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CUCURBITANE TRITERPENOIDS FROM THE LEAVES OF *MOMORDICA FOETIDA*

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Key Word Index—*Momordica foetida*; Cucurbitaceae; triterpenoids; cucurbitacins.

Abstract—The chloroform extract of the leaves of *Momordica foetida* has yielded 3β, 7β, 23ξ-trihydroxycucurbita-5,24-dien-19-al, 3β, 7β; 25-trihydroxycucurbita-5,23-dien-19-al and 3β,7β-dihydroxy-25-methoxycucurbita-5,23-dien-19-al and the novel compounds 5β,19-epoxy-25-methoxycucurbita-6,23-diene-3β,19-diol, 5β,19-epoxycucurbita-6,23-diene-3β,19,25-triol, 5β,19-epoxy-19-methoxycucurbita-6,23-diene-3β,25-diol, 5β,19-epoxy-19,25-dimethoxycucurbita-6,23-dien-3β-ol and 5β,19-epoxy-25-methoxy-cucurbita-6,23-dien-3β-ol.

INTRODUCTION

Momordica foetida Schum., locally known by the Zulu people as iNtshungu, is a perennial herbaceous climber found in Africa south of the Sahara. In KwaZulu-Natal, the Zulus drink a concoction of the root or leaf for the treatment of boils and take an infusion of the runner as a sedative for an irritable stomach [1]. This plant is also reported to be used in KwaZulu-Natal as a remedy for hypertension and is reported to have antidiabetic properties [2]. The leaf is used by the Chagga as an earache remedy [3] and in tropical Africa, the leaf is used to treat roundworm [4]. In Uganda, an infusion of the leaf and roots is used as an abortifacient and ecbolic [5] and in Tanzania the fruit pulp is regarded as poisonous to weevils, moths and ants and is used as a repellant [6]. Previous studies on this plant have resulted in the isolation and identification of sitosteryl glucoside, 5,25-stigmastadien-3β-yl glucoside and 1β-hydroxyfriedel-6-en-3-one [7, 8].

Plant material was bought from a medicinal plant market in Umlazi, Durban and the sample authenticated at the Natal Herbarium, Durban. Three compounds which had been isolated previously from *Momordica charantia*, and five novel compounds were isolated. Structures were assigned using ^{1}H, ^{13}C and 2D NMR spectroscopy.

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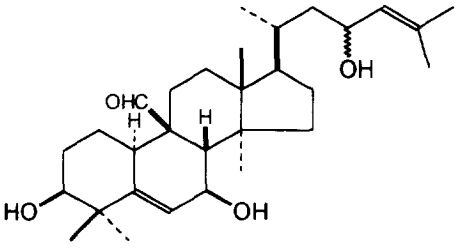
RESULTS AND DISCUSSION

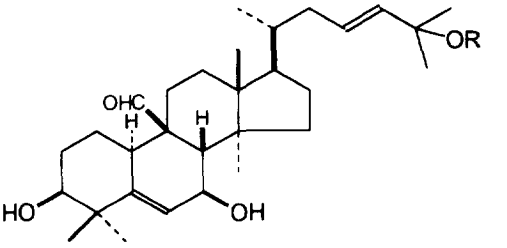
Ground, air-dried leaves of *Momordica foetida* were extracted successively with hexane, chloroform and methanol. The chloroform extract was investigated in this work. The concentrated chloroform extract was extracted with sodium hydroxide solution. The organic phase yielded compounds **1**, **2** and **3**. The alkaline aqueous phase was neutralized and re-extracted with chloroform, yielding compounds **4**, **5**, **6**, **7** and **8**.

Compounds **1**, **2** and **3** were found to be 3β, 7β, 23ξ-trihydroxycucurbita-5,24-dien-19-al, 3β,7β,25-trihydroxycucurbita-5,23-dien-19-al and 3β,7β-dihydroxy-25-methoxycucurbita-5,23-dien-19-al, respectively, which have been isolated previously from *Momordica charantia* [9, 10]. Structures were assigned from NMR and mass spectroscopic data.

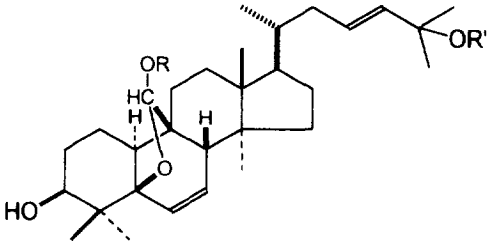
Compound **4** has not been reported previously and was identified as 5β,19-epoxy-25-methoxycucurbita-6,23-dien-3β,19-diol. High resolution mass spectroscopy of **4** indicated a molar mass of 486.7320 g mol^{-1} corresponding to a molecular formula of $C_{31}H_{50}O_3$. The mass spectrum exhibited peaks at *m/z* 471[M-CH_3]$^+$, 440[M-HCO_2H]$^+$, 422[M-HCO_2H-H_2O]$^+$ and 408[M-CH_3OH]$^+$. NMR spectra indicated that the aldehyde group present at C-19 in **1**, **2** and **3** was absent, but showed the presence of a methoxy group (3H, (δ 3.13). The hydroxy group at C-3β was present as in **1**, **2** and **3**. H-3α occurred as a multiplet ($W_{1/2}$ = 6.8 Hz) at δ 3.38 and was coupled to a doublet

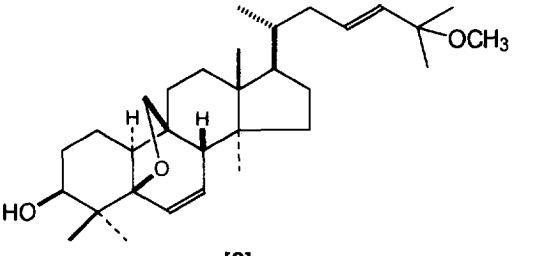


[1]



[2] R = H
[3] R = CH_3





[8]

	[R]	[R']
[4]	H	CH_3
[5]	H	H
[6]	CH_3	H
[7]	CH_3	CH_3

at δ 3.75 which disappeared on addition of D_2O. This confirmed the presence of an axial hydroxy group at C-3β. Compound **4** had two disubstituted double bonds. ^{13}C NMR resonances at δ 128.3*d* and 136.8*d* were ascribed to C-23 and C-24, respectively, as in **2**. The corresponding ^1H NMR resonances occurred at δ 5.42*m* and δ 5.40*d*. The resonances ascribed to the C-5, C-6 double bond in **1**, **2** and **3** were absent, but a second double bond was indicated by resonances at δ 132.7*d* and δ 132.4*d*. The corresponding ^1H NMR resonances occurred at δ 6.06*dd* and δ 5.65*dd*, respectively, and were assigned to H-6 and H-7. H-7 was coupled to H-6 (J = 9.78 Hz) and to H-8 (δ 2.82 *br s*,) H-6 was coupled to H-7 and long range coupled to H-8. H-6 was not further coupled, indicating that no H-5 was present. The NMR spectra indicated the presence of a hemiacetal group in place of the aldehyde for C-19. C-19 occurred as a doublet at δ 105.4 and the corresponding proton resonance occurred at δ 5.11*d*. The doublet at δ 5.11 was coupled to a doublet at δ 2.71. On addition of D_2O to the sample, the resonance at δ 2.71 disappeared and the resonance at δ 5.11 changed to a singlet, confirming the presence of a hydroxy group at C-19. Double bond equivalence calculations indicated the necessity for an additional ring. Since there was no hydrogen present at C-5, an additional ring formed by a C-5, C-19 ether linkage was indicated. C-5 occurred as a singlet at δ 86.6 in the ^{13}C NMR spectrum. Hemiacetal rings open and close in solution and an equilibrium is reached [11]. The ^{13}C NMR spectrum showed a number of minor peaks due to the minor epimer, but the resonances due to the major epimer were clearly recognisable. Following cucurbitacin stereochemistry, the 5,19-hemiacetal ring should be β. No nOe was observed between H-19 and H-8, suggesting that the major epimer was possibly the (*R*)-epimer. Since hydroxy groups were present at C-3β and C-19, the methoxy group was positioned at C-25. Acetylation of **4** yielded the two 19-acetates. The hydroxy group at C-3β did not acetylate as it did for **1** and **2**. A possible reason for this is that the loss in flexibility of ring A due to the 5,19-hemiacetal system imposing a rigid axial orientation to the C-3 hydroxy group making it too sterically hindered for acetylation to take place. Compound **4** was treated with CrO_3–pyridine. The ^1H NMR spectrum of the oxidation product indicated that the H-3α and H-19 resonances had disappeared

indicating the formation of the expected 3-keto, 19-lactone. The ^{13}C NMR spectrum of the oxidation product was poor due to the small amount of sample available. The C-3 resonance present at δ 76.1 in the ^{13}C NMR spectrum of **4** had disappeared, but the C-3 keto group carbon could not be detected due to the weak spectrum. The C-19 lactone carbonyl resonance could be seen at δ 180.7. Compound **4** has not been isolated previously.

NMR spectra for compound **5** were very similar to those of **4**, except that signals ascribed to the methoxy group were absent. Thus, compound **5** was identified as 5β,19-epoxycucurbita-6,23-diene-3β,19,25-triol. Although the ^{13}C NMR spectrum indicated the required 30 carbon atoms, high resolution mass spectroscopy indicated a molecular formula of $C_{29}H_{46}O_2$. The loss of a CH_2O_2 fragment had occurred readily when the mass spectrum of **4** was determined, so it was assumed that the same had occurred here, giving **5** a molecular formula of $C_{30}H_{48}O_4$. Acetylation with acetic anhydride–pyridine again yielded the two possible 19-acetates. Oxidation with CrO_3–pyridine yielded the 3-keto-19-lactone as expected.

Compound **6** was isolated in very small quantities. High resolution mass spectroscopy indicated that the compound had a molar mass of 486.3725 g mol^{-1}, corresponding to a molecular formula of $C_{31}H_{50}O_4$ as for compound **4**. However the NMR spectra of **4** and **6** differed in the fact that a methoxy group three proton resonance occurred at δ 3.37 in **6** while the methoxy group proton resonance occurred at δ 3.13 in **4**. H-19 occurred as a singlet in **6**, indicating that no hydroxy group was present here as in **4**. Instead of the loss of a HCO_2H fragment in the mass spectrum as in **4**, the loss of a HCO_2CH_3 fragment was seen in the mass spectrum of **6**. These facts indicated that the methoxy group was present at C-19 in **6**, instead of at C-25. The compound did not form an acetate on treatment with acetic anhydride–pyridine.

High resolution mass spectroscopy of compound **7** indicated that the compound had a molecular formula of $C_{32}H_{52}O_4$ (500.3865 g mol^{-1}). The ^1H NMR spectrum indicated that the compound was a dimethoxy compound as there were two three-proton singlets at δ 3.37 and δ 3.13. Since H-3α was in its usual position at δ 3.48 and was seen to be coupled to the hydroxyl group proton resonance at δ 3.40, the methoxy groups were placed at C-19 and C-25, respectively. The loss of a HCO_2CH_3 fragment confirmed the placement at C-19. Thus, **7** was identified as 5β,19-epoxy-19,25-dimethoxycucurbita-6,23-dien-3β-ol. Isolation of the 3β-acetate and its 3β-acetate epimer from *Momordica charantia* has been reported [10], but no NMR data for these compounds have been published.

Compound **8** differed from compounds **4**–**7** in that it was neither an acetal nor a hemiacetal as was indicated by the absence of the doublet at δ 105 in the ^{13}C NMR spectrum. The molar mass of 470.3409 g mol^{-1} suggested a molecular formula of $C_{31}H_{50}O_3$. Resonances due to a hydroxy group at C-3β (δ 3.31, $W_{1/2}$ = 6.8Hz) were present and a methoxy group at C-25 was indicated (δ 3.13). The ^{13}C NMR spectra indicated a triplet at δ 79.8 which correlated with a pair of coupled doublets at δ 3.65 and δ 3.49 (J_{gem} = 8.40Hz) in the ^1H NMR spectrum. The double bond equivalence calculation still required the additional ring, thus the triplet at δ 79.8 was assigned to C-19 and this was linked via an oxygen atom to C-5. Compound **8** is thus 5β,19-epoxy-25-methoxycucurbita-6,23-dien-3β-ol. This compound has been isolated previously as the β-D-glucopyranosyl and β-D-allopyranosyl derivatives [12] from *Momordica charantia*, but this is the first report of the aglycone.

EXPERIMENTAL

Powdered, air-dried leaves of *Momordica foetida* Schum. (440 g) were successively extracted with refluxing hexane, $CHCl_3$ and MeOH in a Soxhlet apparatus. The concd $CHCl_3$ extract was extracted with 1 M NaOH. The organic phase yielded **1**, **2** and **3** after concn. and CC over silica gel (Merck 9385) using $CHCl_3$–EtOAc (1 : 1). The alkaline aq. phase was neutralized with 6 M HCl and re-extracted with $CHCl_3$. The concd $CHCl_3$ extract was dried over Na_2SO_4, $CHCl_3$ was removed and repeated CC using hexane–CH_2Cl_2–EtOAc (4 : 3 : 3) yielded **4**, **5**, **6**, **7** and **8**.

The structures of compounds **1**–**8** were elucidated by means of NMR spectroscopic techniques using $CDCl_3$ as a solvent on a Varian Gemini 300 MHz instrument. ^1H NMR spectra were determined at 300 MHz and ^{13}C NMR spectra at 75 MHz. IR spectroscopy was performed on a Galaxy 2020 FTIR and HRMS using a Kratos MS 9150 instrument. MPs were determined using a Koffler microhotstage apparatus, and optical rotations were read on a Perkin-Elmer 241 polarimeter.

Compound **1**. (70 mg), 3β,7β,23ξ-trihydroxycucurbita-5,24-dien-19-al, HRMS: *m/z* at 472.3551 ($C_{30}H_{48}O_4$ requires 472.3552), mp 123–125°, $[\alpha]_D$ + 73.1° ($CHCl_3$, *c* 0.160), acetylated to a triacetate.

Compound **2**. (20 mg), 3β,7β,25-trihydroxycucurbita-5,23-dien-19-al, HRMS: *m/z* at 472.3552 ($C_{30}H_{48}O_4$ requires 472.3552), mp 188–191°, acetylated to a 3β,7β-diacetate.

Compound **3**. (5 mg), 3β,7β-dihydroxy-25-methoxycucurbita-5,23-dien-19-al, HRMS: *m/z* at 486.3663 ($C_{31}H_{50}O_4$ requires 486.3709).

Compound **4**. (12.3 mg), 5β,19-epoxy-25-methoxycucurbita-6,23-diene-3β,19-diol, M^+ at *m/z* 486.3725 ($C_{31}H_{50}O_4$ requires 486.3709), mp 182–184°, $[\alpha]_D$ −55.9° ($CHCl_3$, *c* 0.102), IR ν_{max}^{KBr} cm^{-1}: 3292, 2949, 1649, 1375, 1080. ^1H NMR: δ 6.06 (*dd*, $J_{6,7}$ = 9.78Hz, $J_{6,8}$ = 2.30Hz, H-6), 5.65 (*dd*, $J_{7,8}$ = 3.72Hz, $J_{6,7}$ = 9.78Hz, H-7), 5.42 (*m*, H-23), 5.40 (*d*, H-24), 5.11 (*d*, *J* = 7.98Hz, H-19), 3.75 (*d*, OH), 3.38 (*m*, $W_{1/2}$ = 6.8Hz, H-3α), 3.13 (3H, *s*, OCH_3), 2.82 (*br s*, H-8), 2.71 (*d*, OH), 2.45 (*br t*, *J* = 9.19Hz, H-10), 1.23 (6H, *s*, 3H-26, 3H-27), 1.19 (3H, *d*, 3H-21), 0.89, 0.87,

0.85, 0.83 (ea 3H, 4 × CH_3). ^{13}C NMR: δ136.8 (*d*, C-24), 132.7 (*d*, C-6), 132.4 (*d*, C-7), 128.3 (*d*, C-23), 105.4 (*d*, C-19), 86.6 (*s*, C-5), 76.1 (*d*, C-3), 74.9 (*s*, C-25), 50.3 (*s*, OCH_3), 49.9 (*d*, C-17), 48.5, 48.0 (2*s*, C-9, 14), 45.1 (*s*, C-4), 41.4 (*d*, C-8), 40.6 (*d*, C-10), 39.4 (*t*, C-12), 37.2 (*s*, C-13), 36.1 (*d*, C-9, 14), 45.1 (*s*, C-4), 41.4 (*d*, C-8), 40.6 (*d*, C-10), 39.4 (*t*, C-12), 37.2 (*s*, C-13), 36.1 (*d*, C-20), 33.5 (*t*, C-15), 30.5 (*t*, C-11), 27.9 (*t*, C-16), 27.1 (*t*, C-22), 26.2, 25.8(2*q*, C-26, 27), 23.9 (*q*, C-29), 23.1 (*t*, C-2), 18.7 (*q*, C-21), 17.3 (*t*, C-1), 20.5, 19.7, 14.7 (3*q*, C-28, 30, 18). Compound **4** (2 mg) was oxidized using Sarret's oxidation [13] and yielded 5β,19-epoxy-25-methoxycucurbita-6,23-diene-3,19-dione. ^1H NMR: δ 6.18 (*dd*, $J_{6,7}$ = 9.78Hz, $J_{6,8}$ = 2.30Hz, H-6), 5.80 (*dd*, $J_{6,7}$ = 9.78Hz, $J_{7,8}$ = 3.72Hz, H-7), 5.48 (*m*, H-23), 5.42 (*d*, H-24), 3.13 (3H, *s*, OCH_3), 2.71 (*td*, H-2_{ax}), 1.24 (6H, *s*, 3H-26, 3H-27), 1.20, 1.17, 0.92, 0.91, 0.90 (ea3H, *s*, 5 × CH_3).

Compound **5**. (8.4 mg), 5β,19-epoxycucurbita-6,23-diene-3β,19,25-triol, $[M\text{-}CH_2O_2]^+$ at *m/z* 426.3498 ($C_{29}H_{46}O_2$ requires 426.3498), $[\alpha]_D$ −93.2° ($CHCl_3$, *c* 0.278). IR ν_{max}^{KBr} cm^{-1}: 3365, 2945, 2877, 1651, 1460, 1377, 1082. ^1H NMR: δ 6.06 (*dd*, *J* = 9.80Hz, *J* = 2.30Hz), 5.65 (*dd*, $J_{6,7}$ = 9.80Hz, $J_{7,8}$ = 3.72Hz, H-7), 5.58 (2H, *m*, H-23, H-24), 5.10 (*d*, *J* = 7.80Hz, H-19), 3.40 (*m*, $W_{1/2}$ = 6.8Hz, H-3α), 2.82 (*m*, H-8), 2.45 (*br t*, *J* = 2.19Hz, H-10), 1.29 (6H, *s*, 3H-26, 3H-27), 1.20 (3H, *d*, *J* = 5.70Hz, 3H-21), 0.87, 0.86, 0.85, 0.83(ea 3H, *s*, 4 × CH_3). ^{13}C NMR: δ 139.6 (*d*, C-24), 132.7 (*d*, C-6), 132.4 (*d*, C-7), 125.2 (*d*, C-23), 105.4 (*d*, C-19), 86.6 (*s*, C-5), 76.0 (*d*, C-3), 70.7 (*s*, C-25), 50.0 (*d*, C-17), 48.5, 48.0 (2*s*, C-9, 14), 45.1 (*s*, C-4), 41.4(*d*, C-8), 40.6 (*d*, C-10), 39.1 (*t*, C-12), 38.0 (*t*, C-13), 36.2 (*d*, C-20), 33.5 (*t*, C-15), 30.5 (*t*, C-11), 30.0 (*t*, C-22), 29.8, 27.1 (2*q*, C-26, 27), 27.9 (*t*, C-16), 23.9 (*q*, C-29), 23.1 (*t*, C-2), 17.3 (*t*, C-1), 18.6 (*q*, C-21), 20.4, 19.7, 14.7 (3*q*, C-28, 30, 18).

Compound **6**. (4.9 mg), 5β,19-epoxy-19-methoxycucurbita-6,23-diene-3β,25-diol,$[M]^+$ at *m/z* 486.3725 ($C_{31}H_{50}O_4$ requires 486.3709), mp 102–104°, $[\alpha]_D$ −52.8° ($CHCl_3$, *c* 0.036), ^1H NMR: δ 6.10(*dd*, $J_{6,7}$ = 9.71 Hz, $J_{6,8}$ = 2.30Hz, H-6), 5.57(2H, *m*, H-23, H-24), 5.50 (*dd*, $J_{6,7}$ = 9.71 Hz, $J_{7,8}$ = 3.72 Hz, H-7), 4.40 (*s*, H-19), 3.70(*d*, OH), 3.41(*bs*, $W_{1/2}$ = 6.7Hz, H-3α), 3.37(3H, *s*, OCH_3), 2.29(*m*, H-10), 2.13(*b s*, H-8), 1.29(6H, *s*, 3H-26, 3H-27), 1.23(3H, *d*, 3H-21), 0.88, 0.86, 0.83, 0.84, (ea 3H, *s*, 4 × CH_3). ^{13}C NMR: δ 139.5(*d*, C-24), 133.0(*d*, C-6), 130.5(*d*, C-7), 125.3(*d*, C-23), 114.7(*d*, C-19), 85.1(*s*, C-5), 76.2(*d*, C-3), 70.7(*s*, C-25), 57.3(*q*, OCH_3), 50.1(*d*, C-17), 49.8(*d*, C-8), 48.9(*s*, C-9), 47.9(*s*, C-14), 45.1(*s*, C-4), 39.1(*t*, C-12), 37.9(*d*, C-10), 37.1(*s*, C-13), 36.2(*d*, C-20), 33.5(*t*, C-15), 30.4(*t*, C-11), 30.0, 29.9(2*q*, C-26, 27), 27.8(*t*, C-16), 27.1(*t*, C-22), 24.4(*q*, C-29), 21.4(*t*, C-2), 18.6(*q*, C-21), 16.5(*t*, C-1), 20.6, 20.5, 15.0(3*q*, C-28, 30,18).

Compound **7**. (6.5 mg), 5β, 19-epoxy-19,25-dimethoxycucurbita-6,23-dien-3β-ol, M^+ at *m/z* 500.3874 ($C_{32}H_{52}O_4$ requires 500.3865), $[\alpha]_D$-37.1° ($CHCl_3$, *c* 0.054). IR ν_{max}^{KBr} cm^{-1}: 3516, 2926, 1377, 1109, 1070. ^1H NMR: δ 6.07(*dd*, $J_{6,7}$ = 9.78Hz, $J_{6,8}$ = 2.30Hz, H-6), 5.50(*m*, H-7), 5.45(*m*, H-23), 5.40(*d*, H-24), 4.40(*s*, H-19), 3.37, 3.13(ea 3H, *s*, 2 × OCH_3), 3.48(*m*, $W_{1/2}$ = 6.8Hz, H-3α), 2.24(*m*, H-8), 2.15(*m*, H-10), 1.23(6H, *s*, 3H-26, 3H-27), 0.90, 0.88, 0.87, 0.86, 0.83(ea 3H, 5 × CH_3). ^{13}C NMR: δ 136.8(*d*, C-24), 133.5(*d*, C-6), 130.5(*d*, C-7), 128.4(*d*, C-23), 114.7(*d*, C-19), 85.1(*s*, C-5), 76.2(*d*, C-3), 74.9(*s*, C-25), 57.3(*q*, OCH_3), 50.3(*q*, OCH_3), 50.0(*d*, C-17), 49.8(*d*, C-8), 48.9, 48.0(2*s*, C-9, 14), 45.1(*s*, C-4), 39.4(*t*, C-12), 37.9(*d*, C-20), 37.1(*s*, C-13), 36.1(*d*, C-10), 33.5(*t*, C-15), 30.4(*t*, C-11), 27.8(*t*, C-16)27.1(*t*, C-22), 26.1, 25.8(2*q*, C-26, 27)24.4(*q*, C-29) 21.4(*t*, C-2) 18.7(*q*, C-21), 16.5(*t*, C-1), 20.6, 19.9, 15.0(3*q*, C-28, 30, 11).

Compound **8**. (4.8 mg), 5β, 19-epoxy-25-methoxycucurbita-6,23-dien-3β-ol, $[M]^+$ at *m/z* 470.3632 ($C_{31}H_{50}O_3$ requires 470.3409), mp 139–141°. IR ν_{max}^{KBr} cm^{-1}: 3472, 2943, 1446, 1379, 1080. ^1H NMR: δ 6.00(*dd*, $J_{6,7}$ = 9.78 Hz, $J_{6,8}$ = 2.30Hz, H-6), 5.60(*dd*, $J_{6,7}$ = 9.78Hz, $J_{7,8}$ = 3.72Hz, H-7), 5.47(*m*, H-23), 5.40(*d*, H-24), 3.65(*d*, J_{gem} = 8.40Hz, H-19_A), 3.49(*d*, J_{gem} = 8.40Hz, H-19_B), 3.31 (*m*, $W_{1/2}$ = 6.8Hz, H-3α), 3.13(3H, *s*, OCH_3), 2.32(*m*, H-8), 2.18(*m*, H-10), 1.23(6H, *s*, 3H-26, 3H-27), 1.18, 0.89, 0.87, 0.85, 0.83(ea 3H, *s*, 5 × CH_3). ^{13}C NMR: δ 136.8(*d*, C-24), 131.8(*d*, C-6), 131.5(*d*, C-7), 128.3(*d*, C-23), 87.5(*s*, C-5), 79.8(*t*, C-19), 76.1(*d*, C-3), 74.8(*s*, C-25), 52.0(*d*, C-8), 50.3(*q*, OCH_3), 49.9(*d*, C-17), 48.6(*s*, C-14), 45.5, 45.2(2*s*, C-4, 9), 39.4(*t*, C-12), 38.8(*d*, C-10), 37.2(*s*, C-13), 36.1(*d*, C-20), 33.2(*t*, C-15), 30.8(*t*, C-11), 27.9(*t*, C-16), 27.3(*t*, C-22), 26.1, 25.8(2*q*, C-26, 27), 24.5(*q*, C-29), 23.6(*t*, C-2), 18.7(*q*, C-21), 17.6(*t*, C-1), 20.5, 20.0, 14.9(3*q*, C-28, 30, 18).

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