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Four New Tetranortriterpenoids from *Cedrela odorata* Associated with Leaf Rejection by *Exopthalmus jekelianus*

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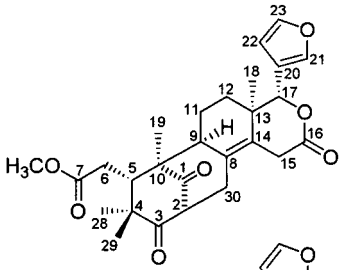
Four new tetranortriterpenoids, 3-deoxo-3β,8β-epoxy-6,14α-dihydroxy-8,14-dihydromexicanolide (cedrodorin, **1**); 3-deoxo-3β,8β-epoxy-6-acetoxy-14α-hydroxy-8,14-dihydromexicanolide (6-acetoxycedrodorin, **2**); 3-deoxo-3β,8β-epoxy-6-deoxy-9α,14α-dihydroxy-8,14-dihydromexicanolide (6-deoxy-9α-hydroxycedrodorin, **3**); and 3-deoxo-3β,8β-epoxy-6,9α,14α-trihydroxy-8,14-dihydromexicanolide (9α-hydroxycedrodorin, **4**), have been isolated from the leaves of *Cedrela odorata* by HPLC. Their molecular structures were determined by 1D and 2D NMR. Three of the compounds are associated with leaf rejection by the polyphagous, folivorous weevil, *Exopthalmus jekelianus*. The importance of these compounds as insect deterrents in *C. odorata*, and their potential value in the selection of insect-resistant clones for timber plantations is discussed.

The Meliaceae includes some of the most economically important tropical trees, notably the Mahoganies (*Swietenia* spp., *Khaya* spp.) and Spanish Cedar (*Cedrela odorata* L.).[1] *C. odorata* is characterized chemically by the presence of tetranortriterpenoids (limonoids),[2,3] a group of compounds that exhibit a wide variety of biological properties. These include insect antifeedant activity[4] and toxicity,[5] and antimalarial,[6] antibacterial,[7] and antifungal[8] activity. Phytochemical studies of timber trees in Meliaceae have focused almost exclusively on the bark and heartwood, rather than leaves or leaf shoots. This is surprising because the establishment of hardwood timber plantations, an economically beneficial conservation strategy for timber production in the tropics,[1] is limited predominantly by insect damage to leaf shoots.[9] This results in early branching and significant loss of timber value. Previous field studies of *C. odorata* in Costa Rica have shown that some clones are less preferred than others by the foliar-feeding, polyphagous weevil, *Exopthalmus jekelianus* White (Curculionidae).[10] The current report describes the isolation and structure elucidation of four new rearranged tetranortriterpenoids from *C. odorata*, three of which are associated with leaf rejection by *E. jekelianus*.

Results and Discussion

The methanolic extract of the leaves of a 6-month-old *C. odorata* clone (X117) was subjected to analysis by HPLC coupled to a photodiode-array detector. This revealed the presence of four major apolar components (**1**−**4**) with UV−vis spectra similar to those of the tetranortriterpenoid limonin,[11] which shows the distinctive feature of a UV maximum at 285 nm due to the presence of a furan ring. In a recent study, rejection of *C. odorata* leaves by the weevil *E. jekelianus* was found to be correlated with the presence of **1**−**3** but not **4**. In addition, when insects took meals from leaves containing **1**−**4**, the meal duration was significantly shorter on leaves containing **1** and **3** than on those from which they were absent.[10] However, the structural identity of compounds **1**−**4** has not been described to date. In the present study, isolation of **1**−**4** in quantities sufficient for structure elucidation was achieved by scaling up the analytical method to semipreparative HPLC, with no apparent loss of resolution.



1 R_1 = OH, R_2 = H; **2** R_1 = OAc, R_2 = H
3 R_1 = H, R_2 = OH; **4** R_1 = OH, R_2 = OH

The ^{1}H and ^{13}C NMR spectra of **1** acquired in $CDCl_3$ contained a number of distinctive resonances, including four *tert*-methyl groups (δ_H 0.94, 1.00, 1.05, and 1.32), a methyl ester (δ_H 3.83; δ_C 52.6 and 175.7), a β-substituted furan (δ_H 6.45, 7.46, and 7.48; δ_C 109.9, 120.9, 140.7, and 143.1) and a lactone (δ_C 170.1). These features are characteristic of compounds classified in the mexicanolide group of rearranged tetranortriterpenoids, many examples of which have been reported previously from *Cedrela* and *Swietenia*.[12] An empirical formula of $C_{27}H_{34}O_9$ was obtained by ESIMS (*m*/*z* 503 $[M + H]^+$) in conjunction with analysis of 1D and DEPT spectra. Exhaustive analysis of 1D ROE, DEPT, DQF−COSY, HSQC, and HMBC experimental data was necessary in order to obtain the molecular structure of **1**. Resonance assignments are summarized in Tables 1

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Table 1. ^{1}H NMR Chemical Shift Assignments (δ) and Coupling Constant Data for Compound **1** in $CDCl_3$ and Compounds **1**−**4** in DMSO-d_6

	compound				
proton	**1**[a]	**1**[b]	**2**[b]	**3**[b]	**4**[b]
2	3.03 (m)	2.86 (m)	2.95 (m)	2.85 (m)	2.83 (m)
3	4.00 (d, 5.8)	3.90 (d, 5.7)	3.98 (d, 5.8)	4.17 (d, 5.4)	3.93 (d, 5.4)
5	2.83 (d, 2.8)	2.82 (d, 4.1)	2.95 (m)	2.94 (m)	2.83 (m)
6	4.36 (br s)	4.15 (m)	4.99 (d, 2.6)	2.11 (dd, 17.3, 11.1) 2.35 (d, 17.3)	4.25 (m)
9	2.04 (dd, 12.2, 4.6)	1.96 (dd, 12.2, 5.0)	2.05 (dd, 11.8, 4.6)		
11α	1.56 (m)	1.42 (m)	1.48 (m)	1.39 (m)	1.54 (m)
11β	1.90 (m)	1.78 (m)	1.74 (m)	2.45 (m)	2.28 (m)
12α	1.74 (m)	1.68 (m)	1.69 (m)	1.79 (m)	1.79 (m)
12β	1.52 (m)	1.25 (m)	1.26 (m)	1.19 (m)	1.18 (m)
15α	2.52 (d, 17.7)	2.48 (d, 17.9)	2.50 (d, 18.0)	2.47 (d, 17.8)	2.44 (d, 18.1)
15β	3.16 (d, 17.7)	2.94 (d, 17.9)	2.96 (d, 18.0)	2.96 (d, 17.8)	2.93 (d, 18.1)
17	6.22 (s)	6.11 (s)	6.07 (s)	6.11 (s)	6.07 (s)
18	1.00 (s)	0.89 (s)	0.89 (s)	0.93 (s)	0.92 (s)
19	1.32 (s)	1.09 (s)	0.93 (s)	0.74 (s)	1.03 (s)
21	7.48 (m)	7.62 (m)	7.65 (m)	7.65 (m)	7.63 (m)
22	6.45 (dd, 1.5, 0.6)	6.48 (m)	6.49 (dd, 1.6, 0.6)	6.51 (m)	6.50 (m)
23	7.46 (t, 1.5)	7.73 (t, 1.6)	7.73 (t, 1.6)	7.75 (t, 1.5)	7.75 (t, 1.6)
28	0.94 (s)	0.85 (s)	0.88 (s)	0.59 (s)	0.85 (s)
29	1.05 (s)	0.98 (s)	0.97 (s)	1.02 (s)	0.96 (s)
30α	2.07 (d, 12.5)	1.82 (d, 12.5)	1.86 (d, 12.6)	2.45 (m)	2.41 (m)
30β	2.54 (dd, 12.5, 6.7)	2.54 (dd, 12.5, 6.8)	2.59 (dd, 12.6, 6.8)	2.45 (m)	2.41 (m)
OCH_3	3.83 (s)	3.67 (s)	3.73 (s)	3.65 (s)	3.67 (s)
$OCOCH_3$			2.03 (s)		
OH-6	2.59 (br s)	5.22 (d, 4.7)			5.28 (d, 4.7)
OH-9				5.46 (s)	5.52 (s)
OH-14		5.14 (s)	5.19 (s)	5.08 (s)	5.08 (s)

[a] Spectra acquired in $CDCl_3$ at 500 MHz and 30 °C. [b] Spectra acquired in DMSO-d_6 at 500 MHz and 37 °C.

Table 2. ^{13}C NMR Chemical Shift Assignments (δ) for Compound **1** in $CDCl_3$ and Compounds **1**−**4** in DMSO-d_6

	compound				
carbon	**1**[a]	**1**[b]	**2**[b]	**3**[b]	**4**[b]
1	214.1	213.6	212.7	213.6	212.6
2	48.9	48.4	48.3	48.3	48.2
3	93.0	92.4	92.0	90.7	92.5
4	38.0	37.3	37.6	37.0	37.5
5	48.5	47.3	46.4	45.0	49.5
6	71.0	70.1	71.6	32.7	70.3
7	175.7	174.8	169.9	173.8	174.8
8	85.2	85.2	85.3	85.8	85.6
9	52.6	52.1	52.2	81.7	82.0
10	51.0	50.1	50.1	56.7	56.2
11	18.2	17.6	17.6	22.8	22.7
12	28.8	28.5	28.5	24.9	24.9
13	40.1	39.8	39.7	39.9	39.7
14	74.4	73.0	73.0	74.4	74.4
15	37.2	36.2	36.1	36.0	35.9
16	170.1	169.4	169.3	169.0	169.0
17	76.4	75.4	75.3	75.5	75.5
18	16.2	16.1	16.1	16.1	16.1
19	18.4	17.6	17.5	10.3	10.7
20	120.9	121.2	121.1	121.1	121.1
21	140.7	140.4	140.5	140.5	140.5
22	109.9	110.0	110.0	110.0	110.0
23	143.1	143.5	143.5	143.6	143.6
28	21.4	20.7	20.7	18.7	20.3
29	29.9	29.5	29.1	27.5	29.5
30	42.9	42.8	42.6	37.2	37.5
OCH_3	52.6	51.3	52.2	51.6	51.2
$OCOCH_3$			169.2		
$OCOCH_3$			20.2		

[a] Spectra acquired in $CDCl_3$ at 67.8 MHz and 30 °C. [b] Spectra acquired in DMSO-d_6 at 67.8 or 125 MHz and 37 °C; δ values for C-13 obtained from the indirectly detected dimension in HMBC experiments.

and 2, and key long-range connectivities are given in Table 1S (Supporting Information). At this stage it was possible to confirm the structure of **1** as that of a rearranged tetranortriterpenoid related to mexicanolide but lacking the 3-oxo group and the 8,14 double bond. The NMR data also indicated the presence of four *O*-substituted carbon atoms (two OH substituents and one O bridge), with two tertiary carbons at δ 93.0 (C-3) and 71.0 (C-6) and two quaternary carbons at δ 85.2 (C-8) and 74.4 (C-14). However, the ^{1}H NMR spectrum of **1** in $CDCl_3$ contained only a single exchangeable proton resonance at δ 2.59 (1H, br s). This showed a cross-peak to the resonance at δ 4.36 (H-6) in the DQF−COSY spectrum allowing assignment to OH-6. The location of the remaining OH group and oxygen bridge among C-3, C-8, and C-14 could not be determined unambiguously, leaving three possible solutions to the structure of **1**. This problem was overcome by acquiring a second set of NMR data in DMSO-d_6. The ^{1}H NMR spectrum of **1** in this solvent was similar to that acquired in $CDCl_3$, although most resonances exhibited solvent-dependent chemical shift variation as expected (Table 1). Two exchangeable resonances were readily identified, at δ 5.14 (1H, s) and 5.22 (1H, d, J = 4.7 Hz). The hydroxyl proton corresponding to the resonance at δ 5.14 showed HMBC connectivities to C-8, C-13, C-14, and C-15, allowing it to be assigned unambiguously to OH-14. In a similar fashion the hydroxyl proton corresponding to the resonance at δ 5.22 was readily assigned to OH-6 on the basis of long-range connectivities to C-5, C-6, and C-7. These data provided a unique solution to the structure of **1**, which was found to be characterized by OH groups at C-6 and C-14 and an epoxy linkage between C-3 and C-8. Compound **1** is therefore 3-deoxo-3,8-epoxy-6,14-dihydroxy-8,14-dihydromexicanolide, a new rearranged tetranortriterpenoid with a rare 3,8-epoxy linkage, which has been assigned the trivial name cedrodorin. A similar example, 3-deoxo-3,8-epoxy-14-hydroxy-8,14-dihydromexicanolide, has been isolated recently from the air-dried fruits of the mangrove, *Xylocarpus granatum* Koenig (Meliaceae) and assigned the trivial name xyloccensin K.[13a] The related 3,8-hemiacetal of 8β-hydroxycarapin has been noted as a natural product in *C. glaziovii* C. DC. and can also be formed synthetically by allylic oxida-

tion of mexicanolide or carapin (the $\Delta^{14,15}$ isomer of mexicanolide) with selenium dioxide.[13b]

The molecular structures of **2**−**4** were determined using NMR data acquired exclusively in DMSO-d_6, due to the importance of the additional information available from the slowly exchanging OH resonances. A direct comparison between the ^{1}H and ^{13}C NMR spectra of **2** and **1** indicated that the compounds were similar. However, the ^{1}H NMR spectrum of **2** lacked a resonance corresponding to OH-6, while additional resonances were present in the ^{1}H and ^{13}C NMR spectra at δ_H 2.03 (3H, s) and δ_C 20.2 and 169.2, confirming the presence of an acetyl group. The H-6 resonance of **2** at δ 4.99 was downfield shifted by +0.84 ppm compared to H-6 in **1**, as expected for acylation at this position. ESIMS of **2** gave a pseudomolecular ion of *m*/*z* 545 ([M + H]$^+$), which, together with NMR data, indicated an empirical formula of $C_{29}H_{36}O_{10}$ and confirmed the presence of an additional acetyl group. Compound **2** is therefore 3-deoxo-3,8-epoxy-6-acetoxy-14-hydroxy-8,14-dihydromexicanolide, the 6-acetoxy derivative of **1** and a second new rearranged tetranortriterpenoid from *C. odorata*.

The ^{1}H and ^{13}C NMR spectra of **3** indicated the presence of an additional CH_2 group (δ_H 2.11 and 2.35; δ_C 32.7) assigned to C-6 on the basis of HMBC connectivities from δ_H 2.11 to δ_C 56.7 (C-10) and 173.8 (C-7) and from δ_H 2.35 to δ_C 45.0 (C-5), 56.7 (C-10), and 173.8 (C-7). Two exchangeable resonances corresponding to OH groups were still present in the ^{1}H NMR spectrum at δ 5.08 (1H, s) and 5.46 (1H, s), despite that fact that the C-6 position lacked the OH group common to **1** and **2**. The resonance at δ 5.08 was readily assigned to OH-14 on the basis of HMBC connectivities to δ_C 36.0 (C-15), 74.4 (C-14), and 85.8 (C-8). Comparison of the 1D and DEPT spectra of **3** with those of **1** and **2** also showed that the resonance of the tertiary carbon corresponding to C-9 appeared to be replaced by a quaternary carbon resonance at δ 81.7. The second OH resonance at δ 5.46 gave HMBC connectivities to both this resonance and those at δ_C 22.8 (C-11), 56.7 (C-10), and 85.8 (C-8), allowing it to be assigned to OH-9. Additional confirmation of these assignments was obtained through site selective excitation of the OH resonances in 1D ROE experiments, using the XSROESY pulse sequence.[14] The remaining HMBC connectivities were the same as those found for **1** and **2**, indicating that all three compounds shared the same molecular framework. ESIMS of **3** gave a pseudomolecular ion of *m*/*z* 503 ([M + H]$^+$), which together with NMR data indicated an empirical formula of $C_{27}H_{34}O_9$. Compound **3** was therefore identified as 3-deoxo-3,8-epoxy-6-deoxy-9,14-dihydroxy-8,14-dihydromexicanolide, or 6-deoxy-9-hydroxycedrodorin.

The ^{1}H NMR spectrum of **4** was of particular interest due to the presence of three exchangeable OH resonances at δ 5.08 (1H, s), 5.28 (1H, d, J = 4.7 Hz) and 5.52 (1H, s). On comparison with the corresponding spectrum of **3**, it was evident that the only other major difference was the replacement of the 6-CH_2 resonance with a CH resonance at δ 4.25 (1H, m), identical in appearance to that of H-6 of **1** at δ 4.15 (1H, m). The OH resonances at δ 5.08 and 5.52 were readily assigned to OH-14 and OH-9, respectively, as they exhibited identical sets of ROE connectivities to the corresponding OH resonances of **3**. In a similar fashion, the OH resonance at δ 5.28 exhibited an identical set of ROE connectivities to the 6-OH resonances of **1**, allowing it to be assigned to 6-OH. ESIMS of **4** gave a pseudomolecular ion of *m*/*z* 519 ([M + H]$^+$), which together with NMR data indicated an empirical formula of $C_{27}H_{34}O_{10}$.

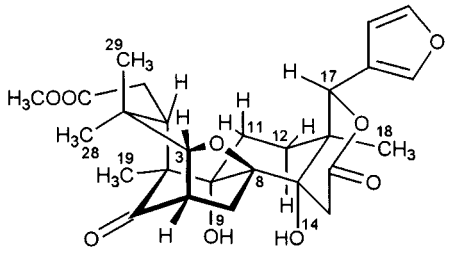

Figure 1. Conformation of **3** based on ROE data.

Compound **4** was therefore identified as 3-deoxo-3,8-epoxy-6,9,14-trihydroxy-8,14-dihydromexicanolide, or 9-hydroxycedrodorin. Compounds **1**−**4** represent a set of new rearranged tertranortriterpenoids distinguished by the presence of a 3,8-epoxy linkage and where structural variation lies with the pattern of substitution at C-6 and C-9.

The stereochemistry of **1**−**4** was investigated using data acquired in 1D ROE experiments (Supporting Information). Compound **3** was used to examine configurational relationships, as it showed the best dispersion of the four *tert*-methyl groups in the ^{1}H NMR spectrum. This allowed ROE connectivities to be assigned without the ambiguity introduced by spillover effects, and also aided the subsequent assignment of corresponding data acquired for the closely related compounds **1**, **2**, and **4**. A representation of the 3D solution structure of **3** is given in Figure 1, based on ROE connectivities, and with reference to previous data obtained by X-ray crystallography and NMR for compounds in the mexicanolide group.[12,15]

These earlier studies indicate that the configuration at C-2, C-5, C-10, C-13, and C-17 is conserved, and that the bicyclo[3,3,1]nonane nucleus adopts a boat−chair conformation. In **3**, strong ROE connectivities were observed between all pairs of combinations of OH-9, H-12α, and OH-14, indicating that these protons are diaxially related. This supports the chair conformation proposed in Figure 1 for the cyclohexane ring fused to the bicyclo[3,3,1]nonane nucleus along the C-9 to C-8 bond. In addition, strong ROE connectivities were observed between OH-9 and OH-14 and the methyl protons H-19 and H-18, respectively. All of these groups adopt α-configurations as shown in Figure 1. The pattern and intensity of ROE connectivities associated with H-3 also indicated an α-configuration for this proton. The configuration of the epoxy linkage is necessarily (3β, 8β) rather than (3β, 8α), which is not possible due to the sterically hindered α-side of the molecule. This is in agreement with crystal structure data obtained for the closely related compound, 3-deoxo-3β,8β-epoxy-14α-hydroxy-8,14-dihydromexicanolide (xyloccensin K).[13a] It is interesting to note that Connolly et al.[13b] concluded that the related 3,8-hemiacetal of 8-hydroxycarapin could only be formed when the 8-hydroxy group adopted the β-configuration, thus giving a 3β,8β-epoxy derivative. In examples that possess an 8α-hydroxy group, such as xyloccensin A, the 1,8-epoxy derivative is always the exclusive product.[13b] Analysis of the ROE data sets obtained for the H-3 and methyl resonances of compounds **1**, **2**, and **4** indicated that the configurational and conformational attributes of compound **3** are common to this group of 3β,8β-epoxy derivatives. It is not clear at this stage why only three of the four compounds are associated with leaf rejection, despite the overall similarity of their molecular structures.

The anti-insect activity of tetranortriterpenoids has been investigated extensively, with particular attention focused on the ring-cleaved example, azadirachtin.[4,5] In contrast, less is known about the activity of compounds in the

mexicanolide class, such as **1**−**4**, with the exception of a series of derivatives (humilinolides A−D), which are insecticides and developmental inhibitors of the European corn borer (*Ostrinia nubilalis* Hübner).[5d] In addition to their association with leaf rejection, the concentration of **1**−**4** in *C. odorata* was found to vary with respect to tree genotype; however, the concentration of the active compounds **1**−**3** was greater than that of the inactive compound **4** in all of the leaf material sampled.[10] A more detailed examination of the tetranortriterpenoid composition of the foliage of specific genotypes of *C. odorata* may strengthen the association between genotype and tetranortriterpenoid profile seen in the present study.

In a wider context, the most serious global constraints to successful *C. odorata* plantations are the mahogany shoot borers *Hypsipyla grandella* Zeller (New World) and *Hypsipyla robusta* Moore (Old World).[9,16] The development of mahogany plantations has been proposed as an ecologically and economically beneficial alternative to felling trees in the wild.[1] New means of providing resistance to *Hypsipyla* will therefore be required in order to limit insect damage and facilitate plantation success.[1,9] In this respect, the insect-deterrent properties of **1**−**3** may be of future value as markers for the selection of insect-resistant clones from germplasm collections, particularly because considerable genetic diversity exists within *C. odorata*.[18]

Experimental Section

General Experimental Procedures. ^{1}H and ^{13}C NMR spectra were acquired on either Varian 500 MHz or JEOL 270 MHz instruments. All chemical shift values (δ) are given in parts per million. Spectra were referenced to residual solvent signals with resonances at $\delta_{H/C}$ 7.25/77.0 ($CDCl_3$) and 2.50/39.5 (DMSO-d_6), relative to TMS. Positive ion first-order MS were recorded using LCMS (Finnigan-Matt LCQ) with an electrospray ionization (ESI) source. HPLC was carried out using a Waters system consisting of a 600E pump, 717 autosampler, and 996 photodiode array detector.

Plant Material. Leaf material of *C. odorata* was collected in July 1996, from a single clone (X117) of a 6-month-old tree growing on an experimental site at Centro Agronomico Tropical de Investigacion y Ensenanza (CATIE) in Turrialba, Costa Rica (altitude, 602 m; 9.53 N, 83.38 W). This clone is still growing in the experimental plot, and a voucher specimen has been deposited in the Herbarium at CATIE.

Extraction and Isolation. Freeze-dried leaves (5 g) of *C. odorata* (X117) were ground to a fine powder and extracted with MeOH at room temperature for 24 h. The extract was filtered and solvent removed in vacuo. The residue was redissolved in 2 mL MeOH and analyzed by HPLC (Merck LiChrospher, 250 × 4.0 mm, 5 μm particle size, 1 mL/min flow rate, isocratic MeCN−MeOH−H_2O 10:41:49). Compounds **1**−**4**, which represented the major apolar components of the MeOH extract, were detected at 210 nm and eluted at 8.5, 11.3, 13.9, and 15.4 min, respectively. Scale-up to semipreparative HPLC (Merck LiChrospher, 250 × 10.0 mm, 10 μm particle size, 4.5 mL/min flow rate, isocratic MeCN−MeOH−H_2O 10:41:49, 150 μL injection volume, 13 injections) was achieved with no loss of resolution and yielded on manual collection **1** (22.0 mg), **2** (5.8 mg), **3** (4.6 mg), and **4** (4.0 mg).

3-Deoxo-3β,8β-epoxy-6,14α-dihydroxy-8,14-dihydromexicanolide (1) (cedrodorin): pale yellow oil (MeOH); UV (MeOH−H_2O) λ_{max} 285 nm; ^{1}H NMR data, see Table 1, Table 1S (DQF−COSY, HMBC correlations), Table 2S (ROE and HMBC correlations for OH protons); ^{13}C NMR data, see Table 2; ESIMS *m*/*z* 503 [M + H]$^+$.

3-Deoxo-3β,8β-epoxy-6-acetoxy-14α-hydroxy-8,14-dihydromexicanolide (2) (6-acetoxycedrodorin): pale yellow oil (MeOH); UV (MeOH−H_2O) λ_{max} 285 nm; ^{1}H NMR data, see Table 1, Table 2S (ROE and HMBC correlations for OH protons); ^{13}C NMR data, see Table 2; ESIMS *m*/*z* 545 [M + H]$^+$.

3-Deoxo-3β,8β-epoxy-6-deoxy-9α,14α-dihydroxy-8,14-dihydromexicanolide (3) (6-deoxy-9α-hydroxycedrodorin): pale yellow oil (MeOH); UV (MeOH−H_2O) λ_{max} 285 nm; ^{1}H NMR data, see Table 1, Table 2S (ROE and HMBC correlations for OH protons), Table 3S (additional ROE connectivities); ^{13}C NMR data, see Table 2; ESIMS *m*/*z* 503 [M + H]$^+$.

3-Deoxo-3β,8β-epoxy-6,9α,14α-trihydroxy-8,14-dihydromexicanolide (4) (9α-hydroxycedrodorin): pale yellow oil (MeOH); UV (MeOH−H_2O) λ_{max} 285 nm; ^{1}H NMR data, see Table 1, Table 2S (ROE and HMBC correlations for OH protons); ^{13}C NMR data, see Table 2; ESIMS *m*/*z* 519 [M + H]$^+$.

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Supporting Information Available: DQF−COSY and HMBC correlations for **1** in $CDCl_3$ (Table 1S), XSROESY and HMBC correlations for the OH protons of **1**−**4** in DMSO-d_6 (Table 2S), and XSROESY connectivities for **3** in DMSO-d_6 (Table 3S). This material is available free of charge via the Internet at http://pubs.acs.org.

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