

THE USE OF TWO-DIMENSIONAL NMR AND RELAXATION REAGENTS TO DETERMINE STEREOCHEMICAL FEATURES IN ACYCLIC SESTERTERPENES

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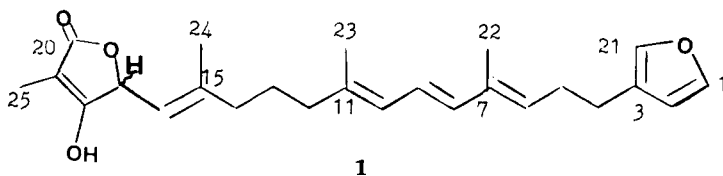
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ABSTRACT.—The structure of a new marine-sponge-derived polyunsaturated acyclic furanosesterterpene, ircinic acid (**1**), and stereochemical features in known sesterterpenes, including ircinin-1 (**2**) and ircinin-2 (**3**), have been elucidated by several nmr strategies.

There are twenty acyclic furanosesterterpenes now known from Dictyoceratid sponges (1). Scrutiny of the data used to establish their structures reveals that, for a majority, uncertainties exist in one or more of their stereochemical or regiochemical features. These uncertainties include ambiguities in trisubstituted double-bond stereochemistry, questions about regiochemical placement of conjugated double bonds, unknown stereochemistry of secondary methyl groups, or undefined stereochemistry of butenolide ring substituents. We now wish to illustrate some nmr strategies that unambiguously solve the stereochemical problems associated with their unsaturated bonds.

The major polar component, suvanine, that is present in *Ircinia* sp. collected from Fiji has been previously described (2). ¹Using ¹³C nmr we observed ircinic acid (**1**) as the main component in the non-polar extract fractions of this sponge and also found **1** from a Truck lagoon sponge. Compound **1** was purified by a combination of solvent partitioning and hplc. The carbon skeleton of **1** was easily recognized to be an acyclic furanosesterterpene by analysis of both ¹H- and ¹³C-nmr spectra. Specifically, both β-substituted furan (¹³C: δ 142.5 d, 138.7 d, 124.5 s, and 110.9 d; ¹H: δ 7.32 brt, and 7.20 brt, and 6.28 brt) and tetroneic acid (¹³C: δ 178.1 s, 175.8 s, 96.3 s, 76.1 d, and 5.9 q) moieties could be identified. In addition, four other double bonds were evident (¹³C: δ 146.6 s, 137.2 s, 135.4 d, 134.6 s, 131.0 d, 125.8 d, 122.8 d, and 117.5 d), and three were associated with vinyl methyls (¹³C: δ 16.9, 16.5, and 12.3) that were each *cis* to an alkyl or alkenyl group. A *trans*-disubstituted double bond was identified by the *J* = 15 Hz to H-9.

Analysis of ircinic acid (**1**) by 2D-nmr experiments provided valuable information to establish the rest of its structure (see Table 1). A ¹H-¹H COSY² experiment iden-



¹A revised structure of suvanine will soon be described: P. Crews, L.V. Manes, M. Kerman, D.J. Faulkner, in preparation.

²No standard abbreviation exists for the various proton and carbon two-dimensional correlated shift experiments. We find it convenient to express them as follows: homocorrelated spectra = ¹H-¹H COSY or homo COSY, heteronuclear scalar correlated spectra = ¹H-¹³C COSY or hetero COSY. It is also important to express the *J* correlation value (normal or long range) employed in these experiments.

TABLE 1. Selected Nmr COSY Results for Ircinic acid (1)

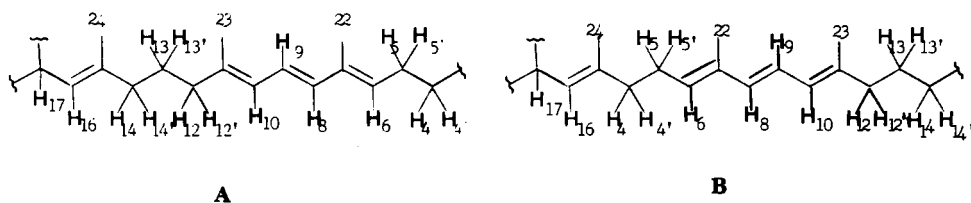
$^1\text{H}-^1\text{H}$ (CDCl ₃) Regular ^a	$^1\text{H}-^1\text{H}$ (CDCl ₃) Long Range ^a	$^{13}\text{C}-^1\text{H}$ (DMSO- <i>d</i> ₆) Long Range ^{b,c}
H-1<-->H-2	H-1<-->H-21 H-2<-->H-4, H-21 H-4<-->H-2, H-6, H-21	C-1<-->H-2, H-21 C-2<-->H-1 C-3<-->H-21 C-6<-->H-8, Me C-7<-->Me C-8<-->H-9, H-10, Me C-9<-->H-8, H-10 C-10<-->H-8, Me C-11<-->H-9, Me C-12<-->H-10, Me C-14<-->Me C-15<-->Me C-16<-->Me C-18<-->H-17, Me-25 C-19<-->Me-25 C-20<-->Me-25 C-21<-->H-1, H-2 C-22<-->H-8 C-23<-->H-10 C-24<-->H-16
H-4<-->H-5 H-5<-->H-6 H-8<-->H-9 H-9<-->H-10 H-12<-->H-13 H-13<-->H-14 H-16<-->H-17	H-8<-->H-10 H-10<-->H-12 H-14<-->H-16 Me<-->H-6, H-10, H-16, H-17	

^aObserved in the super homo COSY spectrum.

^bSee footnote 2.

^cThe three Me's, C-22, C-23, C-24, are isochronous.

tified subunits: H-5, H-5' correlated to H-4, H-4' and to H-6; H-13, H-13' correlated to H-12, H-12' and to H-14, H-14'; H-9 correlated to H-8 and to H-10; and H-17 correlated to H-16. Two partial structures, **A** and **B** were consistent with these data. A $^1\text{H}-^1\text{H}$ SUPER COSY (3) experiment was used to specifically visualize long range proton-proton couplings and allowed the regiochemistry of the conjugated double-bond system to be defined as that shown by **A**. Key correlations were those observed from H-4, H-4' to H-2 and to H-21; from H-16 to H-14, H-14'; and from H-10 to H-12, H-12'. Corroborating evidence came from the $^1\text{H}-^{13}\text{C}$ ($J=140$ Hz) COSY of **1** in which H-4, H-4' correlated to the carbon triplet at δ 24.7. This is the carbon shift expected for the methylene carbon attached at the β position on a furan (1). In the sub-structure **B**, either C-12 or C-14 would be expected at δ 25; however, in the $^1\text{H}-^{13}\text{C}$ COSY spectrum, the protons attached to these carbons correlate to methylene resonances at δ 39.2 and 38.9, respectively. Evidence consistent with substructure **A** and of use in completing assignment of all ^{13}C chemical shifts was also obtained from the long range ($J=9$ Hz)³ $^1\text{H}-^{13}\text{C}$ COSY (Table 1). These included correlations which were as follows: from

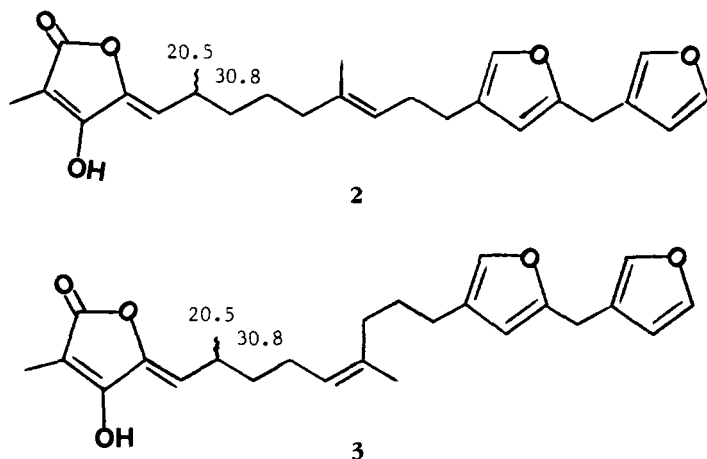


³Although most $^2J_{\text{CH}}$ and $^3J_{\text{CH}}$ are approximately 5 Hz, a $J=9$ Hz value is advantageous because of increased signal to noise (due to shorter delays during τ_m). It is possible, however, to observe different long range correlations at $J=5$ versus $J=10$ Hz, and examples of this can be found in Cimino *et al.* (13) and Camely and Kashman (14).

H-10 to C-23 and to C-12; from H-8 to C-22; from H-17 to C-18; from H-16 to C-24; and from H-25 to C-18, to C-19, and to C-20.

The carbon singlets in ircinic acid (**1**) at δ 146.6, 137.2, and 134.6 were assigned via comparison to model compounds. Although each carbon resonance, in the long range ^1H - ^{13}C COSY, correlated to the proton singlets of the directly attached methyl groups, an unambiguous assignment of the carbon singlets was impossible as the proton resonances for Me-22, Me-23, and Me-24 were nearly isochronous under the COSY nmr conditions at 300 MHz. Similar conclusions were reached from conventional decoupling and a normal hetero and a homo COSY experiment. The assignment of C-24 was confirmed to be δ 16.9, based on a long range SFORD experiment involving irradiation of H-16 (δ 4.89). The H-24 resonance was identified by irradiation of the δ 4.89 (H-16) signal. The C-15 was assigned to the signal at δ 146.3, based on SFORD data from irradiation at δ 4.89.

The previously reported furanosesterterpenes ircinin-1 (**2**) and ircinin-2 (**3**) were

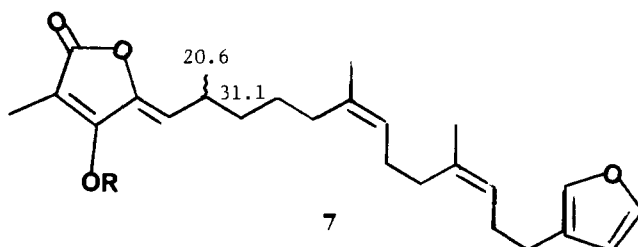
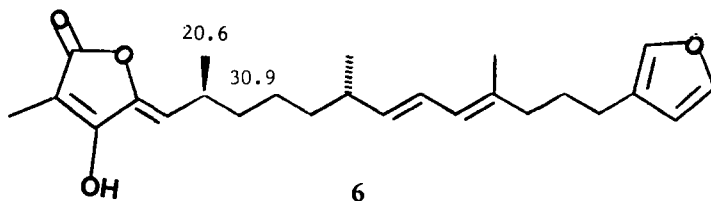
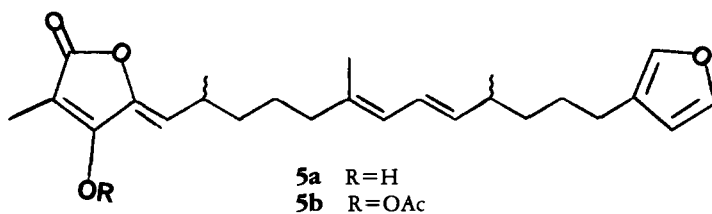
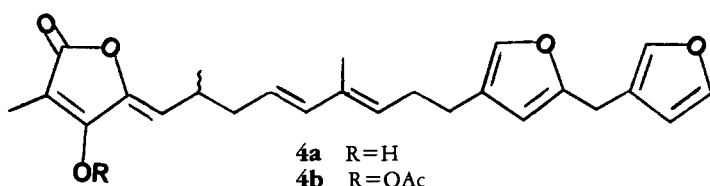


the major components of a species of *Ircinia* collected from the Island of Bora Bora in French Polynesia. Cimino and coworkers (4) were unable to separate ircinin-1 and ircinin-2, but they did determine, by analysis of oxidative ozonolysis products and spectral data, that these two compounds differed in the position of double bonds about C-11. Our further investigation of these compounds was begun to unravel their multiple bond stereochemical features.

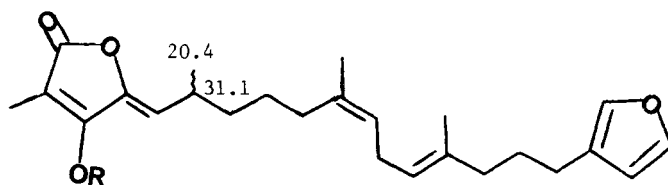
Several ^1H -nmr decoupling experiments were carried out at 360 MHz on both **2** and **3** which confirmed them to be the regiochemical isomers about the central double bond as shown in their respective drawings. Specifically, irradiation (CDCl_3) of the double triplet δ 1.85 (H-13, 13') of ircinin-2 collapsed the triplet at δ 5.05 (H-12) to a singlet and simplified the complex multiplet at δ 1.37 (H-14, 14'), while the triplet δ 2.27 (H-8, 8') remained unchanged. Additionally, irradiation of the quintet at δ 1.55 (H-9, 9') transformed both the triplet at δ 2.27 (H-8, 8') and the double triplet at δ 1.97 (H-10, 10') to singlets. Likewise, for ircinin-1, irradiation (C_6D_6) of the double triplet at δ 2.22 (H-9, 9') collapsed both the doublet at δ 5.22 (H-10) and the triplet at δ 2.35 (H-8, 8') to singlets.

With the exception of groups in the vicinity of the C-11 double bond, the ^{13}C - and ^1H -nmr spectra of **2** and **3** were very similar. The vinyl methyl (C-23) of ircinin-1 had ^{13}C -nmr shifts of δ 15.8 and δ 1.53, which indicated that the double bond geometry must be *E*. Analogously, the vinyl methyl (C-23) shifts of ircinin-2 at δ 24.9 and δ 1.65 indicated a *Z* double bond geometry. The stereochemistry of the double bond exocyclic to the tetrone acid in **2** and **3** was further investigated. This exocyclic double

bond is present in twelve of the sixteen known acyclic furanosesterterpenes possessing a butenolid functionality (1). Addition of the relaxation agent $\text{Gd}(\text{fod})_3$ ⁴ to both ircinin-1 and ircinin-2, in separate 360 MHz ¹H-nmr experiments, showed marked line-broadening of the H-16 proton resonance, while the line-broadening of the C-24 methyl resonance was not as pronounced. All other resonances (including Me-23) displayed only slight broadening, except for Me-25, which was almost completely nulled. Examinations of a Dreiding model of **2** or **3** shows that if the geometry of the exocyclic double bond is *Z*, then the H-16 proton would be closer to the Gd nucleus (complexed to the C-18 OH) than the C-25 methyl and, therefore, should show enhanced line-broadening, as was observed. The proposed *Z* stereochemistry is the same as that which was assigned for furanosesterterpenes **4a** and **5a**, based upon a 0.24 ppm shielding observed for H-16 when the tetrionic acid OH was acetylated (5). This argument for *Z* stereochemistry can be extended to three other similar sesterterpenes because an analogous shielding appears at H-16 when C-18 varies from OH to OAc for: fisciculatin (**6**, 0.59 ppm) (6), **7** (0.53 ppm) (7), and **8** (0.45 ppm) (7). A *Z* stereochemistry across C-16, C-17 can now be suggested for variabilin (**9**), based upon near identity of its ¹³C-nmr shifts (1) at C-15 and C-24 to these same carbons in **2-3**, and **6-8**.

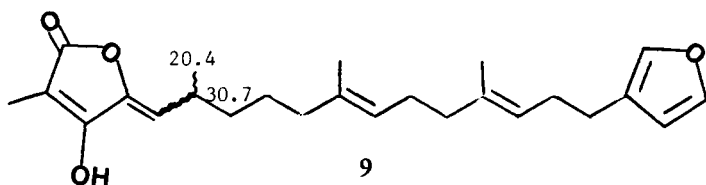


⁴Gd(fod)₃ binds preferentially to strong Lewis bases and causes relaxation and not chemical shift changes of nearby nuclei. The relaxation dependence is r^{-6} where r is the internuclear distance.

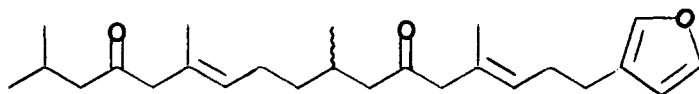


8 [E C-7, C-8 and Z C-10, C-11 can be switched]

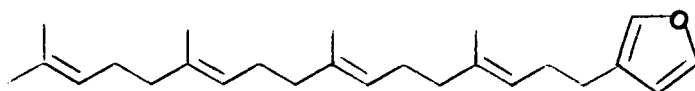
Prof. Jacobs and his co-workers at the University of California at Santa Barbara have discovered that a 1:1 mixture of **2** and **3** reduced motility for sea urchin sperm at 16 $\mu\text{g}/\text{ml}$. A range of biological activities, aside from antimicrobial activity, have been observed for other acyclic sesterterpenes. These include toxicity to numerous predatory marine organisms by idiadione (**10**) (8), toxicity to brine shrimp by furospinulosin-1 (**11**) (9), inhibition of cell division in sea urchin eggs by variabilin (**9**) (10), and inhibition of cell division in sea star eggs by **4a** and **4b** (5).



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10



11

EXPERIMENTAL

Our general analytical, chemical, and chromatographic methods have been described previously (11). The nmr spectra were recorded on a JEOL FX-100 PFT spectrometer operating at 99.5 MHz for ^1H and 25.0 MHz for ^{13}C . High field ^1H -nmr spectra were recorded on a GN-300 spectrometer (at UCSC), or a HXS-360 spectrometer (at Stanford). Multiplicities of ^{13}C -nmr peaks were determined from APT or DEPT data. Mass spectrometry data were obtained on a Finnigan 4000 (6000 LS7 computer system). Hplc was done on a Waters ALC-201, using columns which include a Waters μ -Porasil, or Whatman Partisil, or a Rainin Microsorb C-18. Rotations were measured on a Perkin-Elmer 141 polarimeter.

TWO-DIMENSIONAL NMR PROCEDURES.—Standard pulse sequences (12) were used for the homo COSY (12),⁵ the super homo COSY (3), and the hetero COSY (12).⁶ For the hetero COSY experiment spectral acquisition parameters were 14254 Hz in the F_2 dimension and 2322 Hz in F_1 with a relaxation pulse delay of 1 sec. A total of 128 evolution increments of 125 μsec each were employed beginning at an initial delay period of 10 μsec . The initial 128×1024 data matrix was zero filled, then transformed to give a 128×1024 matrix. Apodization by a double exponential multiplication function was employed in each

⁵See Figure 37a in Benn and Gunther (12).

⁶See Figure 35 in Benn and Gunther (12).

dimension. Detection of correlations was facilitated by utilizing the delay $\tau_1 = 0.5/J$ preceding the polarization transfer pulse and a refocussing delay of $\tau_2 = 0.3/J$ with τ_s , respectively, for $J = 140$ Hz, 3.5 msec and 2.0 msec, and for $J = 9$ Hz, 55.6 and 33.3 msec. For the homonuclear ^1H COSY and super COSY experiments, spectral acquisition parameters were 2404 Hz in the F_1 and F_2 dimensions. A total of 512 evolution increments of 416 μsec each were employed beginning at an initial delay period of 416 μsec . Initial dimension of the data matrices was 512×1024 , and transformation gave 512×512 matrices which were symmetrized. Apodization by sinusoidal multiplication was employed in each dimension. The super COSY experiment employed delays ($\tau = 0.25/J$) during t_m (mixing) for $J = 7$ Hz (35.7 msec). See Table 1 for additional information about the long range hetero COSY experiment (13, 14).

COLLECTION AND ISOLATION PROCEDURES.—*UCSC specimens.*—*Ircinia* sp. was collected from Suva Harbor, Fiji Islands during the summers of 1983, 1984, and 1985. The other *Ircinia* was collected from the lagoon of Bora Bora Island, French Polynesia, during the summer of 1982. Details about the taxonomy of these sponges are given by Manes *et al.* (2). These collections were immediately extracted with CH_2Cl_2 , and the crude oil concentrates were returned to the University of California at Santa Cruz for further examination. Each crude oil was examined by ^{13}C nmr, and the oils were successively partitioned between wet MeOH and the series: hexanes, CCl_4 , and CH_2Cl_2 . Each solvent fraction was usually examined by ^{13}C nmr. Flash chromatography followed by hplc was used for isolation and purification.

U.O. specimen.—This was collected from Truk lagoon in September 1984, and was kept frozen until workup.

Ircinic acid (1).—Freshly collected sponge (7.5 kg, wet weight) from Fiji in 1983 yielded a dark, viscous crude oil (6 g). ^{13}C nmr showed that the CCl_4 partition fraction (2.04 g) contained 1 as the major component. Repeated hplc of a portion (1.2 g) of the CCl_4 partition fraction, first by normal phase (3:2 hexanes-EtOAc, Waters porasil M9 10/50 column), then by reverse phase (MeOH, Regis C18 10 μ) gave 1 as an oil (650 mg). The Truk lagoon sponge (1.4 kg) was soaked in EtOH (4 liters) for 1 day (dry wt, 162 g), and the solvent evaporated to give a brown oil. Trituration of this oil with 200 ml of CHCl_3 gave CHCl_3 -soluble material, which was subjected to silica gel flash chromatography starting with CHCl_3 and then progressing to $\text{CHCl}_3/\text{MeOH}$ mixtures as eluent, collecting 200 ml fractions. Fraction 19 [CHCl_3 -MeOH (95:5)] was chromatographed by hplc (silica gel) and CHCl_3 -MeOH (98:5:1.5) to give 1 as an oil, 180 mg, $\approx 90\%$ pure by ^{13}C - and ^1H -nmr analysis. All further efforts to purify this oil failed, and the oil decomposed within a few weeks, even if kept cold (5°). Physical properties are: nmr (300 MHz, CDCl_3 , assignments by ^1H - ^1H and ^1H - ^{13}C COSY), ^1H - δ 1.47 (bm, H-13, -13'), 1.62 (s, Me-25), 1.67 (s, Me-22 & Me-23), 1.70 (s, Me-24), 1.94 (bt, $J = 7.7$ Hz, H-12, -12' and H-14, -14'), 2.30 (pent, $J = 7.7$ Hz, H-5, -5'), 2.40 (t, $J = 7.7$ Hz, H-4, -4'), 4.89 (d, $J = 9.2$ Hz, H-16), 5.3 (d, $J = 9.2$ Hz, H-17), 5.38 (t, $J = 7.7$ Hz, H-6), 5.85 (d, $J = 10.7$ Hz, H-10), 6.05 (d, $J = 16.8$ Hz, H-8), 6.28 (bt, $J = 3$ Hz, H-2), 6.22 (dd, $J = 15.3$, 10.7 Hz, H-9), 7.20 (bt, $J = 2$ Hz, H-21), 7.32 (bt, $J = 2$ Hz, H-1), ^{13}C - δ 178.1 (s, C-20), 175.8 (s, C-18), 146.6 (s, C-15), 142.5 (d, C-1), 138.7 (d, C-21), 137.2 (s, C-7), 135.4 (d, C-8), 134.6 (s, C-11), 131.0 (d, C-6), 125.8 (d, C-10), 124.5 (s, C-3), 122.8 (d, C-9), 117.5 (d, C-16), 110.9 (d, C-2), 96.3 (s, C-19), 76.1 (d, C-17), 39.2 (t, C-12), 38.9 (d, C-14), 28.8 (t, C-5), 25.4 (t, C-13), 24.7 (t, C-4), 16.9 (q, C-24), 16.5 (q, C-23), 12.3 (q, C-22), 5.9 (q, C-25); ms m/z 396 (M^+ , $\text{C}_{25}\text{H}_{32}\text{O}_4$), 381 (M^+ -Me), 227, 213, 201 (cleavage between C-11 and C-12), 161 (cleavage between C-9 and C-10), 135 (base peak, cleavage between C-7 and C-8).

Ircinin-1 (2).—Repeated normal-phase hplc (Waters porasil M9) of the crude CH_2Cl_2 extract, first in 3:2 hexanes-EtOAc, then in 4:1 hexanes-EtOAc, gave fractions containing ircinin-1 (2) slightly contaminated with 3 and completely pure ircinin-2 (3). Compound 2 displayed the following properties. Oil, $[\alpha]^{19.5\text{D}}$ (MeOH) = -34.12° ; ^1H nmr (360 MHz, C_6D_6) δ 0.93 (d, H-24, $J = 7.5$ Hz), 1.22 (m, H-14, -14'), 1.36 (p, H-13, -13', $J = 8.0$ Hz), 1.50 (s, H-23), 1.60 (s, H-25), 1.93 (m, H-12, -12'), 2.22 (m, H-9, -9'), 2.35 (t, H-8, -8', $J = 7.5$ Hz), 2.85 (m, H-15), 3.52 (s, H-4, -4'), 5.22 (t, H-10, $J = 8.0$ Hz), 5.27 (d, H-16, $J = 9.6$ Hz), 5.82 (s, β -furan), 6.14 (s, β -furan), 7.02 (s, α -furan), 7.08 (s, α -furan), 7.15 (s, α -furan); ^{13}C nmr (25 MHz, CDCl_3) δ 173.0 (s, C-20), 163.1 (s, C-18), 153.8 (s, C-5), 143.1 (s, C-17), (142.8 (d, C-1), 139.6 (d, C-21 or C-22), 137.3 (d, C-21 or C-22), 135.3 (s, C-11), 125.7 (s, C-3), 124.1 (d, C-10), 121.5 (s, C-7), 116.6 (d, C-16), 111.1 (d, C-2), 107.3 (d, C-6), 99.1 (s, C-19), 39.4 (t, C-12), 36.5 (t, C-14), 30.8 (d, C-15), 28.4 (t, C-9), 25.5 (t, C-4 or C-13), 25.2 (t, C-4 or C-13), 24.1 (t, C-8), 20.5 (q, C-24), 15.8 (q, C-23), 6.0 (q, C-25).

Ircinin-2 (3).—Isolation was as described above and the following physical properties were observed. Oil $[\alpha]^{19.5\text{D}}$ (MeOH) = -40.20° ; ^1H nmr (360 MHz, CDCl_3) δ 1.0 (d, H-24, $J = 7.5$ Hz), 1.37 (m, H-14, -14'), 1.55 (p, H-9, -9', $J = 8.0$ Hz), 1.6 (s, H-23), 1.76 (s, H-25), 1.85 (dt, H-13, -13', $J = 6.8$, 8.1 Hz), 1.97 (dt, H-10, -10', $J = 1.8$, 8.1 Hz), 2.27 (t, H-8, -8', $J = 8.6$ Hz), 2.75 (m, H-15), 3.69 (s, H-4, -4'), 5.05 (t, H-12, $J = 6.8$ Hz), 5.18 (d, H-16, $J = 9.5$ Hz), 5.86 (s, β -furan), 6.28 (s, β -furan), 7.04 (s, α -furan), 7.25 (s, α -furan), 7.33 (s, α -furan); ^{13}C nmr (25 MHz, CDCl_3) δ 173.4 (s, C-20), 163.1 (s, C-18), 154.0 (s, C-5), 143.1 (s, C-17), 142.7 (d, C-1), 139.6 (d, C-21 or C-22), 137.4 (d, C-22 or C-

21), 135.9 (s, C-11), 125.9 (s, C-3), 124.8 (d, C-12), 121.5 (s, C-7), 116.9 (d, C-16), 111.2 (d, C-2), 107.4 (d, C-6), 99.1 (s, C-19), 37.4 (t, C-14), 31.5 (t, C-10), 30.8 (d, C-15), 28.3 (t, C-9), 25.7 (t, C-4), 24.4 (t, C-8), 23.3 (t, C-13), 24.9 (q, C-23), 20.5 (q, C-24), 6.1 (q, C-25).

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