** contains an attached long-chain ester moiety. HSQC Experiments allowed to correlate each C-atom with its respective H-atom. Thus, it was possible to correlate the signals of H–C(3) (δ(C) 80.60; δ(H) 4.48), H–C(19) (δ(C) 129.77; δ(H) 4.86), and CH_2(2′) (δ(C) 34.54; δ(H) 2.27).

The initial analysis of the HMBC plots allowed to establish the correlations between δ(H) 4.48 (H–C(3)) with δ(C) 173.68 (C=O) and with the Me signals at δ(C) 27.99 (Me(23)) and at δ(C) 16.59 (Me(24)). The C=O signal also correlated with δ(H) 2.27 (CH_2(2′)). These data confirmed that **1** is a triterpene of the olean-18-ene type having a long-chain ester attached at C(3). The molecular ion observed in the MS at *m/z* 692 defined the chain length and contributed to establish the structure of compound **1** as being (3β)-olean-18-en-3-yl stearate.

The HSQC and HMBC data of **1**, together with the literature data of (3β)-olean-18-en-3-yl acetate [13], were used to complete the attribution of all ^{1}H- and ^{13}C-NMR chemical shifts. The HMBC revealed the correlation of δ(C) 129.77 (C(19)) with δ(H) 0.93 (Me(29)) and 0.94 (Me(30)), and of δ(H) 4.86 (H–C(19)) with δ(C) 38.41 (C(13)) and 34.35 (C(17)) (*Table*). Correlations of δ(H) 1.02 with δ(C) 37.70 (C(16)), 34.35 (C(17)), 142.68 (C(18)), and 37.39 (C(22)) were also observed, demonstrating that δ(H) 1.02 corresponded to Me(28) (δ(C) 25.27). The Me signals at δ(H) 0.74 and 1.08 correlated with δ(C) 40.79 (C(8)) and 43.35 (C(14)). However, as only the correlations δ(H) 0.74/δ(C) 38.41 (C(13)) and 27.53 (C(15)), were detected, δ(H) 0.74 was attributed to Me(27). Similarly, the correlations δ(H) 1.08/δ(C) 34.87 (C(7)) and 51.14 (C(9)) allowed to assign δ(H) 1.08 to Me(26).

The signal at δ(C) 51.14 (C(9)) also presented correlation with another Me signal at δ(H) 0.89. The latter correlated with δ(C) 38.63 (C(1)), 55.60 (C(5)), and 37.17 (C(10)), in accord with its assignment to Me(25). The δ(C) of C(5) showed correlation with an intense signal at δ(H) 0.85, arising from Me(23) and Me(24) which could not be distinguished (overlapping signals). The Me signal at δ(H) 0.85 showed correlation with δ(C) 80.60, previously attributed to C(3), and H–C(3) at δ(H) 4.48 correlated with δ(C) 55.60 (C(5)), 27.99 (C(23)), and 16.59 (C(24)), and also with δ(C) 173.68 (C(1′)). These correlations confirmed the position of the stearyloxy group at C(3) of the PCTT ring A. The Me signal at δ(H) 0.88 (Me(18′)) correlated with δ(C) 31.92 (C(16′)) and 22.68 (C(17′)). The remaining δ(H) and δ(C) of the side chain were attributed by comparison with NMR data of triterpene esters [9][14][15].

The COSY experiments were used to confirm the assignments of CH_2(3′), CH_2(6), CH_2(12), and CH_2(15). Analysis of NOESY plots allowed to establish the configuration of **1**. Thus, NOEs between H–C(3) and H–C(5), Me(23), H_{ax}–C(1), and H_{eq}–C(2) were observed (*Fig. 2*). The NOEs between H–C(19) and CH_2(12), Me(29), and Me(30) were due to the presence of the olefinic C-atoms in rings D and E, confirming the distortion of the chair conformation of these rings, which renders possible these correlations. Moreover, the following NOEs were observed: Me(25)/Me(24), Me(26), H_{ax}–C(6), and H_{ax}–C(11); H–C(13)/Me(28), Me(26), and H_{ax}–C(15); H–C(9)/H–C(5) and Me(27); and Me(28)/Me(30), H–C(13), and H_{ax}–C(21).

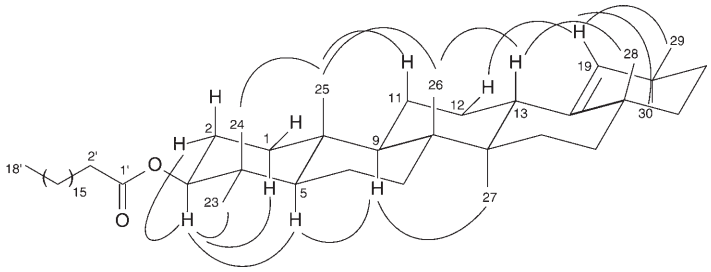

Fig. 2. *Some ^{1}H,^{1}H-correlations observed in the NOESY plot of (3β)-olean-18-en-3-yl stearate* (**1**)

The IR spectra of compounds **2** and **3** showed a broad band at 1731 cm^{-1}, suggesting the presence of an ester group in both compounds. The ^{1}H- and ^{13}C-NMR, HSQC,

HMBC, COSY, and NOESY data and their comparison with literature data established the structures of **2** and **3**.

The ^{1}H- and ^{13}C-NMR spectra of **2** showed signals at δ(H) 5.12 (t, J = 3.48 Hz), at δ(C) 124.38 (CH) and 139.67 (C), indicating a triterpene structure of the ursane type [16]. The analysis of the HSQC plot revealed correlations of the signals of C(3) (δ(C) 80.64; δ(H) 4.51), of C(12) (δ(C) 124.38; δ(H) 5.12), and of C(2′) (δ(C) 34.88; δ(H) 2.29) corresponding to a H−C−NO group. The HMBC plot showed that H−C(3) was correlated with δ(C) 28.13 (Me(23)), 16.84 (Me(24)), 23.68 (C(2)), 55.32 (C(5)), and 38.50 (C(1)) and also with δ(C) 173.54 (C(1′)=C=O). These data suggested that the long-chain ester group was bonded to C(3). The size of this side chain was determined by a quantitative ^{13}C-NMR experiment. Integration of the side-chain δ(C) signals revealed the presence of 16 CH_2 groups. Adding to these results the signals of C=O and the terminal Me group established the C_{18} aliphatic side chain. The molecular ion at m/z 692 observed in the MS confirmed the structure of (3β)-urs-12-en-3-yl stearate for compound **2** [9]. The attributions of the ^{1}H- and ^{13}C-NMR signals were performed with the aid of HSQC, HMBC, COSY, and NOESY data and were in accord with the literature [9]. For the ^{13}C-NMR data, see *Exper. Part*.

The NMR spectra of **3** showed signals at δ(H) 4.49 and δ(C) 109.36 (CH_2) and also at 150.96 (C), indicating that it was a triterpene of the lupane type [13]. The HMBC plot revealed a correlation of δ(C) 173.69 (C=O), with δ(H) 4.49 (H−C(3)). This observation suggested the presence of a long-chain ester group at C(3). Comparison of the ^{13}C-NMR data with those of (3β)-lup-20(29)-en-3-yl palmitate [10] suggested the structure of a long-chain aliphatic ester derivative of lupeol for **3**. The size of this side chain was determined by a quantitative ^{13}C-NMR experiment. Integration of the side-chain δ(C) signals revealed the presence of 16 CH_2, 1 C=O, and 1 terminal Me group, *i.e.*, of a C_{18} side chain. Comparison of the NMR and MS data of **3** with the literature data [12] established the structure of (3β)-lup-20(29)-en-3-yl stearate. For the ^{13}C-NMR data, see *Exper. Part*.

Experimental Part

General. M.p. (uncorrected): *Mettler FP 80 HT*. CC = Column chromatography. TLC: silica gel *G-60*/$F_{254\,nm}$ (0.25 mm; *Merck*) plates, previously activated at 100°; detection by UV light, I_2 vapor, or vanillin in perchloric acid soln. [17]. IR Spectra (KBr): *Shimadzu IR-408* spectrophotometer; in cm^{-1}. GC/MS: *Shimadzu-GC-MS-QP5050* equipment.

NMR Spectra. Bruker-DRX-400-Advance spectrometer, at 400 or 100 MHz and 300 K, and equipped with an inverse-detection 5-mm multinuclear head ^{1}H/^{13}C (90° pulse widths of 6.44 μs and 7.50 μs for ^{1}H and ^{13}C, resp.). A sample of **1**, **2**, or **3** was dissolved in $CDCl_3$ (0.5 ml) and transferred to a 5-mm (o.d.) tube; $SiMe_4$ was used as internal standard. 1D ^{1}H- and ^{13}C-NMR spectra were acquired under standard conditions. ^{1}H-NMR spectra were obtained by using a sweep width of 11990.41 Hz over 65536 data points and multiplied by an exponential factor corresponding to a 0.30-Hz line broadening prior to *Fourier* transformation. ^{13}C-NMR spectra were obtained by using a sweep width of 31.847 Hz. The quantitative ^{13}C-NMR experiments were carried out with a direct-detection 5-mm dual probe, and by using an inverse-gated decoupling standard pulse program to NOE suppression. A total of 3081 transients with 65000 data points were collected by using a spectral width of 24000 Hz and the 20.0-s delay between pulses, to permit full relaxation of all C-atoms. The total experiment time of each sample was 20 h. The FID was obtained with 32.00 data points and processed with the *Gaussian* function (LB = −1.0, GB = 0.01). All 2D NMR spectra were obtained with gradient pulses. Two-dimensional inverse (H detection) to heteronuclear shift-correlation spectra were obtained with a 5-mm multinuclear inverse detection probe with gradient coil (90° pulse width of 6.44 μs and 9.80 μs for ^{1}H and ^{13}C, resp.). For HSQC (^1J(C,H) detection), a delay for long-range evolution time of 65 ms was used. A total of 16 transients with 1024 data points were collected. The same conditions were used for HMBC (detection of ^nJ(C,H); n = 2 and 3) experiments. Sine and squared sine-bell windows were used for processing the second and first dimensions, resp. Standard pulse sequences were used for the 2D ^{1}H,^{1}H-NOESY experiments, with the 400 ms mixing time. The F_1 dimension was 20000 Hz with 512 data point. Sixteen transients were

collected for each time increment and processed in each dimension by using a QSINE function. 2D ^{1}H,^{1}H-COSY-GP were carried out under standard conditions, with a sweep width of 5341.88 Hz over 2048 data points. Sine bells were used in both dimensions. Data processing was carried out on the *SGI* workstation with *Bruker* (*DRX 400*) micro programs and the XWIN-NMR 3.1 version program for *Windows XP*.

Plant Material and Compound Isolation. *Maytenus salicifolia* REISSEK (Celastraceae) was collected in Ouro Branco Mountain, located near Ouro Branco City, Minas Gerais State, Brazil. A voucher (N° OUPR 18094) of this plant is deposited at the Herbário Jose Badini of the Universidade Federal de Ouro Preto, MG, Brazil. The leaves were dried on *Kraft* paper at r.t. and with forced air circulation. After being dried and grounded in a mill, the leaves (1000 g) were exhaustively extracted with hexane at r.t. for 3 weeks. After evaporation of the solvent, the hexane extract (23.38 g) was submitted to CC (silica gel (*Merck*, 70–230 mesh; 380 g), polarity gradient with hexane, $CHCl_3$, AcOEt, and MeOH, pure or in mixtures): 188 fractions (TLC control). *Fr. 11–15* furnished a colorless wax (395 mg) that was submitted to CC (silica gel (*Merck*, 70–230 mesh; 200 g, with 2% $AgNO_3$ (*w*/*w*)), cyclohexane/$CHCl_3$ 85:15): **1** (3.0 mg) and **2** (209.4 mg) as white waxes. The remaining material was eluted with AcOEt and identified by IR and NMR spectra as a mixture of long-chain saturated hydrocarbons (162.0 mg). From *Fr. 23–29*, a colorless wax (581.0 mg) was obtained that was submitted to CC (silica gel (*Merck*, 70–230 mesh; 300 g, with 2% $AgNO_3$ (*w*/*w*)), cyclohexane/$CHCl_3$ 8:2): **3** (26 mg) as a white wax. The remaining material was eluted with AcOEt furnishing a greasy mixture constituted by long-chain saturated hydrocarbons (433.0 mg).

(3β)-Urs-12-en-3-yl Stearate (**2**): ^{13}C-NMR ($CDCl_3$): 173.68 (C(1′)); 139.66 (C(13)); 124.38 (C(12)); 80.64 (C(3)); 59.13 (C(18)); 55.32 (C(5)); 47.69 (C(9)); 42.13 (C(14)); 41.58 (C(22)); 40.09 (C(8)); 39.70 (C(20)); 39.65 (C(19)); 38.51 (C(1)); 37.77 (C(4)); 36.85 (C(10)); 34.87 (C(2′)); 33.78 (C(17)); 32.92 (C(7)); 31.95 (C(16′)); 31.29 (C(21)); 29.72 (C(11′), C(12′), C(13′)); 29.71 (C(10′)); 29.69 (C(9′)); 29.68 (C(8′)); 29.66 (C(14′)); 29.60 (C(7′)); 29.49 (C(15′)); 29.38 (C(6′)); 29.28 (C(5′)); 29.20 (C(4′)); 28.77 (C(28)); 28.14 (C(16)); 28.13 (C(23)); 26.65 (C(15)); 25.20 (C(3′)); 23.68 (C(2)); 23.41 (C(11)); 23.27 (C(27)); 22.70 (C(17′)); 21.40 (C(30)); 18.29 (C(6)); 17.52 (C(29)); 16.91 (C(26)); 16.84 (C(24)); 15.75 (C(25)); 14.12 (C(18′)).

(3β)-Lup-20(29)-en-3-yl Stearate (**3**): ^{13}C-NMR ($CDCl_3$): 173.69 (C(1′)); 150.96 (C(20)); 109.36 (C(29)); 80.65 (C(3)); 55.44 (C(5)); 50.40 (C(9)); 48.35 (C(18)); 48.04 (C(19)); 43.03 (C(17)); 42.88 (C(14)); 40.91 (C(8)); 40.03 (C(22)); 38.43 (C(1)); 38.11 (C(13)); 37.87 (C(4)); 37.14 (C(10)); 35.65 (C(16)); 34.88 (C(2′)); 34.27 (C(7)); 31.94 (C(16′)); 29.88 (C(21)); 29.71 (C(9′), C(10′), C(11′), C(12′), C(13′)); 29.69 (C(8′)); 29.65 (C(14′)); 29.60 (C(7′)); 29.48 (C(15′)); 29.37 (C(6′)); 29.27 (C(5′)); 29.19 (C(4′)); 28.00 (C(23)); 27.48 (C(15)); 25.19 (C(3′)); 25.15 (C(12)); 23.78 (C(2)); 22.70 (C(17′)); 20.99 (C(11)); 19.31 (C(30)); 18.24 (C(6)); 18.03 (C(28)); 16.59 (C(24)); 16.18 (C(25)); 16.01 (C(26)); 14.55 (C(27)); 14.11 (C(18′)).

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