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# CYCLOARTANE TRITERPENE GLYCOSIDES FROM *ASTRAGALUS TRIGONUS*

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**Key Word Index**—*Astragalus trigonus*; Fabaceae; Leguminales; roots; cycloartane triterpene glycoside; trigonoside I, II and III; astragaloside I and II.

**Abstract**—Three new cycloartane glycosides, trigonoside I, II and III, and the known astragalosides I and II were isolated from the roots of *Astragalus trigonus*. The structures of the new glycosides were totally elucidated by high field (600 MHz) NMR analyses as cycloastragenol-6-*O*-*β*-xylopyranoside, cycloastragenol-3-*O*-[α-L-arabinopyranosyl(1 → 2)-*β*-D-xylopyranosyl]-6-*O*-*β*-D-xylopyranoside and cycloastragenol-3-*O*-[α-L-arabinopyranosyl (1 → 2)-*β*-D-(3-*O*-acetyl)-xylopyranosyl]-6-*O*-*β*-D-xylopyranoside.

## INTRODUCTION

The genus *Astragalus* L. has 37 species indigenous to Egypt, it belongs to the family Fabaceae of the order Leguminales [1, 2].

Extracts from different *Astragalus* species have shown cytotoxic activities in animals [3] and have been used for the treatment of leukaemia and uterine cancer patients [4]. Cycloartane triterpene glycosides were isolated from several Egyptian *Astragalus* species [5–10]. Recently, we found that some of these glycosides have antitumour activity against some human tumour cell lines and, also, AIDS antiviral activity [6, 7]. From the aerial parts of *A. trigonus* DC., the major 6-oxocycloartan-3*β*,16*β*-diglucoside was previously isolated [10]. We now report on the isolation and characterization of the three new cycloartane triterpene glycosides (**1–3**) together with astragalosides I and II, from the roots of *A. trigonus* DC.

## RESULTS AND DISCUSSION

The structures of compounds **1–3** were established by a combination of one-dimensional and two-dimensional NMR techniques, operating at 600 MHz. Compound **1**, the less polar one, was used as a model compound to fully assign proton resonances and coupling constants of the aglycone, it being common to all products. For the sake of clarity we report in the tables the proton NMR coupling constants for compound **1** and for the sugar moieties of the three isolated compounds **1–3**; proton and carbon assignments of compounds **2** and **3** are reported in the experimental. The proton and carbon NMR analyses, the E-COSY [11] and the ROESY [12] experiments allowed to assign the aglycone the structure of cycloastragenol [20(*R*),24(*S*)-epoxy-9*β*,19cyclolanostan-3*β*,6α,16*β*,25-tetrol]. Cycloastragenol is commonly found in many cycloartane glycosides from *Astragalus* species [13].

Compound **1** showed a molecular peak at *m/z* 645 $[M + Na]^+$ in the FAB mass spectrum, corresponding to the molecular formula $C_{35}H_{58}O_9$. The structure, configuration and conformation of the pentose unit linked to the aglycone were determined by running a 1D TOCSY [14] experiment, which allows determination of both chemical shifts and coupling constants of the sugar moiety and define it as a *β*-D-xylopyranoside. The site of linkage to the aglycone was determined by a HMBC [15] experiment as position-6. From these spectroscopic data we could assign **1** the structure of cycloastragenol-6-*O*-*β*-xylopyranoside, a new compound which we named trigonoside I.

Compound **2** showed a molecular peak at *m/z* 909 $[M + Na]^+$ in the FAB mass spectrum corresponding to the molecular formula $C_{45}H_{74}O_{17}$. The one-dimensional TOCSY experiment allowed to identify the sugar moiety as constituted of two *β*-D-xylopyranosyl units and one α-L-arabinopyranosyl unit. The coupling constants of the α-L-arabinopyranosyl unit accommodate it in a preferred

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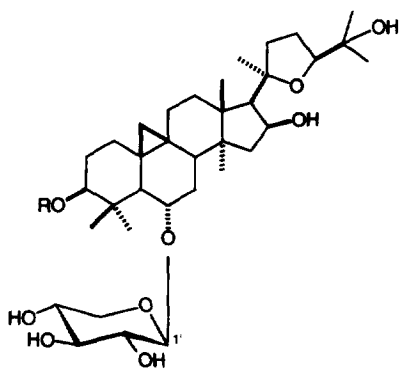
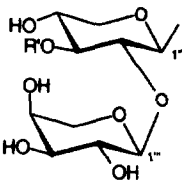
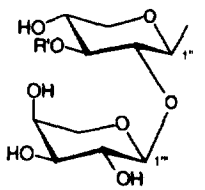


| | R | R' |
|---|---|---|
| 1 | H | |



| | | |
|---|---|---|
| 2 | | H |



| | | |
|---|---|---|
| 3 | | COMe |

$^4C_1$ conformation [16]. Of the three saccharidic units, one β-D-xylopyranose is linked at position C-6 to the aglycone, another β-D-xylopyranose is linked to position C-3 of the aglycone and carries the α-L-arabinopyranose unit, linked to C-2. These assignments were made possible by the combined interpretation of the HMBC and ROESY spectra. Compound **2** has been assigned the structure of cycloastragenol-3-*O*[α-L-arabinopyranosyl (1 → 2)-β-D-xylopyranosyl]-6-*O*-β-D-xylopyranoside, a new compound which we named trigonoside II.

Compound **3** showed a molecular ion at *m/z* 951 $[M + Na]^+$ in the FAB mass spectrum, corresponding to the molecular formula $C_{47}H_{76}O_{18}$. Three monosaccharidic units were determined as in compound **3**, plus the presence of an acetyl group. This could be located at C-3 of the β-D-xylopyranosyl unit linked to position C-3 of the aglycone, as determined by HMBC experiments. Compound **3** was assigned the structure of cycloastragenol 3-*O*-[α-L-arabinopyranosyl(1 → 2)-β-D-(3-*O*-acetyl)-xylopyranosyl]-6-*O*-β-D-xylopyranoside, a new compound which we named trigonoside III.

Together with these three new saponins, from *A. trigonus* we also isolated astragaloside I and II, previously found in *A. trigonus* [5, 7].

## EXPERIMENTAL

*Plant material. Astragalus trigonus* DC. was collected from El-Agami, west of Alexandria, Egypt, in April 1991. The plant was previously identified in the Department of Botany, Faculty of Science, Cairo University. Voucher specimens were also deposited in the herbarium of Faculty of Science, University of Alexandria, Egypt.

*General methods.* FAB-MS were obtained on a VG 7070 mass spectrometer using NBA as matrix. NMR: All spectra were measured on samples of about 10 mg dissolved in 750 μl of pyridine-$d_5$, in 5 mm tubes. Spectra were registered in phase sensitive mode at 28° on a Varian Unity 600 spectrometer, operating at 599.919 MHz for $^1H$ and at 150.858 for $^{13}C$, equipped with a triple resonance indirect detection probe ($^1H\{^{13}C, ^{15}N\}$), a waveform generator on both the observing and the decoupling channel and running the Varian Software Vnmr 4.3a. The 1D experiments were run with the States–Haberkorn method [17] and the 2D ones with collection of 2 sets of data (Hypercomplex method). The 1D and 2D spectral widths used were 6000 Hz for $^1H$ and 15300 Hz for $^{13}C$. All spectra were referencered to TMS through internal signals. The DQF-COSY [18] spectra were acquired with 2048 points in F2, 512 complex increments in F1, 16 scans per increment and a final data matrix of 4k × 2k points. The TOCSY spectra [19] were acquired with a 80 msec mixing time, a MLEV-17 [20] spin-lock field of 10 kHz flanked by two 2 msec trim pulses, 1024 points in F2, 256 complex increments in F1, 8 scans per increment and a final data matrix of 2k × 1k points. The ROESY spectra [12] were acquired with a 400 msec mixing time, a MLEV-17 spin-lock field of 3 kHz obtained with small flip-angle pulses (30°), 1024 points in F2, 256 complex increments in F1, 8 scans per increment and a final data matrix of 2k × 1k points. The E-COSY spectra [11] were acquired with 4096 points in F2, 1024 complex increments in F1, 32 scans per increment and a final data matrix of 8k × 4k points. The HMQC spectra [21] were acquired with a nulling time of 300 msec, 1024 data points in F2, 256 complex increments in F1, 8 scans per increment, a final data matrix of 2k × 1k points and a MPF7 [22] waveform generator-based $^{13}C$-decoupling sequence during the acquisition. The HMBC spectra [15] were acquired with 1024 points in F2, 256 complex increments in F1, 32 scans per increment and a final data matrix of 2k × 1k points. For each sample one HMBC spectrum was optimized for a $^nJ_{C-H}$ of 8 Hz and another one for a $^nJ_{C-H}$ of 4 Hz, with $n = 2 \div 4$. All 2D spectra were transformed with a cosine-squared weighting function in both dimension, except for the HMBC ones where a sinebell function was applied in F2 and a cosine squared in F1, together with a mixed mode display of the spectra (magnitude mode in F2 and phase sensitive mode in F1). Selective excitation spectra, 1D-TOCSY [14] were acquired using waveform generator-based BURP shaped pulses [23], mixing times ranging from 80 to 150 msec and a MLEV-17 spin-lock field of 10 kHz preceded by a 2 msec trim pulse. The repetition rates for all kind of spectra were about 1.5 sec.

*Extraction and isolation.* The air-dried powdered roots of *A. trigonus* DC. (2 kg) were extracted with 95% EtOH. The extract was concd to 200 ml which was added slowly with continuous stirring to water (1 l), left 5 hr at room temp. then filtered from the pptd resin. The filtrate was partitioned into petrol, $Et_2O$, $CHCl_3$, EtOAc and *n*-BuOH, successively. The residue after evapn of the EtOAc (20 g) was chromatographed on silica gel. Elution with $CHCl_3$–MeOH mixtures yielded **1** (80 mg; 9:1), astragaloside I (150 mg 4:1) and astragaloside II (180 mg; 3:1). On the other hand, the *n*-BuOH soluble fraction (30 g) was chromatographed on silica gel previously wetted with EtOAc. Elution with EtOAc–MeOH mixtures yielded astragaloside II (60 mg; 9:1), **3** (120 mg; 4:1) and **2** (160 mg; 7:3).

*Compound* **1** (*Trigonoside I*). Mp 226° ($Et_2O$); $[\alpha]_D^{25} = +25$ (MeOH; *c* 0.58), FAB-MS *m/z*: 645 $[M + Na]^+$, $^1H$ and $^{13}C$ NMR see Tables 1–3.

*Compound* **2** (*Trigonoside II*). Mp 243° (dec) (EtOH–$Et_2O$ 1:1); $[\alpha]_D^{25} = -30$ (pyridine; *c* 1.29), FAB-MS *m/z*. 909 $[M + Na]^+$, $^1H$ NMR: $\delta$ 5.03 (H-16ax), 3.87 (H-24$\alpha$), 3.77 (H-6ax), 3.37 (H-3 ax), 3.10 (H-22$\alpha$), 2.57 (H-17ax), 2.33 (H-15ax), 2.29 (H-23$\alpha$), 2.24 (H-2eq), 2.09 (H-8ax), 2.06 (2H-7), 2.03 (H-23$\beta$), 1.95 (H-2ax), 1.82 (H-5ax), 1.81 (H-15eq), 1.77 ($CH_3$-28), 1.67 (H-11eq), 1.66 (H-12ax), 1.64 (H-22$\beta$), 1.56 ($CH_3$-26), 1.53 (H-1ax), 1.51 (H-12eq), 1.48 (H-11ax), 1.38 ($CH_3$-18), 1.32 ($CH_3$-29), 1.28 ($CH_3$-21), 1.28 ($CH_3$-27), 1.27 (H-1eq), 1.15 ($CH_3$-30), 0.61 (H-19B), 0.11 (H-19A), $^{13}C$ NMR: $\delta$ 87.85 (C-3), 87.45 (C-20), 81.84 (C-24), 77.46 (C-6), 73.55 (C-16), 71.32 (C-25), 58.21 (C-17), 52.02 (C-5), 46.25 (C-14), 45.79 (C-15), 45.33 (C-13), 43.37 (C-8), 42.76 (C-4), 35.04 (C-22), 33.66 (C-12), 33.15 (C-7), 32.00 (C-1), 30.18 (C-2), 28.79 (C-21), 28.30 (C-26), 28.04 (C-10), 27.74 (C-28), 27.22 (C-27), 26.59 (C-23), 26.42 (C-11), 25.68 (C-19), 21.40 (C-9), 20.18 (C-18), 19.92 (C-30), 16.50 (C-29).

*Compound* **3** (*Trigonoside III*). Mp 264° (dec) (pyridine–MeOH 1:1); $[\alpha]_D^{25} = -45$ (pyridine; *c* 0.82), FAB-MS *m/z*: 951 $[M + Na]^+$, $^1H$ NMR: $\delta$ 4.98 (H-16ax), 3.83 (H-24$\alpha$), 3.67 (H-6ax), 3.19 (H-3ax), 3.04 (H-22$\alpha$), 2.53

Table 1. $^1H$ NMR chemical shifts of **1** (after exchange with $D_2O$) as determined by E-COSY and ROESY experiments (600 MHz, pyridine-$d_5$, $\delta$ in ppm from internal TMS)

| H | $\delta$(ppm) | Mult. | *J* (Hz) | Significant cross-peak correlations in the ROESY spectrum |
|---|---|---|---|---|
| 1ax | 1.57 | *ddd* | 12.0, 13.2, 4.5 | 3ax, 2eq, 5ax |
| 1eq | 1.26 | *ddd* | 13.2, 4.5, 3.0 | 11eq |
| 2eq | 2.02 | *m* | | 3ax |
| 2ax | 1.92 | *m* | | 19A |
| 3ax | 3.55 | *dd* | 11.2, 5.0 | 1ax, 2eq, 5ax |
| 5ax | 1.88 | *d* | 8.4 | 3ax, 30 |
| 6ax | 3.84 | *ddd* | 5.0, 7.1, 8.4 | 19B, 29 |
| 7eq | 2.14 | *ddd* | 5.0, 12.9, 5.3 | 15ax |
| 7ax | 1.94 | *ddd* | 7.1, 12.9, 9.4 | 15eq |
| 8ax | 2.04 | *dd* | 5.3, 9.4 | 18, 30 |
| 11eq | 1.82 | *ddd* | 14.7, 9.3, 5.5 | 1eq |
| 11ax | 1.37 | *ddd* | 14.7, 8.4, 6.9 | 19A |
| 12ax | 1.66 | *ddd* | 9.3, 6.9, 13.2 | 17ax |
| 12eq | 1.55 | *ddd* | 5.5, 8.4, 13.2 | |
| 15eq | 2.30 | *dd* | 8.0, 12.9 | 16ax, 15ax, 30, 7eq |
| 15ax | 1.84 | *dd* | 6.9, 12.9 | 18 |
| 16ax | 5.04 | *ddd* | 7.9, 8.0, 6.9 | 17ax, 15eq, 30 |
| 17ax | 2.55 | *d* | 7.9 | 16ax, 30, 21 |
| 18 | 1.41 | *s* | | 22$\alpha$, 8ax, 7, 15ax |
| 19B | 0.63 | *d* | 4.6 | 6ax, 8ax, 29 |
| 19A | 0.21 | *d* | 4.6 | 29, 2ax |
| 21 | 1.32 | *s* | | 17ax |
| 22$\alpha$ | 3.11 | *ddd* | 11.2, 9.0, 12.3 | 24$\alpha$, 22$\beta$, 18 |
| 22$\beta$ | 1.68 | *ddd* | 12.3, 9.7, 3.0 | 22$\alpha$ |
| 23$\alpha$ | 2.31 | *dddd* | 5.6, 12.8, 11.2, 3.0 | 24$\alpha$ |
| 23$\beta$ | 2.04 | *ddt* | 12.8, 9.7, 9.0 | |
| 24$\alpha$ | 3.88 | *dd* | 9.0, 5.6 | 22$\alpha$, 23$\alpha$, 26, 27 |
| 26 | 1.53 | *s* | | 24$\alpha$ |
| 27 | 1.30 | *s* | | 24$\alpha$ |
| 28 | 1.85 | *s* | | 3ax, |
| 29 | 1.35 | *s* | | 6ax, 19A, |
| 30 | 1.08 | *s* | | 16ax, 15ax, 17ax, |

Table 2. $^{13}$C NMR assignments for **1**, and $^{n}$C–H connectivities as determined by the HMBC experiment

| Carbon | δ(ppm) | Mult. | Connected protons |
|---|---|---|---|
| 1 | 32.55 | *t* | 0.63 (19A), 0.21 (19B) |
| 2 | 31.23 | *t* | |
| 3 | 78.35 | *d* | 1.85 (28), 1.35 (29) |
| 4 | 42.59 | *s* | 1.85 (28), 1.35 (29) |
| 5 | 52.38 | *d* | 1.85 (28), 1.35 (29), 2.15 (7), 0.63 (19A), 0.21 (19B) |
| 6 | 78.80 | *d* | 4.88 (1′), 2.15 (7), 2.04 (8) |
| 7 | 34.33 | *t* | 2.04 (8) |
| 8 | 45.17 | *d* | 1.08 (30), 1.41 (18), 0.63 (19A), 0.21 (19B) |
| 9 | 21.33 | *s* | 2.04 (8). 1.94 (7ax), 0.63 (19A), 0.21 (19B) |
| 10 | 29.23 | *s* | 1.88 (5), 0.63 (19A), 0.21 (19B) |
| 11 | 26.53 | *t* | 0.63 (19A), 0.21 (19B) |
| 12 | 33.67 | *t* | 1.41 (18) |
| 13 | 45.40 | *s* | 5.04 (16), 2.56 (17), 2.31 (15ax), 1.41 (18), 1.08 (30) |
| 14 | 46.07 | *s* | 2.31 (15ax), 2.15 (7), 2.04 (8), 1.41 (18), 1.08 (30) |
| 15 | 46.44 | *t* | |
| 16 | 73.67 | *d* | 2.56 (17) |
| 17 | 58.40 | *d* | 2.31 (15ax), 1.41 (18), 1.32 (21) |
| 18 | 21.05 | *q* | 2.56 (17) |
| 19 | 28.10 | *t* | 1.88 (5) |
| 20 | 87.62 | *s* | 3.11 (22α), 1.32 (21) |
| 21 | 28.86 | *q* | 2.56 (17), |
| 22 | 36.16 | *t* | 2.56 (17), 1.32 (21) |
| 23 | 26.68 | *t* | |
| 24 | 81.94 | *s* | 1.56 (26), 1.30 (27) |
| 25 | 71.58 | *s* | 1.56 (26), 1.30 (27) |
| 26 | 28.31* | *q* | 1.30 (27) |
| 27 | 27.26* | *q* | 1.56 (26) |
| 28 | 28.99 | *q* | 1.35 (29) |
| 29 | 16.47 | *q* | 3.55 (3), 1.88 (5), 1.85 (28) |
| 30 | 20.02 | *q* | 2.31 (15ax), 2.04 (8) |

*Values interchangeable within their columns.

Table 3. $^{1}$H and $^{13}$C NMR assignments (δ in ppm, *J* (Hz), significant $^{n}$H–C as determined from a HMBC experiment) of the sugar moieties of compounds **1–3**

| | | Carbon | Proton | Mult. | *J* (Hz) | Significant $^{n}$H–C carbon connections |
|---|---|---|---|---|---|---|
| Compound **1** | | | | | | |
| 6-*O*-Xyl | 1′ | 105.82 | 4.88 | *d* | 7.0 | C-6 |
| | 2′ | 75.45 | 3.99 | *t* | 7.0 | |
| | 3′ | 78.55 | 4.14 | *t* | 7.0 | |
| | 4′ | 71.19 | 4.16 | *dd* | 7.0, 4.8 | |
| | 5′ | 67.12 | 4.31eq | *dd* | 11.1, 4.8 | |
| | | | 3.70ax | *dd* | 11.1, 9.6 | |
| Compound **2** | | | | | | |
| 6-*O*-Xyl | 1′ | 105.90 | 4.82 | *d* | 7.0 | C-6 |
| | 2′ | 75.50 | 3.96 | *dd* | 8.5, 7.4 | |
| | 3′ | 78.39 | 4.11 | *t* | 8.4 | |
| | 4′ | 71.13 | 4.16 | *dt* | 12.0, 4.9 | |
| | 5′ | 67.03 | 4.29eq | *dd* | 10.9, 4.6 | |
| | | | 3.66ax | *dd* | 11.6, 9.4 | |

*Continued*

Table 3. *Continued*

| | | Carbon | Proton | Mult. | *J* (Hz) | Significant $^{B}H$–C carbon connections |
|---|---|---|---|---|---|---|
| 3-*O*-Xyl | 1″ | 105.49 | 4.78 | *d* | 7.7 | C-3 |
| | 2″ | 83.73 | 4.07 | *dd* | 6.6, 9.5 | |
| | 3″ | 77.56 | 4.14 | *m* | | |
| | 4″ | 71.18 | 4.16 | *m* | | |
| | 5″ | 66.73 | 4.25eq | *dd* | 11.0, 3.4 | |
| | | | 3.57ax | *dd* | 11.0, 8.3 | |
| 3-*O*-Ara | 1‴ | 106.88 | 5.16 | *d* | 7.0 | C-2″ |
| | 2‴ | 73.74 | 4.57 | *t* | 7.0 | |
| | 3‴ | 74.38 | 4.19 | *dd* | 8.9, 4.1 | |
| | 4‴ | 69.23 | 4.27 | *q* | 2.8 | |
| | 5‴ | 67.18 | 4.40eq | *dd* | 11.9, 1.5 | |
| | | | 3.78ax | *bd* | 11.9 | |
| *Compound* **3** | | | | | | |
| 6-*O*-Xyl | 1′ | 105.74 | 4.75 | *d* | 7.9 | C-6 |
| | 2′ | 75.44 | 3.93 | *dd* | 8.3, 7.3 | |
| | 3′ | 78.29 | 4.09 | *t* | 8.7 | |
| | 4′ | 71.13 | 4.13 | *dt* | 4.5, 8.8 | |
| | 5′ | 66.97 | 4.26eq | *dd* | 11.0, 4.2 | |
| | | | 3.63ax | *dd* | 11.4, 9.0 | |
| 3-*O*-Xyl | 1″ | 104.17 | 4.86 | *d* | 5.5 | C-3 |
| | 2″ | 77.18 | 4.22 | *dd* | 4.9, 6.9 | |
| | 3″ | 75.46 | 5.58 | *t* | 7.1 | –*CO*$CH_3$ |
| | 4″ | 68.48 | 4.09 | *dt* | 7.7, 4.6 | |
| | 5″ | 65.04 | 4.31eq | *dd* | 11.4, 3.9 | |
| | | | 3.67ax | *dd* | 11.6, 7.6 | |
| 3-*O*-Ara | 1‴ | 105.23 | 4.96 | *d* | 6.7 | C-2″ |
| | 2‴ | 72.29 | 4.34 | *dd* | 9.1, 7.4 | |
| | 3‴ | 74.40 | 4.08 | *dd* | 8.5, 4.0 | |
| | 4‴ | 69.26 | 4.24 | *dt* | 2.5, 2.5, 2.8 | |
| | 5‴ | 67.10 | 4.29eq | *dd* | 12.1, 2.1 | |
| | | | 3.70ax | *bd* | 11.9 | |

(H-17ax), 2.28 (H-15eq), 2.23 (H-23α), 2.14 ($\underline{CH_3}$–CO), 2.10 (H-2eq), 2.03 (H-8ax), 2.01 (H-23β), 2.00 (2H-7), 1.85 (H-2ax), 1.78 (H-15ax), 1.72 (H-5ax), 1.65 (H-11eq), 1.62 (H-22β), 1.61 (H-12ax), 1.58 ($CH_3$-28), 1.53 ($CH_3$-26), 1.46 (H-12eq), 1.43 (H-1ax), 1.41 (H-11ax), 1.32 ($CH_3$-18), 1.26 ($CH_3$-21), 1.26 ($CH_3$-26), 1.25 ($CH_3$-29), 1.20 (H-1eq), 1.08 ($CH_3$-30), 0.55 (H-19B), 0.07 (H-19A). $^{13}C$ NMR: δ170.93 ($CH_3$-$\underline{CO}$), 88.50 (C-3), 87.56 (C-20), 81.85 (C-24), 77.59 (C-6), 73.53 (C-16), 71.49 (C-25), 58.23 (C-17), 52.09 (C-5), 46.34 (C-14), 45.72 (C-15), 45.42 (C-13), 43.70 (C-8), 42.71 (C-4), 35.11 (C-22), 33.67 (C-12), 33.28 (C-7), 31.94 (C-1), 29.85 (C-2), 28.81 (C-21), 28.31 (C-10), 28.27 (C-26), 27.88 (C-28), 27.22 (C-27), 26.65 (C-23), 26.49 (C-11), 26.15 (C-19), 21.63 ($\underline{CH_3}$–CO), 21.43 (C-9), 20.43 (C-18), 19.78 (C-30), 16.59 (C-29).

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