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New Eunicellin-Based Diterpenoids from the Gorgonian *Eunicella verrucosa*

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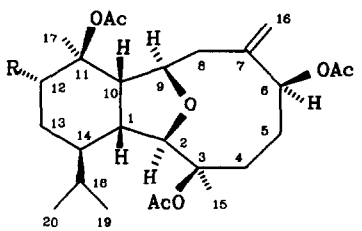
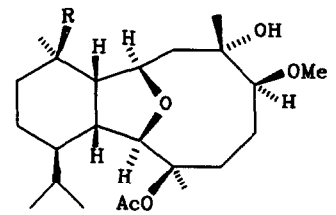
Abstract: Five new eunicellin-based diterpenoids named palmonine A, B, C, D and E have been isolated from the gorgonian *Eunicella verrucosa*. Their structures have been established by spectroscopic methods and their relative stereochemistry defined by extensive NOEDS experiments.

Eunicellin-based diterpenoids belong to a class of marine natural products characterized for possessing a cladiellane skeleton made up of four isoprene units linked head to tail. Although this skeleton occurs most frequently in the Alcyonacea[2-6] this type of compounds has also been isolated from the gorgonacean corals.[7-13]

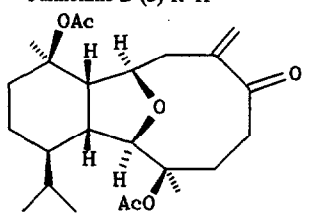
Eunicellin (**1**), the first compound of this class to be described, was isolated from the gorgonian coral *Eunicella stricta*.[7] Although there have been some chemical studies of species of the genus *Eunicella*,[14,15] eunicellin remains as the only compound possessing a cladiellane skeleton reported from this genus.



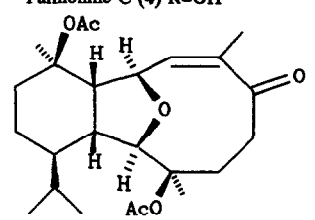
Eunicellin (**1**) R=OAc
Palmonine B (**3**) R=H



Palmonine A (**2**) R=OAc
Palmonine C (**4**) R=OH



Palmonine D (**5**)



Palmonine E (**6**)

In the course of our investigations of the metabolites of marine organisms from the southern coast of Spain we obtained specimens of the gorgonian *Eunicella verrucosa* Verrill (Gorgonaceae) collected in Palmones at Algeciras Bay. The chemical study of *Eunicella verrucosa* has led to the isolation and

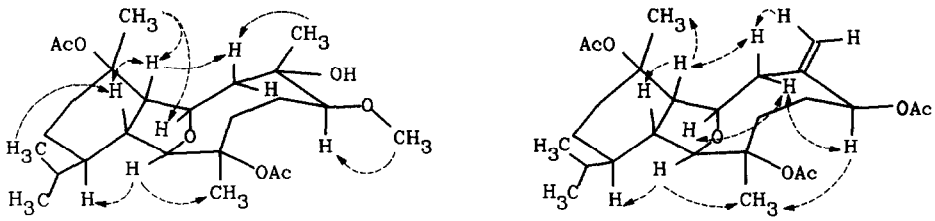
characterization of five new eunicellin-based diterpenes: palmonine A (**2**) and B (**3**) as the major compounds together with three other minor palmonines (**4-6**).

Specimens of *Eunicella verrucosa* were collected by hand using SCUBA, dried and extracted with methanol. Chromatography of the methanol soluble material on silica gel followed by final purification using HPLC allowed isolation of the following compounds: palmonine A (**2**, 0.0155% dry wt), palmonine B (**3**, 0.0060% dry wt), palmonine C (**4**, 0.0002% dry wt), palmonine D (**5**, 0.0014% dry wt) and palmonine E (**6**, 0.0010% dry wt).

Palmonine A (**2**) was isolated as a colorless oil. The molecular formula, $C_{25}H_{42}O_7$, was obtained from the high resolution mass measurement. The presence of two acetate groups were indicated by the IR absorption at 1723 cm^{-1}, the ^1H NMR signals at ∂ 1.99 (s,3H) and 2.11 (s,3H) and the ^{13}C NMR signals at 22.3 (q), 22.6 (q), 169.9 (s) and 170.3 (s). The ^1H NMR signal at 3.33 (s,3H) and the ^{13}C NMR signal at 56.9 (q) clearly indicated the presence of a methoxyl group. Since the ^{13}C NMR did not contain any olefinic signal the diterpenoid skeleton must therefore be tricyclic. The isopropyl group signals at 1.70 (m,1H), 0.81 (d,3H) and 0.94 (d,3H) together with two methine carbons bearing oxygen at 92.1 and 75.9 that were correlated on the XHCORR experiment to the signals at ∂ 3.48 (brs, H-2) and 4.08 (m, H-9), respectively, supported that **2** had an eunicellin carbon skeleton. The remaining oxygen was assigned to a tertiary alcohol upon analysis of the IR absorption at 3451 cm^{-1} and the ^{13}C NMR singlet at ∂ 76.4.

The location of the oxygen functionalities on the eunicellin skeleton as well as the stereochemistry were defined on the bases of COSY, HMBC and NOEDS experiments. The methyl attached to the hydroxyl group appeared as a singlet at ∂ 1.12 and in the HMBC experiment showed long range couplings to the C-7, C-8 and C-6 carbon signals. The methyl groups geminal to the acetoxyl groups appeared as singlets at ∂ 1.39 and 1.48 that were correlated in HMBC experiment to the C-3, C-2 and C-4, and to C-11, C-10 and C-12 carbon signals, respectively. Therefore the hydroxyl group must be located on C-7, and the acetoxyl groups to C-3 and C-11. A similar rationale indicated that the methoxy group must be attached to C-6 since the geminal proton signal at ∂ 4.10 (m,1H) showed long range couplings to C-7 and -O<u>C</u>H$_3$.

The stereochemistry of palmonine A (**2**) was determined by extensive NOEDS experiments. Irradiation of the Me-17 signal caused enhancement of the H-10 and H-9 signals, irradiation of H-10 signal resulted in enhancement of H-1 signal and irradiation of Me-19 signal produced enhancement of H-1 signal. These data support the stereochemistry proposed for the six member ring and the H-1,H-10 ring junction protons. Irradiation of the H-2 signal enhanced the H-14 and Me-15 signals confirming the β orientation for the isopropyl group and defining the stereochemistry at C-3. Irradiation both of H-10 and Me-16 signals caused enhancement on the H-8β signal at ∂ 1.85 in agreement with the α orientation of the hydroxyl group. The stereochemistry at C-6 was defined since irradiation of the methoxyl group signal caused enhancement exclusively on the geminal proton signal at ∂ 4.10 indicating that the methoxyl group lack connection through the space with H-2, H-9 and Me-15 and suggesting a β orientation for the methoxyl group (see figure 1).



Palmonine A (2) Palmonine B (3)

Figure 1. Selected NOE (indicated by arrows) for palmonine A (2) and palmonine B (3).

Palmonine B (3) was isolated as a colorless oil. The molecular formula, $C_{26}H_{40}O_7$, was deduced from the high resolution mass measurement. The signals on the ^1H NMR spectrum at ∂ 1.95 (s,3H), 1.98 (s,3H), 2.01 (s,3H) and 5.15 (dd,J=3.7,11.6,1H) together with the ^{13}C NMR data, in particular, a doublet at ∂ 76.4 indicated that **3** must be a triacetate: two of the acetoxyl groups adjacent to fully substituted carbon atoms and, the third one attached to a methine carbon. In addition, two broad singlets on the ^1H NMR spectrum at ∂ 5.22 and 5.40 together with the ^{13}C NMR signals at ∂ 118.4 (t) and 146.4 (s) indicated that palmonine B (**3**) contained an exocyclic double bond.

Comparison of the spectral data of palmonine B (**3**) with those of palmonine A (**2**) strongly suggested that **3** had the same carbon skeleton and stereochemistry with a 6β-acetoxy substituent and a C-7,C-16 double bond instead of the methoxyl and hydroxyl groups present in **2**. It is worth noting that the ^1H NMR signals of the allylic protons at ∂ 2.44 (d,J=13.8,1H) and 3.07 (m,1H) were correlated to the C-8 signal at 41.0 (t) on the HXCORR experiment. The structure and stereochemistry was confirmed by a series of NOEDS experiments. Irradiation of the H-10 caused enhancements on the H-1, H-8β and Me-17 signals, and irradiation of H-2 signal enhanced the H-14 and Me-15 signals. These results support the similarities between **2** and **3**. Furthermore irradiation of the H-6 signal caused enhancements on the H-8α and Me-15 signals whereas irradiation of the vinylic proton H-16 enhanced the H-8β signal supporting the proposed structure and stereochemistry for palmonine B (**3**) (see figure 1).

Palmonine C (**4**), obtained as a colorless oil, was the minor metabolite whose structure was determined from *E. verrucosa* (1 mg). The small amount available prevented high quality spectroscopic data being obtained. The molecular formula, $C_{23}H_{40}O_6$, was obtained from the high resolution mass measurement. The ^1H NMR spectrum clearly indicated that the structure of palmonine C (**4**) was very similar to that of palmonine A (**2**) though unambiguously showed that only one acetoxyl group was present on its structure. The main differences observed were the significant upfield shifts of Me-17 signal at ∂ 1.16 (s,3H) and H-10 signal at ∂ 2.81 (brt,J=6.4,1H). It was therefore assumed that palmonine C (**4**) was the 11-deacetoxy derivative of **2**.

Palmonine D (**5**) was isolated as a colorless oil. The HRFABMS indicated a molecular formula

$C_{24}H_{36}O_6$. Comparison of the ^1H NMR and ^{13}C NMR of **5** with those of **3** indicated a great similarity between both structures. However some differences were observed: The ^{13}C NMR spectrum of **5** showed a singlet at ∂ 205.4 and lacked one acetoxyl group and the geminal methine carbon signals. The IR spectrum contained a band at 1680 cm^{-1} due to an α,β-unsaturated ketone. These spectral features indicated that in palmonine D (**5**) the C-6 was oxidized to a ketone. Nuclear Overhauser effect difference spectroscopy provided confirmation to the proposed structure. Irradiation of the Me-17 signal resulted in enhancement of the H-10 and the H-8β signals, irradiation of the H-10 signal caused enhancements of the H-1 and H-8β signals and irradiation of the H-8β signal produced and enhancement of one of the vinylic protons at C-16. The stereochemistry at C-3 and C-14 is identical to the other members of the series as confirmed by the enhancements produced on H-14 and Me-15 signals upon irradiation of the H-2 signal.

Palmonine E (**6**) was obtained as white crystals, mp. 152-153 °C. The molecular formula $C_{24}H_{36}O_6$ obtained from a HRFABMS indicated that **6** was an isomer of **5**. The broad singlet at ∂ 5.36 on the ^1H NMR together with the signals at ∂ 124.9 (d) and 138.4 (s) on the ^{13}C NMR spectrum suggested that palmonine E (**6**) contained a trisubstituted endocyclic double bond. Furthermore, a broad singlet at ∂ 1.80 on the ^1H NMR spectrum assigned to a vinylic methyl group together with the correlations between the vinylic protons signals at ∂ 5.36 and the H-9 signal at ∂ 4.35 on the COSY experiment and with the C-9 at ∂ 77.9 on the XHCORR experiment indicated that the double bond was located on C-7,C-8.

The Z geometry of the double bond was ascertained by two NOEDS experiments. Irradiation of the Me-16 signal caused enhancement only of the H-8 signal. Irradiation of the H-8 signal produced enhancements on the Me-16, H-9, H-10 and Me-17 signals. These data could be accommodated by structure **6**.

Despite eunicellin type diterpenes have been proposed[9] as the logical biosynthetic intermediates from cembranes to the asbestin diterpenes, none of these types of compounds have been found among the metabolites from *Eunicella verrucosa*.

EXPERIMENTAL

Infrared spectra were recorded in a Perkin-Elmer 881 spectrophotometer. ^1H-NMR and ^{13}C-NMR spectra were made on a Varian Gemini-400 at 400 Mhz and 100 MHz respectively using $SiMe_3$ as internal reference. An asterisk indicates interchangeable signals. Mass spectra were recorded on VG 12250 or on a Kratos MS 80RFA spectrometers. Optical rotations were measured in a Perkin-Elmer 881 polarimeter. Melting points (uncorrected) were determined on a Reichert-Jung apparatus. All solvents were distilled from glass prior to use.

Extraction and isolation: The gorgonian *Eunicella verrucosa* (515.5 g, dry weight) was collected in Palmones (Spain) in July 1990 air-dried in the shade and extracted with methanol. The methanolic extract was evaporated under reduced pressure and the aqueous residue was extracted with dichloromethane (5x500 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent evaporated to give dark orange oil (8 g), which was chromatographed on a silica column (26x5.5 cm) using solvents of increasing polarity from hexane to diethyl-ether and subsequently chloroform-methanol. Fractions eluted with 20% ether in hexane contained palmonine B (**3**, 29 mg, 0.0058% dry weight), 30% ether in hexane contained a 1:1 mixture of palmonine D (**5**, 7mg,

0.0014% dry weight) and palmonine E (**6**, 5 mg, 0.0010% dry weight) that was separated and purified by high-performance liquid chromatography on LiChrosorb (15% EtOAc in hexane eluent). Fractions eluted with 50% ether in hexane contained palmonine A (**2**, 80 mg, 0.016% dry weight) and fractions eluted with 70% ether in hexane contained Palmonine C (**4**, 1 mg, 0.0002% dry weight).

Palmonine A (2): Colorless oil, $[\alpha]_D$= +43.4 (c=1.04, $CHCl_3$); **IR** (film) 3458, 2926, 1723, 1187, 1144, 1078, 1021 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) ∂ 4.10 (d, 1H, *J*= 6.3 Hz, H-6), 4.08 (m, 1H, H-9), 3.48 (brs, 1H, H-2), 3.33 (s, 3H, -OCH_3), 3.18 (brt, 1H, *J*= 6.8 Hz, H-10), 2.70 (dd, 1H, *J*= 8.7, 14.4 Hz, H-4β), 2.13 (dd, 1H, *J*= 6.8, 11.22 Hz, H-1), 2.11 (s, 3H, -OAc), 2.10 (m, 1H, H-12), 1.99 (s, 3H, -OAc), 1.95 (m, 1H, H-8α), 1.85 (m, 1H, H-8β), 1.7 (m, 1H, H-18), 1.65 (m, 1H, H-4α), 1.6 (dd, 1H, *J*= 8.7, 16.8 Hz, H-5), 1.48 (s, 3H, H-17), 1.41 (m, 1H, H-12), 1.39 (s, 3H, H-15), 1.32 (m, 2H, H-13), 1.3 (m, 1H, H-5), 1.2 (m, 1H, H-14), 1.12 (s, 3H, H-16), 0.94 (d, 3H, *J*= 6.8 Hz, H-20), 0.81 (d, 3H, *J*= 6.8 Hz, H-19); **^{13}C-NMR** ($CDCl_3$) ∂ 170.3 (s, -$\underline{C}OCH_3$), 169.9 (s, -$\underline{C}OCH_3$), 92.1 (d, C-2), 90.8 (d, C-6), 86.2 (s, C-3), 82.2 (s, C-11), 76.4 (s, C-7), 75.9 (d, C-9), 56.9 (q, -OCH_3), 52.6 (d, C-10), 46.9 (t, C-8), 42.5 (d, C-14), 42.3 (d, C-1), 37.1 (t, C-4), 32.4 (t, C-12), 29.0 (d, C-18), 26.7 (t, C-5), 24.8 (q, C-17), 23.7 (q, C-16), 23.1 (q, C-15), 22.6 (q, -CO$\underline{C}H_3$), 22.3 (q, -CO$\underline{C}H_3$), 21.8 (q, C-20), 17.5 (t, C-13), 15.3 (q, C-19); **EIMS** (70 Ev) *m/z* 436 (6), 394 (3), 334 (14), 177 (23), 115 (28), 43 (100); **HREIMS** Obsd. *m/z*= 437.2828 (M-OH$^·$), $C_{25}H_{41}O_6$ requires *m/z*= 437.2903; obsd. *m/z*= 436.2825 $(M-H_2O)^+$, $C_{25}H_{40}O_6$ requires *m/z*= 436.2825; obsd. *m/z*= 394.2685 $(M-AcOH)^+$, $C_{23}H_{38}O_5$ requires *m/z*= 394.2719.

Palmonine B (3): Colorless oil, $[\alpha]_D$=-35,8 (c= 1.0, $CHCl_3$); **IR** (film) 2955, 1731, 1247, 1044 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) ∂ 5.40 (brs, 1H, H-16), 5.22 (brs, 1H, H-16), 5.15 (dd, 1H, *J*= 3.7, 11.6, H-6), 4.08 (dd, 1H, *J*= 4.6, 11.7, H-9), 3.57 (brs, 1H, H-2), 3.07 (m, 2H, H-8α,10), 2.44 (d, 1H, *J*= 13.8, H-8β), 2.22 (dd, 1H, *J*= 7.3, 11.7, H-1), 2.18 (m, 2H, H-4,12), 2.05 (m, 1H, H-5), 2.01 (s, 3H, -OAc), 1.85 (m, 2H, H-4,18), 1.84 (m, 1H, H-5), 1.98 (s, 3H, -OAc), 1.95 (s, 3H, -OAc), 1.54 (s, 3H, H-15), 1.53 (s, 3H, H-17), 1.44 (m, 1H, H-12), 1.39 (m, 1H, H-13), 1.33 (m, 1H, H-13), 1.2 (m, 1H, H-14), 0.95 (d, 3H, *J*= 6.9, H-20), 0.78 (d, 3H, *J*= 6.9, H-19); **^{13}C-NMR** ($CDCl_3$) ∂ 170.2 (s, -$\underline{C}OCH_3$), 170.0 (2xq, -$\underline{C}OCH_3$), 146.4 (s, C-7), 118.4 (t, C-16), 90.3 (d, C-2), 84.7 (s, C-3), 82.3 (s, C-11), 78.8 (d, C-9), 76.4 (d, C-6), 45.8 (d, C-10), 43.0 (d, C-14), 41.5 (d, C-1), 41.0 (t, C-8), 32.5 (t, C-12)*, 32.3 (t, C-5)*, 29.6 (t, C-4), 27.5 (d, C-18), 25.5 (q, C-17), 22.5 (q, -CO$\underline{C}H_3$), 22.4 (2xq, C-15, -CO$\underline{C}H_3$), 21.7 (q, C-20), 21.4 (q, -CO$\underline{C}H_3$), 18.1 (t, C-13), 15.2 (q, C-19); **EIMS** (70 Ev) *m/z* 404 (4), 344 (3), 302 (7), 284 (10), 43 (100); **HREIMS** Obsd. *m/z*= 464.2752 $(M)^+$, $C_{26}H_{40}O_7$ requires *m/z*= 464.2774; obsd. *m/z*= 404.2546 $(M-AcOH)^+$, $C_{24}H_{36}O_5$ requires *m/z*= 404.2562.

Palmonine C (4): amorphous powder; IR (film) 3390, 2930, 1720, 1200, 1140, 1060, 1015 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) ∂ 4.06 (m, 2H, H-6,9), 3.55 (brs, 1H, H-2), 3.37 (s, 3H, -OCH_3), 2.81 (brt, 1H, *J*= 6.4 Hz, H-10), 2.4 (m, 1H, H-12), 2.3 (dd, 1H, *J*= 14.8, 11.5 Hz, H-5), 2.18 (m, 1H, H-1), 1.99 (s, 3H, -OAc), 1.94 (m, 1H, H-8), 1.82 (m, 1H, H-8), 1.73 (dd, 1H, *J*= 14.8, 3.6 Hz, H-5), 1.71 (m, 1H, H-18), 1.46 (s, 3H, H-15), 1.4 (m, 3H, H-4, 12, 13), 1.3 (m, 1H, H-13), 1.2 (m, 2H, H-4, 14), 1.16 (s, 6H, H-16, 17), 0.94 (d ,3H, *J*= 6.9 Hz, H-20), 0.82 (d, 3H, *J*= 6.9 Hz, H-19); **HRFABMS** Obsd. *m/z*= 545.1868 $(M+Cs)^+$,$C_{23}H_{40}O_6Cs$ requires *m/z*=545.1878.

Palmonine D (5): Colorless oil, $[\alpha]_D$=+7.3 (c=0.7, $CHCl_3$); **IR** (film) 2933, 1723, 1627, 1444, 1077 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) ∂ 5.57 (d, 1H, *J*= 1.38 Hz, H-16), 5.2 (brs, 1H, H-16), 3.85 (ddd, 1H, *J*= 4.9, 7.2, 9.7 Hz, H-9), 3.53 (brs, 1H, H-2), 3.39 (brdd, 1H, *J*= 6.6, 7.2, H-10), 2.95 (dd, 1H, *J*= 4.9, 13.7 Hz, H-8α), 2.77 (dd, 1H, *J*= 7.2, 13.7 Hz; H-8β), 2.67 (dd, 1H, *J*=8.4, 12.8 Hz, H-5), 2.62 (t, 1H, *J*=12.8 Hz, H-5), 2.20 (dd, 1H, *J*= 6.6, 12.1 Hz, H-1), 2.17 (m, 1H, H-4), 2.12 (s, 3H, -OAc), 2.09 (m, 1H, H-4), 2.05 (m, 1H, H-12), 2.02 (s, 3H, -OAc), 1.69 (m, 1H, H-18), 1.53 (s, 3H, H-17), 1.42 (m, 1H, H-12), 1.40 (s, 3H, H-15), 1.37 (m, 2H, H-13), 1.16

(s, 1H, H-14), 0.92 (d, 3H, *J*=6.9 Hz, H-20), 0.79 (d, 3H, *J*= 6.9 Hz, H-19); **^{13}C-NMR** ($CDCl_3$) ∂ 205.3 (s, C-6), 170.24 (s, -$\underline{C}OCH_3$) , 170.12 (s, -$\underline{C}OCH_3$), 148.3 (s, C-7), 119.4 (t, C-16), 90.6 (d, C-2), 84.3 (s, C-3), 81.4 (s, C-11), 78.4 (d, C-9), 49.2 (d, C-10), 42.9 (d, C-1), 41.6 (d, C-14), 41.4 (t, C-8), 35.1 (t, C-5)*, 33.4 (t, C-4)*, 33.9 (t, C-12)*, 28.2 (d, C-18), 25.4 (q, C-17), 22.5 (2xq, C-15, -CO$\underline{C}H_3$), 22.2 (q, -CO$\underline{C}H_3$), 21.6 (q, C-20), 17.8 (t, C-13), 15.0 (q, C-19); **EIMS** (70 Ev) *m/z* 360 (57), 318 (20), 300 (36), 99 (41), 43 (100); **HRFABMS** Obsd. *m/z*= 553.1563 $(M+Cs)^+$, $C_{24}H_{36}O_6Cs$ requires *m/z*= 553.1565; obsd. *m/z*= 505.1629 $(M+Rb)^+$, $C_{24}H_{36}O_6Rb$ requires *m/z*= 505.1629.

Palmonine E (6): white crystals, mp 152-153°C; $[\alpha]_D$=-17,25 (c= 0.4, $CHCl_3$); **IR** (film) 2928, 1722, 1692, 1282, 1146, 1064, 1016 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) ∂ 5.36 (brs, 1H, H-8) 4.35 (brd, 1H, *J*= 10.8 Hz, H-9), 3.67 (brs, 1H, H-2), 3.37 (ddd, 1H, *J*= 10.8, 6.4, 1.4, H-10), 2.64 (ddd, 1H, *J*= 14.3, 7.8, 2 Hz, H-4β), 2.45 (td, 1H, *J*= 12.4, 1.9 Hz, H-5), 2.23 (dd, 1H, *J*= 6.7, 11.9, H-1), 2.22 (m, 1H, H-12), 2.14 (m, 1H, H-5), 2.09 (m, 1H, H-4), 2.08 (s, 3H, -OAc), 2.02 (s, 3H, -OAc), 1.80 (brs, 3H, H-16), 1.7 (m, 1H, H-18), 1.57 (s, 3H, H-17), 1.43 (m, 3H, H-12,13), 1.40 (s, 3H, H-15), 1.22 (m, 1H, H-14), 0.94 (d, 3H, *J*=6.9 Hz, H-20), 0.74 (d, 3H, *J*= 6.9 Hz, H-19); **^{13}C-NMR** ($CDCl_3$) ∂ 205.0 (s, C-6), 170.1 (s, -$\underline{C}OCH_3$), 170.4 (s, -$\underline{C}OCH_3$), 138.4 (s, C-7), 124.9 (d, C-8), 91.2 (d, C-2), 83.7 (s, C-3), 81.5 (s, C-11), 77.9 (d, C-9), 50.1 (d, C-10), 43.1 (d, C-1), 41.1 (d, C-14), 37.5 (t, C-5), 33.9 (t, C-4), 32.9 (t, C-12), 28.2 (d, C-18), 25.5 (q, C-17), 22.5 (q, C-15), 22.4 (q, -CO$\underline{C}H_3$), 21.9 (q, -CO$\underline{C}H_3$), 21.6 (q, C-20), 19.1 (q, C-16), 17.9 (t, C-13), 14.9 (q, C-19); **EIMS** (70 eV) *m/z* 360 (57), 318 (100), 300 (36), 231 (43), 99 (41), 43 (49); **HRFABMS** Obsd. *m/z*= 553.1559 $(M+Cs)^+$, $C_{24}H_{36}O_6Cs$ requires *m/z*= 553.1565; obsd. *m/z*= 421.2589 $(M+1)^+$, $C_{24}H_{37}O_6$ requires *m/z*= 421.2590.

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