# Lupane Pentacyclic Triterpenes Isolated from Stems and Branches of *Maytenus imbricata* (Celastraceae)

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Four lupane pentacyclic triterpenes were isolated from the hexane extract of stems and branches of *Maytenus imbricata* MART. *ex* REISSEK: 3-oxolup-20(30)-en-29-al (**1**), 30-hydroxylup-20(29)-en-3-one (**2**), (11$\alpha$)-11-hydroxylup-20(29)-en-3-one (**3**), and (3$\beta$)-lup-20(30)-ene-3,29-diol (**4**). The structural identification of **1**–**4** was achieved by $^1$H- and $^{13}$C-NMR techniques, including 2D experiments (HSQC, HMBC, and NOESY).

**Introduction.** – Many specimens of *Maytenus* (Celastraceae) are used in folk medicine in different Brazilian regions. These species present a variety of secondary metabolites including flavonoids, glycosides, maitansinoids, alkaloid and non-alkaloid sesquiterpenes, friedelanes, oleananes, lupanes, quinonoid triterpenes, and pentacyclic triterpenes of the other series [1]. Pentacyclic triterpenes are commonly isolated from plants of the Celastraceae family, and they were found to have pharmacological properties such as antiseptic, anti-asthmatic, and antimicrobial actions [2][3], antispermatogenic [4], antispasmodic [5], analgesic and anti-ulcer [6][7], insecticidal [8][9], antitumoral [10], and molluscicidal, allelopathic, and anti-inflammatory effects [11].

*Maytenus imbricata* MART. *ex* REISSEK is found in Cerrado regions in the states of Minas Gerais and Bahia, Brazil. The botanical description of *M. imbricata* is reported in [12].

The present phytochemical study of *Maytenus imbricata* resulted in the isolation and identification of the following triterpenes: 3-oxolup-20(29)-en-30-al[1]) (**1**), 30-hydroxylup-20(29)-en-3-one (**2**), (11$\alpha$)-11-hydroxylup-20(29)-en-3-one (**3**), and (3$\beta$)-lup-20(29)-ene-3,30-diol[1]) (**4**). The structural elucidation was achieved by $^1$H- and $^{13}$C-NMR techniques, including 2D experiments (HSQC, HMBC, NOESY, and COSY), and GC/MS analysis.

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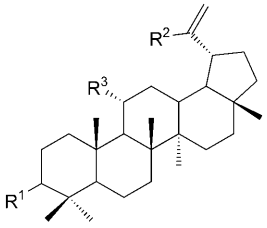
[1]) For convenience, the numbering of compounds **1** and **4** is identical to that of **2** and **3**; for systematic names, see *Exper. Part.*

**Results and Discussion.** – The $^1$H- and $^{13}$C-NMR spectra of compounds **1**–**4** (*Fig. 1*) showed a very similar profile with respect to the signals of the lupane moiety C(29)[1] (=$CH_2$) and C(20) (C=) [13]. The structure elucidation of these compound were based on differences observed in their spectroscopic data.




| Lupane | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **1** | =O | CHO | H |
| **2** | =O | $CH_2OH$ | H |
| **3** | =O | Me | OH ($\alpha$) |
| **4** | OH ($\beta$) | $CH_2OH$ | H |

Fig. 1. *Structures of lupanes isolated from* Maytenus imbricata

The mass spectra of **1** showed peaks at *m*/*z* 205 and 189 corresponding to characteristic fragments of lupane compounds. The presence of a peak at *m*/*z* 438 (24%, $M^+$) along with NMR data allowed to establish the molecular formula $C_{30}H_{46}O_2$. Detailed analysis of further spectral data (see *Table 1*) and their comparison with known data confirmed the structure of 3-oxolup-20(29)-en-30-al[1]) for **1**. Compound **1** was first isolated by *Kumar* and co-workers [15] from *Gymnosporia emarginata* (Celastraceae) bark, but the structural elucidation was based mainly on data obtained from chemical transformations, and only incomplete NMR data were reported.

The $^{13}$C-NMR spectrum of **1** showed the presence of 27 signals which were attributed (DEPT-135 experiment) to 6 Me, 10 $CH_2$, and 4 CH groups and 7 quaternary C-atoms. The presence of two C=O groups was established by the resonances at $\delta$(C) 217.92 (C=O) and at $\delta$(C) 194.99 (CHO). With these signals as the starting point, a detailed study of HMBC, HSQC, and NOESY data was carried out. The HMBC contour plot showed correlations of $\delta$(C) 217.92 with $\delta$(H) 2.49 (*ddd*, $CH_2$), 1.89 (*ddd*, $CH_2$), 1.07 (*s*, Me), and 1.02 (*s*, Me); thus $\delta$(C) 217.92 was assigned to C(3). Based on this and the HSQC data, $\delta$(C) 34.16 ($\delta$(H) 2.49) and at 39.66 ($\delta$(H) 1.89) were attributed to C(2) and C(1), respectively. Moreover, $\delta$(C) 26.65 ($\delta$(H) 1.07) and 21.09 ($\delta$(H) 1.02) were assigned to C(23) and C(24), respectively. The NOESY correlation $\delta$(H) 5.91 ($H_a$–C(29))/9.52 (H–C(30))[1]) indicated that H–C(30) of the aldehyde group is in *cis* position to the olefinic $H_a$–C(29), in aggreement with [16] (see *Fig. 2*). The signal of $H_b$–C(29) correlated with the signals of Me(27), $H_\alpha$–C(21), and $H_\alpha$–C(18). These interactions confirmed the lupane skeleton of **1**. Also the NOESY correlations Me(28) ($\delta$(H) 0.83) $H_\beta$–C(22), $H_\beta$–C(15), $H_\beta$–C(21), and $H_\beta$–C(19) were observed. From these data, it was possible to assign $\delta$(C) 32.73, not detected in the $^{13}$C-NMR spectrum, to C(21) and $\delta$(H) 2.75 to H–C(19). The assignment of the chemical shifts of C(19) and C(18) were based on published data for (3$\beta$)-3-hydroxylup-20(29)-en-30-al[1]) [16]. The resonance signals for these C-atoms were not observed in the $^{13}$C-NMR spectrum, probably due to the large relaxation times. This fact was also observed by *Reynolds* and co-workers [16] for (3$\beta$)-3-hydroxylup-20(29)-en-30-al[1]).

Similarly to **1**, the spectroscopic data of **2** (see also [15]) established its structure as 30-hydroxylup-20(29)-en-3-one (**2**).

In the $^1$H-NMR spectrum (*Table 2*) of **2**, a *dd* at $\delta$(H) 4.15 ($J$ = 1.4, 14.5 Hz) and a *m* at $\delta$(H) 4.07 ($CH_2OH$), as well as a *s* at $\delta$(H) 4.91 and a *dd* at $\delta$(H) 4.94 ($J$ = 1.5, 13.2 Hz) (2 olefinic H) were observed. The $^{13}$C-NMR spectrum exhibited the presence of 29 C-signals which were assigned (DEPT-135 experiment) to 6 Me, 11 $CH_2$, and 5 CH groups and 7 quaternary C-atoms. The signal at $\delta$(C) 26.67 showed an increased intensity compared to that of the other C-signals due to two superimposed signals. The HMBC contour plot revealed a correlation of $\delta$(C) 26.67 with $\delta$(H) 1.27 ($H_\beta$–C(11)) and 1.02 (Me(24)). These data allowed us to

Table 1. *$^1H$-(400 MHz) and $^{13}C$-NMR (100 MHz) Data for Compound* **1**. $CDCl_3$ solution; $\delta$ in ppm, $J$ in Hz.

| | HSQC | | HMBC ($^{13}C \rightarrow {}^1H$) | $^1H,^1H$ Correlation | |
|---|---|---|---|---|---|
| | $\delta$(C) | $\delta$(H) | | COSY | NOESY |
| C(3) | 217.92 | | $CH_2$(1), $CH_2$(2), Me(23), Me(24) | | |
| C(4) | 47.37 | | Me(23), Me(24) | | |
| C(8) | 40.81 | | H–C(9), Me(26), Me(27) | | |
| C(10) | 36.92 | | Me(25), H–C(9), H–C(5) | | |
| C(14) | 42.83 | | Me(26), Me(27) | | |
| C(17) | 43.32 | | Me(28) | | |
| C(20) | 157.21 | | H–C(30) | | |
| H–C(5) | 55.06 | 1.30–1.40 (*m*) | Me(23), Me(24), Me(25) | $H_\alpha$–C(1) | |
| H–C(9) | 49.68 | 1.30–1.40 (*m*) | Me(25), Me(26) | | |
| H–C(30)[1]) | 194.99 | 9.52 (*s*, CHO) | $CH_2$(29) | | $H_a$–C(29) |
| H–C(13) | 37.93 | | Me(27) | | |
| | | 1.64–1.70 (*m*) | | | |
| H–C(18) | 47.70 | | | | |
| H–C(19) | 47.70 | 2.75 (*m*) | | | |
| $CH_2$(1) | 39.66 | 1.89 (*ddd*, $J$ = 13.2, 7.6, 4.3, $H_\alpha$); 1.30–1.40 (*m*, $H_\beta$) | $CH_2$(2), Me(25) | $H_\alpha$–C(2) | |
| $CH_2$(2) | 34.16 | 2.49 (*ddd*, $J$ = 15.6, 9.9, 7.5, $H_\alpha$); 2.39 (*ddd*, $J$ = 15.6, 7.6, 4.4, $H_\beta$) | $CH_2$(1) | | |
| $CH_2$(6) | 19.70 | 1.40–1.44 (*m*) | $CH_2$(7) | $CH_2$(7) | |
| $CH_2$(7) | 33.66 | 1.44–1.50 (*m*) | $CH_2$(6), Me(26) | $CH_2$(6) | |
| $CH_2$(11) | 21.52 | 1.30–1.34 (*m*) | | | |
| $CH_2$(12) | 27.64 | 1.00–1.10 (*m*) | H–C(13), H–C(18) | | |
| $CH_2$(15) | 27.40 | 1.00–1.10 (*m*) | Me(27) | | |
| $CH_2$(16) | 35.39 | 1.40–1.50 (*m*) | | | |
| $CH_2$(21) | 32.73 | 2.10–2.20 (*m*) | | | |
| $CH_2$(22) | 39.96 | 1.40–1.30 (*m*) | | | |
| $CH_2$(29)[1]) | 133.05 | 5.91 (*s*, $H_a$) 6.29 (*s*, $H_b$) | H–C(30), H–C(19) | | H–C(30) H–C(18), $CH_2$(21), Me(27) |
| Me(23) | 26.65 | 1.07 (*s*) | | H–C(5), Me(24) | |
| Me(24) | 21.09 | 1.02 (*s*) | | H–C(5), Me(23) | |
| Me(25) | 15.91 | 0.92 (*s*) | | $H_\alpha$–C(1), H–C(5), H–C(9) | |
| Me(26) | 15.81 | 1.05 (*s*) | | H–C(9), $CH_2$(7) | |
| Me(27) | 14.39 | 0.94 (*s*) | | H–C(13), $CH_2$(15) | |
| Me(28) | 17.84 | 0.83 (*s*) | $CH_2$(16), $CH_2$(22) | | $H_\beta$–(15), H–C(19), $H_\beta$–C(21), $H_\beta$–C(22) |

attribute $\delta$(C) 26.67 to C(23) and C(12) accounting for the 30 C-atoms of the pentacyclic triterpene structure. A correlation between $\delta$(H) 4.91 and $\delta$(C) 65.01 (C(30)) and 43.77 (C(19)) and also between $\delta$(C) 154.71 (C(20)) and $\delta$(H) 4.13 (H–C(30)) allowed to assign the OH group as attached to C(30). The assignments of the other C-atoms of **2** were carried out as for **1**.

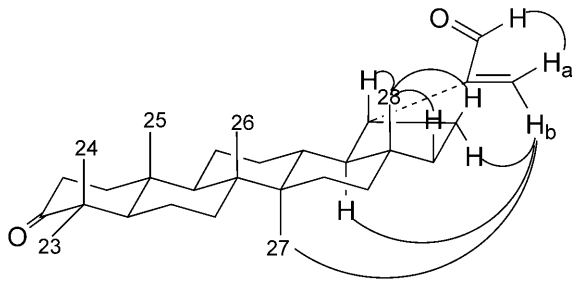



Fig. 2. *NOE Correlations observed for compound* **1** *isolated from* Maytenus imbricata

Compound **3** was first isolated from *Maytenus obtusifolia*; however, some of our NMR assignments presented for compound **3** (*Table 3*) are different from the $^1$H- and $^{13}$C-NMR signals reported in [18]. The data of **3** established its structure as (11$\alpha$)-11-hydroxylup-20(29)-en-3-one.

As for compound **2**, the $^{13}$C-NMR spectrum of **3** showed a signal at $\delta$(C) 47.63 with enhanced intensity as compared to that of the others indicating a superposition of two C-signals. This fact was confirmed by the HMBC and HSQC experiments which established correlations between $\delta$(C) 47.63 and $\delta$(H) 1.09 (Me(23)), 1.06 (Me(24)), and 0.79 (Me(28)). From these data, it was possible to attribute the signal at $\delta$(C) 47.63 to C(4) and C(18). In the $^1$H-NMR spectrum, the signal at $\delta$(H) 3.91 was clearly observed as a *dt*, the coupling constants $J = 10.8$ and 5.1 Hz indicating that H–C(11) is in axial position. The position and configuration of this H-atom were confirmed by the NOESY correlations $\delta$(H) 3.91 (H–C(11))/1.07 (Me(25), Me(26)), 1.81 (H–C(13) axial), and 1.90 (H–C(12) equatorial). The HMBC correlation $\delta$(C) 54.87 (C(9))/$\delta$(H) 3.91 confirmed the position of the OH group at C(11). The signal of H$_\alpha$–C(1) was observed as a *ddd* at $\delta$(H) 2.67 ($J = 13.7$, 8.1, 5.6 Hz). The HMBC correlations $\delta$(C) 218.34 (C(3))/$\delta$(H) 1.06 and 1.09 confirmed that $\delta$(H) 1.09 arose from a Me group (Me(24)). The Me(28) signal assignment was established by the correlation $\delta$(H) 0.79 $\delta$(C) 43.05 (C(17)). This attribution differs from that reported in [18], where $\delta$(H) 0.79 was attributed to Me(24) and $\delta$(H) 0.79 to Me(28). The attributions of the signal of C(12) ($\delta$(C) 37.44) and C(15) ($\delta$(C) 27.41) were confirmed by the HSQC, NOESY, and COSY data (*Table 3*); these attributions are inverted in [18]. The $^1$H,$^1$H-COSY plot revealed the correlation of $\delta$(H) 2.67 (H$_\alpha$–C(1)) with the *m* of low intensity at $\delta$(H) 1.60 – 1.70 which allowed us to attribute the latter to H$_\beta$–C(1). The HMBC plot showed the correlations $\delta$(C) 218.84 (C(3))/$\delta$(H) 2.67 (H$_\alpha$–C(1)), 1.60 – 1.70 (H$_\beta$–C(1)), 2.42 – 2.52 (CH$_2$(2)), 1.09 (Me(23)), and 1.06 (Me(24)). Moreover, the correlations $\delta$(H) 2.67 (H$_\alpha$–C(1))/$\delta$(C) 54.76 (C(5)), 38.20 (C(10)), 34.21 (C(2)), and 16.71 (C(25)) were observed. The NOESY correlation H$_a$–C(29)/Me(30) and the lack of a correlation H$_b$–C(29)/Me(30) confirmed the assignments of $\delta$(H) 4.72 (H$_b$–C(29)), 4.59 (H$_a$–C(29)), and 1.69 (Me(30)). Also the NOESY correlations H$_b$–C(29)/H$_\alpha$–C(18), H$_\beta$–C(19), and H$_\alpha$–C(21) were observed, suggesting that the propenyl group freely rotates around the C(19)–C(20) bond. Similar information has been reported for (3$\beta$)-3-hydroxylup-20(29)-en-30-al[1]), isolated from *Russelia equisetiformis* [16].

The data of compound **4** were in agreement with the reported data of the triterpene (3$\beta$)-lup-20(29)-ene-3,30-diol[1]) isolated from *Maerua oblongifolia* (Capparaceae) [19].

The analysis of the $^1$H- and $^{13}$C-NMR data of **4** (see *Exper. Part*) indicated the presence of two OH groups. The 2 *d* at $\delta$(H) 4.16 and 4.11 (C*H*$_2$OH), a *dd* at $\delta$(H) 3.19 (C*H*OH) and a *s* at $\delta$(H) 4.99 and a *dd* at $\delta$(H) 5.00 (2 olefinic H) suggested a labdenediol structure. The $^{13}$C-NMR spectrum showed the presence of 29 signals which were attributed (DEPT-135 experiment) to 5 Me, 12 CH$_2$ and 6 CH groups and 6 quaternary C-atoms. A signal at $\delta$(H) 0.78 with high intensity indicated the superposition of two Me signals which was confirmed also by the HMBC correlations $\delta$(H) 0.78/$\delta$(C) 28.08 (C(23)), 55.38 (C(5)), 39.89 (C(22)), and 43.03 (C(17)). The latter established that $\delta$(H) 0.78 Me(24) arose from both Me(24) and Me(28). The location and configuration of the

Table 2. *$^1H$- (400 MHz) and $^{13}C$-NMR (100 MHz) Data for Compound* **2**. $CDCl_3$ solution; $\delta$ in ppm, $J$ in Hz.

| | HSQC | | HMBC ($^{13}C \rightarrow {}^1H$) | $^1H,^1H$-COSY |
|---|---|---|---|---|
| | $\delta$(C) | $\delta$(H) | | |
| C(3) | 218.25 | | $CH_2$(1), $CH_2$(2), Me(23), Me(24) | |
| C(4) | 47.32 | | Me(23), Me(24) | |
| C(8) | 40.79 | | Me(27) | |
| C(10) | 36.86 | | Me(25) | |
| C(14) | 42.85 | | Me(27) | |
| C(17) | 43.01 | | Me(28) | |
| C(20) | 154.71 | | $CH_2$(30) | |
| H–C(5) | 54.87 | 1.30–1.40 (*m*) | Me(23), Me(24), Me(25) | |
| H–C(9) | 49.68 | 1.40–1.45 (*m*) | Me(25), $CH_2$(11) | |
| H–C(13) | 38.11 | 1.60–1.70 (*m*) | Me(27) | |
| H–C(18) | 48.83 | 1.45–1.50 (*m*) | H–C(19), $CH_2$(22) | |
| H–C(19) | 43.77 | 2.29 (*td*, $J$ = 11.2, 5.4) | H–C(18), $CH_2$(22), $CH_2$(29) | H–C(18) |
| $CH_2$(1) | 39.58 | 1.89 (*ddd*, $J$ = 13.2, 8.6, 7.5, $H_\alpha$) | $CH_2$(2), Me(25) | |
| | | 1.30–1.40 (*m*, $H_\beta$) | | |
| $CH_2$(2) | 34.14 | 2.49 (*ddd*, $J$ = 15.7, 7.5, 9.7, $H_\alpha$) | $CH_2$(1) | $CH_2$(1) |
| | | 2.40 (*ddd*, $J$ = 15.7, 7.7, 4.5, $H_\beta$) | | |
| $CH_2$(6) | 19.67 | 1.40–1.50 (*m*) | $CH_2$(7) | |
| $CH_2$(7) | 33.57 | 1.40–1.50 (*m*) | | |
| $CH_2$(11) | 21.55 | 1.45–1.48 (*m*, ($H_\alpha$) | H–C(9), H–C(12) | |
| | | 1.20–1.30 (*m*, $H_\beta$) | | |
| $CH_2$(12) | 26.67 | 1.13 (*td*, $J$ = 12.6, 4.4) | $CH_2$(11), Me(27) | |
| $CH_2$(15) | 27.39 | 1.00–1.10 (*m*, $H_\alpha$) | Me(27) | |
| | | 1.60–1.80 (*m*, $H_\beta$) | | |
| $CH_2$(16) | 35.40 | 1.40 (*m*, $H_\alpha$) | Me(28) | |
| | | 1.50–1.55 (*m*, $H_\beta$) | | |
| $CH_2$(21) | 31.75 | 1.30–1.40 (*m*, $H_\alpha$) | | H–C(19) |
| | | 2.00–2.10 (*m*, $H_\beta$) | | |
| $CH_2$(22) | 39.82 | 1.26–1.40 (*m*) | H–C(18), H–C(19), Me(28) | $CH_2$(21) |
| $CH_2$(29) | 106.87 | 4.94 (*dd*, $J$ = 13.2, 1.5, $H_b$) | H–C(19) | $CH_2$(30) |
| | | 4.91 (*s*, $H_a$) | $CH_2$(30) | |
| $CH_2$(30) | 65.01 | 4.15 (*dd*, $J$ = 14.5, 1.4) | $CH_2$(29) | |
| | | 4.07 (*m*) | | |
| Me(23) | 26.67 | 1.07 (*s*) | H–C(5), Me(24) | |
| Me(24) | 21.04 | 1.02 (*s*) | H–C(5), Me(23) | |
| Me(25) | 15.98 | 0.93 (*s*) | $H_\alpha$–C(1), H–C(5), H–C(9) | |
| Me(26) | 15.80 | 1.06 (*s*) | H–C(9) | |
| Me(27) | 14.46 | 0.96 (*s*) | $CH_2$(12), H–C(13), $CH_2$(15) | |
| Me(28) | 17.72 | 0.79 (*s*) | $CH_2$(16), $CH_2$(22) | |

OH-group were assigned *via* HSQC, HMBC, and NOESY experiments. The HMBC plot showed the correlations $\delta$(C) 78.77 (C(3))/$\delta$(H) 0.98 (Me(23)) and 0.78 (Me(24)), $\delta$(H) 0.78 (Me(24)/$\delta$(C) 55.38 (C(5)), $\delta$(H) 3.19 (H–C(3))/$\delta$(C) 38.94 (C(1)), 28.08 (C(23)), and 15.49 (C(24)), $\delta$(H) 4.95 ($CH_2$(29))/$\delta$(C) 43.78 (C(19)), 64.63 (C(30)) and 155.16 (C(20)), and $\delta$(C) 155.16 (C(20)/$\delta$(H) 4.14 ($CH_2$(30)), and 2.29 (H–C(19)).

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Table 3. *$^1H$- (400 MHz) and $^{13}C$-NMR (100 MHz) Data for Compound* **3**. $CDCl_3$ solution; $\delta$ in ppm, $J$ in Hz.

| | HSQC | | HMBC ($^{13}C \rightarrow {}^1H$) | $^1H,^1H$ Correlation | |
|---|---|---|---|---|---|
| | $\delta(C)$ | $\delta(H)$ | | COSY | NOESY |
| C(3) | 218.84 | | $CH_2(1)$, $CH_2(2)$, Me(23), Me(24) | | |
| C(4) | 47.63 | | $CH_2(6)$, Me(23), Me(24) | | |
| C(8) | 42.41 | | $CH_2(6)$, Me(26), Me(27) | | |
| C(10) | 38.20 | | $H_\alpha$–C(1), Me(25) | | |
| C(14) | 42.61 | | $CH_2(16)$, Me(26), Me(27) | | |
| C(17) | 43.05 | | Me(28), $CH_2(16)$ | | |
| C(20) | 150.20 | | $CH_2(21)$, H–C(18), H–C(19), Me(30) | | |
| H–C(5) | 54.76 | 1.49 (*m*) | $H_\alpha$–C(1), Me(23), Me(24), Me(25) | | |
| H–C(9) | 54.87 | 1.46 (*m*) | H–C(11), Me(25), Me(26) | | |
| H–C(11) | 70.49 | 3.91 (*dt*, $J = 10.8, 5.1$) | H–C(9) | | $CH_2(12)$, H–C(13), Me(25), Me(26) |
| H–C(13) | 37.17 | 1.83 (*ddd*, $J = 13.2, 11.4, J = 3.8$) | Me(27), H–C(18) | | H–C(11), Me(26), Me(28) |
| H–C(18) | 47.63 | 1.41 (*m*) | Me(28), $CH_2(16)$ | | |
| H–C(19) | 47.70 | 2.34–2.43 (*m*) | $CH_2(29)$, Me(30) | | $CH_2(12)$, $CH_2(21)$, Me(28), $H_b$–C(29) |
| $CH_2(1)$ | 42.07 | 2.67 (*ddd*, $J = 13.7, 8.1, 5.6$, $H_\alpha$); 1.60–1.70 (*m*, $H_\beta$) | H–C(5), Me(25) | $H_\alpha$–C(1) $H_\alpha$–C(2) | |
| $CH_2(2)$ | 34.21 | 2.42–2.52 (*m*) | $H_\alpha$–C(1) | | |
| $CH_2(6)$ | 19.64 | 1.46 (*m*) | H–C(5), $CH_2(7)$ | | |
| $CH_2(7)$ | 34.27 | 1.43 (*m*) | $CH_2(6)$, Me(26) | | |
| $CH_2(12)$ | 37.44 | 1.94–2.00 (*m*) | H–C(13), H–C(18) | | |
| $CH_2(15)$ | 27.41 | 1.60–1.70 (*m*) | $CH_2(16)$, Me(27) | $H_\beta$–C(15) | |
| $CH_2(16)$ | 35.40 | 1.50 (*m*, $H_\alpha$) 1.41 (*m*, $H_\beta$) | $CH_2(15)$, H–C(18), Me(28) | | |
| $CH_2(21)$ | 29.78 | 1.90–1.96 (*m*, $H_\alpha$) 1.40 (*m*, $H_\beta$) | H–C(18), H–C(19), H–C(22) | | |
| $CH_2(22)$ | 39.80 | 1.44 (*m*, $H_\alpha$) 1.20 (*m*, $H_\beta$) | $CH_2(21)$, Me(28) | | |
| $CH_2(29)$ | 109.95 | 4.59 (*dq*, $J = 2.3, 1.4$, $H_a$); 4.72 (*d*, $J = 2.3$, $H_b$) | Me(30), H–C(19) | | Me(30), $H_\alpha$–C(18), $H_\beta$–C(19), $H_\alpha$–C(21) |
| Me(23) | 27.46 | 1.09 (*s*) | H–C(5), Me(24) | | |
| Me(24) | 20.77 | 1.06 (*s*) | H–C(5), Me(23) | | |
| Me(25) | 16.71 | 1.07 (*s*) | $H_\alpha$–C(1), H–C(9) | | |
| Me(26) | 16.86 | 1.07 (*s*) | H–C(9), $CH_2(7)$ | | |
| Me(27) | 14.42 | 0.98 (*s*) | $CH_2(15)$ | | |
| Me(28) | 18.08 | 0.79 (*s*) | $CH_2(16)$, $CH_2(22)$, H–C(18) | | |
| Me(30) | 19.37 | 1.69 (*s*) | $CH_2(29)$, H–C(19) | | |

## Experimental Part

*General.* TLC: silica gel *G-60/$F_{254nm}$* plates (0.25 mm; *Merck*) previously activated in an oven at 100°; detection with UV light, $I_2$ vapor, acid soln. of vanillin (0.1 g/100 ml of phosphoric acid (50% aq. soln.) or phosphomolybdic acid) [20]. M.p.: *MQAPF-301/MicroQuímica* or *Mettler FP82*. IR (KBr) Spectra: *Perkin-Elmer 1000* spectrophotometer; in $cm^{-1}$. NMR Spectra: *Bruker DRX-400-Avance* spectrometer, at 400 ($^1H$) or

100 MHz ($^{13}C$); $CDCl_3$ solns. (5–10 mg of sample/0.5 ml of solvent) and $SiMe_4$ as internal standard; $\delta$ in ppm, $J$ in Hz; NOESY: standard pulse sequence with 350 ms of mixture time; HSQC: 5-mm probe of inverse detection equipped with a field-gradient coil; HMBC: field gradient obtained by a standard pulse sequence; data processing with a workstation and the XWIN-NMR vs. 3.1 program for Windows XP. CI-MS: *Shimadzu GC-MS-QP5050* equipment; in *m/z* (rel. %).

*Plant Material, Extraction, and Compound Isolation. Maytenus imbricata* MART. ex REISSEK (Celastraceae) was collected in the 'Morro de Santana' region, Ouro Preto City, Minas Gerais, Brazil. A voucher specimen was deposited at the Herbarium of the Botany Department of Universidade Federal de Viçosa (UFV), Viçosa, Minas Gerais, Brazil (Collection No. 27780). The cleaned stems and branches were dried at r.t. and ground to powder (883.36 g), which was submitted to hexane extraction in a *Soxhlet* apparatus for 24 h. On evaporation of the extract hexane, a white solid precipitated (8.29 g). This solid gave a positive *Liebermann–Burchard* test for pentacyclic triterpenes. A sample of 500 mg of this solid was submitted to column chromatography (CC; (*Merck* $SiO_2$ (70–230 mesh, 15 g), benzene, hexane/AcOEt 7:3, hexane/AcOEt 1:1, and MeOH) yielding 33 fractions. *Fr. 1–23* (150 ml each) were eluted with benzene and *Fr. 24–33* (500 ml each) with other eluents. The combined *Fr. 1* and *2* (= *Fr. A*; 118 mg) were resubmitted to CC ($CH_2Cl_2$): *Fr. A.1–A.29* (5 ml each). The combined *Fr. A.14–A.29* afforded **1** (18 mg). *Fr. 12–23* (= *Fr. B*) were resubmitted to CC (hexane/AcOEt 8:2): *Fr. B.1–B.156* (10 ml each). The combined *Fr. B.51–B.66* yielded **2** (289,7 mg) and the combined *Fr. B.122–B.156* **3** (18 mg). The combined *Fr. 26* and *27* (= *Fr. c*; 210 mg) of the initial CC, eluted with hexane/AcOEt 7:3, were dissolved in $CHCl_3$, and after 24 h, the formed white solid (25 mg) was submitted to CC (hexane/AcOEt 4:1): *Fr. C.1–C.35* (10 ml). The combined *Fr. C.21–C.35* gave **4** (21 mg).

*3-Oxolup-20(29)-en-30-al*[1] (= *3-Oxolup-20(30)-en-29-al* **1**): White powder. M.p. 177–181° ([15]: 193–194°). IR (KBr): 2940, 2862, 1701, 1683, 1640, 920. $^1H$- and $^{13}C$-NMR: *Table 1*. MS: 438 (24, $M^{+\bullet}$, $C_{30}H_{46}O_2^+$), 382 (1, $[M-C_3H_2O]^+$), 232 (12, $[M-C_{14}H_{22}O]^+$), 203 (47, $[M-C_{16}H_{19}O]^+$), 55 (100).

*30-Hydroxylup-20(29)-en-3-one* (**2**): White powder. M.p. 178–181° ([15]: 186–187°). IR (KBr)): 3548, 3079, 2957, 2939, 2866, 1380, 1697, 1644, 1455, 1075, 1010. $^1H$- and $^{13}C$-NMR: *Table 2*. MS: 440 (10, $M^{+\bullet}$, $C_{30}H_{48}O_2$), 422 (5, $[M-H_2O]^+$), 234 (7, $[M-C_{14}H_{22}O]^+$), 221 (23, $[M-C_{17}H_{25}O]^+$), 205 (61, $[M-C_{16}H_{27}O]^+$), 55 (100).

*(11α)-11-Hydroxylup-20(29)-en-3-one* (**3**): White powder. M.p. 156–159°. IR (KBr): 3500–3000, 2940, 2850, 1700–1650, 1400–1385. $^1H$- and $^{13}C$-NMR: *Table 3*. MS: 440 (4, $M^{+\bullet}$, $C_{30}H_{48}O_2^+$), 423 (15, $[M-OH]^+$), 218 (15, $[M-C_{15}H_{26}O]^+$), 41 (100).

*(3β)-Lup-20(29)-ene-3,30-diol* (= *(3β)-Lup-20(30)-ene-3,29-diol* **4**): White powder. M.p. 199–201° ([19]: 230–232°). IR (KBr): 3500–3100, 3000–2700. $^1H$-NMR (400 MHz, $CDCl_3$): 0.60–0.70 (*m*, H–C(5)); 0.78 (*s*, Me(24)); 0.78 (*s*, Me(28)); 0.83 (*s*, Me(25)); 0.85–0.90 (*m*, $H_\beta$–C(1)); 0.94 (*s*, Me(27)); 0.98 (*s*, Me(23)); 1.02 (*s*, Me(26)); 1.00–1.10 (*m*, $H_\beta$–C(12)); 1.00–1.20 (*m*, $H_\beta$–C(7)); 1.15–1.20 (*m*, $H_\beta$–C(11)); 1.23 (*m*, H–C(9)); 1.20–1.30 (*m*, $H_\alpha$–C(22)); 1.30–1.35 (*m*, $H_\alpha$–C(21)); 1.30–1.35 (*m*, $H_\alpha$–C(11)); 1.30–1.40 (*m*, $H_\beta$–C(22)); 1.35–1.40 (*m*, $H_\alpha$–C(7)); 1.37–1.40 (*m*, $H_\beta$–C(6)); 1.40 (*m*, $H_\alpha$–C(12)); 1.44 (*m*, H–C(18)); 1.35–1.50 (*m*, $CH_2$(16)); 1.50 (*m*, $H_\alpha$–C(6)); 1.50–1.60 (*m*, 1 H–C(15)); 1.60–1.65 (*m*, $H_\alpha$–C(1)); 1.60–1.65 (*m*, 1 H–C(2)); 1.60–1.65 (*m*, H–C(13)); 1.65–1.70 (*m*, 1 H–C(15)); 1.70–1.75 (*m*, 1 H–C(2)); 2.29 (*td*, $J$ = 11.4, 5.6, H–C(19)); 3.19 (*dd*, $J$ = 10.5, 5.2, H–C(3)); 4.11 (*d*, $J$ = 14.7, 1 H–C(30)); 4.16 (*d*, $J$ = 4.7, 1 H–C(30)); 4.99 (*s*, $H_a$–C(29)); 5.00 (*dd*, $J$ = 2.8, 1.6, $H_b$–C(29)).$^{13}C$-NMR (100 MHz, $CDCl_3$): 14.56 (C(27)); 15.40 (C(24)); 16.01 (C(25)); 16.14 (C(26)); 17.73 (C(28)); 18.35 (C(6)); 21.02 (C(11)); 26.66 (C(12)); 27.46 (C(2)); 27.46 (C(15)); 28.08 (C(23)); 31.79 (C(21)); 33.36 (C(7)); 35.52 (C(16)); 37.19 (C(10)); 38.05 (C(13)); 38.80 (C(4)); 38.94 (C(1)); 39.89 (C(22)); 40.89 (C(8)); 42.81 (C(14)); 43.03 (C(17)); 43.78 (C(19)); 48.86 (C(18)); 50.44 (C(9)); 55.38 (C(5)); 64.63 (C(30)); 78.77 (C(3)); 106.42 (C(29)); 155.16 (C(20)). MS: 442 (3, $M^{+\bullet}$, $C_{30}H_{50}O_2^+$), 424 (4, $[M-H_2O]^+$), 384 (5, $[M-C_3H_2O]^+$), 220 (18, $[M-C_{15}H_{24}O]^+$), 205 (14, $[M-C_{16}H_{29}O]^+$), 43 (100), 41 (85).

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