

JUNCINS A-F, SIX NEW BRIARANE DITERPENOIDS FROM
THE GORGONIAN *JUNCELLA JUNCEA*

S. ISAACS, S. CARMELY, and Y. KASHMAN*

Sackler Faculty of Exact Sciences, School of Chemistry, Tel Aviv University,
Ramat Aviv 69978, Tel Aviv, Israel

ABSTRACT.—Six new diterpenoids, juncins A-F [2–7], possessing the known briarane skeleton have been isolated from a gorgonian collected from the Red Sea. The structures and relative stereochemistry of the juncins were determined by extensive ^1H and ^{13}C 1D and 2D nmr spectral analysis.

Briarein A [1] isolated from the gorgonian *Briareum asbestinum* was the first reported example of these novel bicarbocyclic diterpenes (1–5). Diterpenes with the same skeleton as briarein A have been subsequently reported from octocorals belonging to the order Pennatulacea and also from Gorgonacea. Most recently a novel briarane diterpenoid was also isolated from a Mediterranean nudibranch and from its octocoral prey (6).

Our investigation of the gorgonian *Junceella juncea* Pallas (Gorgonaceae) has resulted in the isolation and identification of six new briarane diterpenes, 2–7. *J. juncea* was collected from sites in the entrances to the Gulf of Eilat and Gulf of Suez, Red Sea. The CH_2Cl_2 -soluble extract of the freeze-dried horny coral was separated by repeated chromatographies on Si gel and RP-18 columns; a total of six compounds have been isolated and identified. These compounds, designated juncins A [2], B [3], C [4], D [5], E [6], and F [7], were isolated in yields of 0.001–0.008% (dry wt). The mass spectra of the juncins, together with their ^1H - and ^{13}C -nmr spectra (Tables 1 and 2) suggested the briarane skeleton. Characteristic in the mass spectra of 2–7 were the pairs of peaks differing by 2 amu with a relative intensity of 1:3, suggesting one chlorine atom in each compound.

Juncin A [2] had the molecular formula $\text{C}_{26}\text{H}_{33}\text{ClO}_{10}$ (hreims, see Experimental), m/z 541/543 (3:1, $[\text{MH}]^+$, cims), and showed a uv absorption at λ 220 nm (ϵ 9000) and ir absorptions at ν 3520, 1780, 1730, and 1720 cm^{-1} , typical for an alcohol, a γ -lactone, and one or more ester functionalities. Comparison of the ^1H -nmr spectrum of 2 with that of 1 (7) (Table 1) and the ^{13}C -nmr spectrum with that of ptilosarcone [8] (8) (Table 2) suggested for 2 the same substituted ten-membered ring system as in compounds 1 and 8 and in addition an acetate and an exocyclic epoxide. The positions of the latter two functionalities were unequivocally determined by COSY and difference nOe measurements to be at C-14 and C-11, respectively. The resonance line assignments of both protons and carbons of the molecule was assisted by an HMQC (9) experiment that established all C-H connectivities and, hence, also all pairs of geminal protons.

The COSY experiment established the following correlations: H-2 to H-3, -4, and Me-15; H-3 to H-4; H-4 to H-6, -16a, -16b; H-6 to H-7, -16a, -16b; H-7 to 8-OH; H-9 to H-10; H-10 to H-20a and Me-15; H-12eq to H-12ax, -13ax, -13eq, -14; H-12ax to H-13ax, -13eq, -20b; H-13eq to H-13ax, -14; H-13ax to H-14; H-17 to Me-18; H-20a to H-20b. These connectivities established the C-1 (including Me-15) to C-8, C-9 to C-14, and C-17 to C-18 segments of the molecule, leaving unconnected the C-1 to C-14 and C-8 to C-9 and C-17 bonds and the manner of the closure of the γ -lactone. The suggested briarane diterpenoid structure was unequivocally established by difference nOe measurements summarized in Figure 1. The latter experiment, together with the measured coupling constants (Table 1), also determined the relative

TABLE 1. ¹H-nmr Data of Juncins A [2], B [3], C [4], D [5], E [6], and F [7] and Briarein A [1] in CDCl₃.^a

Proton	Compound						
	2	3	4 ^b	5	6	7 ^c	1 ^d
H-2	6.46(d,9)	6.20(d,9)	6.32(d,9)	6.37(d,9.7)	6.25(d,10)	6.00(d,8.3)	6.12(10)
H-3	5.66(dd,9,11)	5.62(dd,9,12)	5.70(dd,9,11)	5.75(dd,9.7,11.3)	5.75(dd,10,12)	1.64(m) ^{e,f} 2.32(m) ^{e,f}	5.84(12,10)
H-4	5.92(d,11)	5.96(d,12)	5.92(d,11)	5.92(d,11.3)	5.96(d,12)	2.50(m) ^{e,f} 2.38(m) ^{e,f}	6.00(12)
H-6	5.11(d,3.2)	5.18(d,2.9)	5.12(dd,3,1)	5.12(dd,3.1,1.2)	5.10(d,3.1)	4.63(d,3.2)	5.12(3.7,1.1)
H-7	4.78(d,3.2)	4.97(d,2.9)	4.78(d,3)	4.75(d,3.1)	4.75(d,3.1)	4.45(brs)	4.87(3.7)
H-9	4.82(d,4)	5.31(d,5.3)	4.92(m,ΔW _{1/2} =8 ^f)	4.98(m,ΔW _{1/2} =7)	4.93(d,1.8)	5.75(m,ΔW _{1/2} =3)	5.58(6)
H-10	3.22(d,4)	3.50(m,ΔW _{1/2} =13)	3.92(m,ΔW _{1/2} =9)	3.92(m,ΔW _{1/2} =9)	3.95(m,ΔW _{1/2} =4)	3.70(m,ΔW _{1/2} =3)	3.10(6)
H-12eq	1.15(m) ^g	2.30(m) ^g	4.62(τ,3.5)	4.56(τ,3.3)	4.87(d,3.3)	4.35(τ,3.2)	4.87(3.2,5)
H-12ax	2.22(m) ^g	2.23(m) ^g	2.15(m) ^{g,h}	2.10(m) ^{e,f}	5.20(τ,3.3)	2.02(m) ^{e,f}	1.99(17.3,4.3)
H-13eq	1.77(m) ^{e,f}	1.82(m) ^{e,f}	2.15(m) ^{g,h}	2.25(m) ^{e,f}	5.25(d,3.3)	2.28(m) ^{e,f}	2.35(17.2,8.2,5)
H-13ax	1.92(m) ^{e,f}	1.92(m) ^{e,f}	4.96(τ,3.8)	4.92(τ,3.4)	1.30(6)	4.85(τ,2.8)	5.71(3.4,2.8)
H-14	4.88(brs)	4.79(τ,1)	1.20(6)	1.19(6)	5.76(brs) ^g	1.16(6)	1.40(6)
Me-15	1.05(6)	1.10(6)	5.77(6)	5.76(6) ^h	5.76(brs) ^g	5.82(6) ^h	5.48(1,1)
H-16a	6.04(6)	5.90(brs) ^h	5.72(6)	5.70(6) ^h	2.86(q,7)	5.51(6) ^h	5.60(1,1)
H-16b	5.95(6)	5.88(brs) ^h	2.71(q,7.5)	2.88(q,7)	1.25(d,7)	2.96(q,7)	3.14(7,7.7)
H-17	2.53(q,7)	2.56(q,7.3)	1.22(d,7.5)	1.22(d,7)	2.92(d,3)	1.25(d,7)	1.34(7)
Me-18	1.21(d,7)	1.20(d,7.3)	2.85(brs) ^g	2.85(d,2.8)	2.73(d,3)	2.82(d,3.6)	1.54(6)
H-20a	2.64(d,2.6)	4.84(brs)	2.85(brs) ^g	2.72(brs,ΔW _{1/2} =10)	3.10(6)	2.36(d,3.6)	
H-20b	3.12(τ,2.6)	4.94(brs)	3.12(6)	3.10(6)	1.96(6)	3.42(6)	
8-OH	3.19(6)	2.95(6)	2.04(6)	2.00(6)	1.97(6)	1.97(6)	
OAc's	2.09(6)	2.02(6)	2.10(6)	2.03(6)	1.99(6)	2.00(6)	
	2.22(6)	2.17(6)	2.17(6)	2.07(6)	2.07(6)	2.22(6)	
				2.17(6)	2.12(6)		
					2.18(6)		

^aReported as chemical shift (multiplicity, coupling constant).

^b2.06 (m), 2.25 (m), 2.10 (m), 0.95 (d,6.2), 0.99 (d,6.2)—the isovaletrate signals.

^c2.5 (sep,7), 1.16 (d,7), 1.19 (d,7)—the isobutyrate signals.

^dData are from Wratton *et al.* (7).

^eAssignments obtained from the 2D-COSY experiments.

^fAssignments are interchangeable.

^gOverlapping signals.

^hAssignments based on comparison to the other juncin compounds.

TABLE 2. ^{13}C nmr of Juncins A [2], C [4], D [5], and E [6] in CDCl_3 .^a

Carbon	Compound				
	2	4 ^b	5	6	8 ^c
C-1	47.8 s	47.6 s	47.7 s	47.1 s	44.72 s
C-2	71.6 d	70.7 d	70.6 d	70.8 d ^d	76.01 d
C-3	130.5 d	130.4 d	130.5 d	130.0 d	131.06 d
C-4	128.2 d	128.2 d	128.3 d	128.5 d	128.02 d
C-5	137.0 s	137.3 s	137.2 s	137.2 s	136.56 s
C-6	62.2 d	63.8 d	62.2 d	64.0 d	62.91 d
C-7	78.6 d	78.7 d	78.7 d	78.7 d	72.16 d
C-8	81.3 s	80.0 s	80.0 s	80.4 s	82.85 s
C-9	70.4 d	72.6 d ^e	73.0 d ^e	73.1 d ^d	77.92 d
C-10	38.3 d	33.4 d	33.3 d	32.8 d	38.86 d
C-11	59.3 s	57.9 s	57.8 s	57.1 s	
C-12	25.0 t ^d	72.4 d	72.9 d	73.5 d ^d	
C-13	29.6 t ^d	29.8 t	29.6 t	66.8 d ^d	
C-14	74.1 d	72.6 d ^e	73.0 d ^e	74.7 d ^d	
C-15	14.4 q	14.3 q	14.3 q	14.4 q	13.64 q
C-16	116.9 t	116.8 t	117.0 t	117.1 t	117.79 t
C-17	47.8 d	48.4 d	48.0 d	48.4 d	46.28 d
C-18	7.4 q	8.3 q	8.4 q	8.4 q	7.07 q
C-19	174.9 s	175.6 s	175.6 s	173.1 s	174.50 s
C-20	50.5 t	49.7 t	49.5 t	49.5 t	
OAc's	21.1 q	21.1 q	21.0 q ^e	20.5 q	
	21.2 q	21.3 q	21.0 q ^e	20.7 q	
	21.4 q	22.8 q	21.2 q ^e	20.9 q	
			21.2 q ^e	21.1 q	
				21.4 q	
	169.6 s	169.0 s	169.0 s	164.3 s	
	170.2 s ^e	169.9 s	169.7 s ^e	164.4 s	
	170.2 s ^e	170.1 s	169.7 s ^e	169.5 s	
			170.3 s	169.7 s	
				170.3 s	

^aReported as chemical shift, multiplicity.

^b ^{13}C values of the isovalerate: 172.3 s, 43.3 t, 33.4 d, 24.9 q (2C).

^cData from Hendrickson and Cardellina (8).

^dAssignments are interchangeable.

^eOverlapping signals.

stereochemistry of the various chiral centers, namely, the same $1R^*$, $2S^*$, $6S^*$, $7R^*$, $8R^*$, $9S^*$, $10S^*$, $11S^*$, $12R^*$, $14S^*$, $17R^*$ configurations as in compounds **1** (1–5) and **8** (8).

The structure for **3**, $\text{C}_{26}\text{H}_{33}\text{ClO}_9$, obtained in minute amounts only, followed directly from the identification of **2**. Comparison of the ^1H -nmr spectra (Table 1) determined the 11,20-deoxyjuncin A structure for **3**. Juncin B is, most likely, the biogenetic precursor of **2**. The structure of **3** was confirmed by a COSY experiment which established the following correlations: H-2 to H-3, -4; H-3 to H-4; H-4 to H-6, -16a, -16b; H-6 to H-7, -16a; H-9 to H-10; H-12ax to H-12eq, -13ax, -13eq, -20b; H-12eq to H-14; H-13ax to H-13eq, -14; H-16a to H-16b; H-17 to Me-18; H-20a to H-20b.

Juncins C [4], D [5], and E [6] all possess the same ten-membered ring as juncins A [2] and B [3] but differ in the cyclohexane unit and in case of **4** also in one of the four ester groups.

Juncin C [4], $\text{C}_{31}\text{H}_{41}\text{ClO}_{12}$ (hreims), possesses in addition to three acetates an isovalerate ester, as suggested by the ^1H nmr [δ 0.99 (d, $J = 6.2$, Me-25), 0.95 (d,

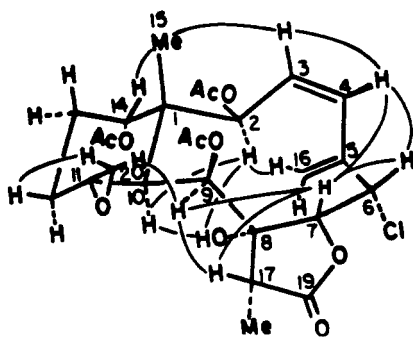
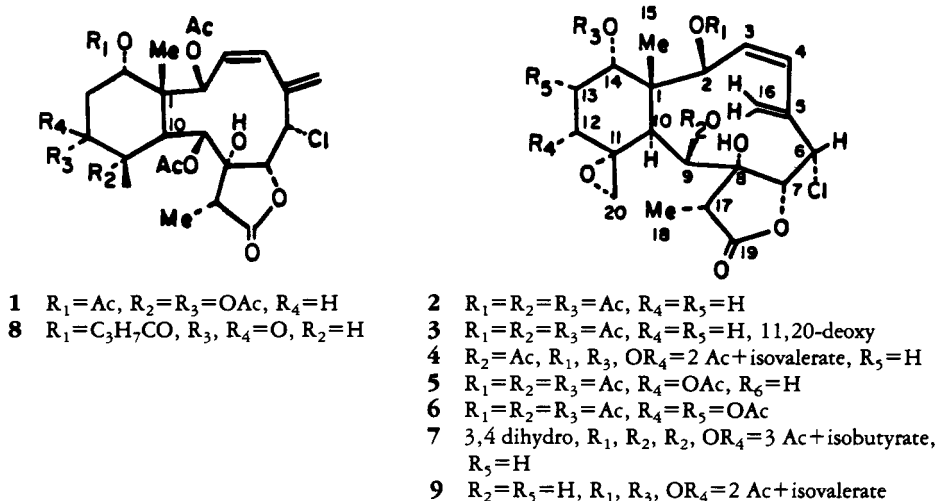


FIGURE 1. Difference nOe measurements of juncin D [5].

$J = 6.2$, Me-24), 2.10 (m, H-23), 2.06 (m, H-22'), 2.25 (m, H-22)], which was assigned by a COSY experiment (H-22 correlates to H-22' and H-23 and H-23 to Me-24 and Me-25). The isovalerate was also in full agreement with the $[\text{M} - \text{C}_5\text{H}_{10}\text{O}_2]^+$ ($\text{M} - 102$ amu) fragment observed in the mass spectrum. The location of the fourth ester, at C-12, was determined by the COSY experiment. Furthermore, a coupling of less than 1 Hz between H-12 and H-14 due to a W-arrangement determined the 1,3-diequatorial configuration for the latter two protons.

The latter stereochemistry was confirmed by nOe's measured between H-14 and Me-15 and between H-12 and H-20a. The position of the isovalerate, however, could not be determined. It has already been shown for the briaran diterpenoids that no nmr differences exist between methines carrying acetate or other esters (10), thus excluding nmr measurements for the determination of the location of the isovalerate.

Mild basic hydrolysis of 4 afforded the 8,9-dihydroxy compound 9. The C-9 position of the newly formed alcohol was established by double irradiations (see Experimental). Under stronger basic conditions or by treatment of 4 with the Zn/Cu couple (11) no selectivity in the hydrolysis of the esters could be observed. The small available amount of juncin C excluded other possible series of reactions.

Juncin D [5], $\text{C}_{28}\text{H}_{35}\text{ClO}_{12}$, a tetraacetate, possesses almost the same nmr spectrum, apart from the isovalerate, as that of 4 (Tables 1 and 2). A COSY experiment (see Experimental) confirmed the 2,9,12,14-tetraacetate structure for 5.

Juncin E [6], $\text{C}_{30}\text{H}_{37}\text{ClO}_{14}$, m/z 657/659 (3:1) $[\text{MH}]^+$, is a pentaacetate (Tables 1

and 2). Four of the acetates are the same as in juncin D, and the fifth was determined to be on C-13. The equatorial configuration of the latter acetate ($J_{13ax,14eq} = J_{12eq,13ax} = 3.3$ Hz) was established by nOe enhancements observed on H-3, H-13, and H-14 while irradiating the Me-15 group.

The last compound, juncin F [7], $C_{30}H_{41}ClO_{12}$, m/z 629/631 (3:1), $[MH]^+$, was also isolated in a small amount only. From the 1H -nmr spectrum (Table 1) it was found that the diene present in compounds 1-6 was replaced in 7 by an exocyclic methylene (C-5=C-16). Furthermore 7 carries three acetates and one isobutyrate [δ_H 1.16 (d, $J = 7$, Me-24), 1.19 (d, $J = 7$, Me-23), 2.50 (septet, $J = 7$, H-22); $[M - C_4H_8O_2]^+$ ($M^+ - 88$ mu)]. All four esters were determined to be on the same carbon atoms as in juncins C and D. However, for the same reasons discussed in the case of juncin C, we could not determine the location of the isobutyrate ester. The structure of 7 was confirmed by a COSY experiment showing the following correlations (the numbers with primes point to one out of a pair of methylene protons—the one resonating at higher field): H-2 to H-3', Me-15; H-3 to H-3', -4, -4'; H-3' to H-4, -4'; H-4 to H-4', -16a, -16b; H-4' to H-16b; H-6 to H-7, -16b; 8-OH to H-9; H-9 to H-10; H-10 to H-20a, Me-15; H-12 to H-13ax, -13eq, -14; H-13ax to H-13eq, -14; H-14 to Me-15; H-16a to H-16b; H-17 to Me-18; H-20a to H-20b. The suggested stereochemistry of the acetate at C-2 of 7 was based on the vicinal coupling constants ($J_{2,3'} = 8.3$, $J_{2,3} = 0$), which are similar to the ones measured for minabein 3 ($J = 7, 2$) isolated by Ksebati and Schmitz from a *Minabae* sp. (12).

A literature search for similar 11,20-functionalized compounds disclosed junceellin (13) and junceellin B (14) isolated from the Chinese gorgonian *Junceella squamata* and praelolide isolated from the Chinese gorgonian *Plerauroides praelonga* (15).

The juncins are closely related to the most recently reported junceelloides, isolated from *Junceella fragilis* (16).

Worth mentioning are the H-9 to H-10 coupling constants (Table 1). Cardellina and coworkers (8, 10) already have pointed out the changes of this J value with the substituent at C-11. Our findings show that other changes in substitutions of the cyclohexane unit, even if C-11 remains unchanged, change significantly the $J_{9,10}$ coupling constant, most likely because of changes in the conformation of the ten-membered ring.

EXPERIMENTAL

Ir spectra were recorded on a Perkin-Elmer Model 177 spectrophotometer. Uv spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer. Low-resolution mass spectra were recorded on a Finnigan-4021 mass spectrometer, source temperature 220-230°, pressure of reagent gases for ci spectra: CH_4 , 0.28 Torr and NH_3 , 0.15-0.20 Torr; the electron energies in ei mode were 25-35 eV. 1H - and ^{13}C -nmr spectra were recorded on a Bruker AM-360 spectrometer equipped with an Aspect 3000 computer and operating at 360.1 and 90.5 MHz for 1H and ^{13}C , respectively. All chemical shifts are reported with respect to TMS ($\delta = 0$). Hrms were taken on a VG 70 VSEQ instrument.

The 2D-nmr experiments were measured on samples in $CDCl_3$ at 298°K. The 1H - 1H shift correlation experiments were performed with a COSY 45 sequence. The two-dimensional maps were composed of $512 \times 2K$ data point spectra. A 1-sec recycle delay was allowed between each pulse sequence. Quadrature detection was applied in both dimensions by using the 16-step phase cycling for N-type peak selection. Data were multiplied with sine bell shaping function, zero-filled to $1K \times 2K$ and then Fourier transformed and symmetrized. For 1H and ^{13}C nmr of the various compounds see Tables 1 and 2.

COLLECTION AND EXTRACTION.—*J. juncea* was collected at depths of 15-25 m in the entrances to the Gulf of Eilat and the Gulf of Suez, Red Sea. The specimens were frozen immediately after collection. The freeze-dried organism (250 g) was then extracted with CH_2Cl_2 to give after evaporation a gum (1.1 g). A voucher specimen was kept in our collection in TA-YK 1690.

ISOLATION OF THE BRIARANE DITERPENOID 2-7.—The crude material was chromatographed on a dry-packed column of Merck Kieselgel H. The column was eluted successively with petroleum ether-

EtOAc (8:2 to 3:2) by applying a vacuum to the receiving flask. The material was divided into three fractions. Chromatography of the second fraction (100 mg) on an RP-18 column eluted with MeOH-H₂O (1:1) gave juncin A (20 mg, 0.008% dry wt) and juncin F (3 mg, 0.001%). The second fraction (210 mg) was first chromatographed again on a Kieselgel H column eluted with petroleum ether/EtOAc, and various combined fractions were separately applied to a RP-18 column. Elution of the latter column with H₂O with increasing percentages of MeOH gave juncin C [4] (40 mg, 0.016%), juncin D [5] (15 mg, 0.006%), juncin B [3] (3 mg, 0.001%), and juncin E [6] (15 mg, 0.005%). All six compounds were obtained as amorphous powders which could not be crystallized.

Tlc of the new compounds [Si gel eluted with petroleum ether-EtOAc (1:1)] showed for compounds 6, 5, 4, 2, 7, and 3 *R_f* values of 0.20, 0.26, 0.36, 0.37, 0.43 and 0.57, respectively.

Juncin A [2].—[α]²⁵_D -79° (c = 0.02, CHCl₃); hreims *m/z* 540.1752 for C₂₆H₃₃ClO₁₀ (required 540.1762); ir (CHCl₃) 3520, 1780, 1730, 1720 cm⁻¹; cims (CH₄) *m/z* (rel. int.) [MH]⁺ 541/543 (22,9), 481/483 (17,4), 421/423 (49,19), 361/363 (54,21), 325 (64), 307 (49), 279 (34), 261 (21), 251 (35), 243 (100), 225 (27).

Juncin B [3].—[α]²⁵_D -55° (c = 0.003, CHCl₃); ir (CHCl₃) 3540, 1780, 1750, 1730, 1720 cm⁻¹; cims (CH₄) *m/z* (rel. int.) [MH]⁺ 525/527 (4,1), 491 (18), 465/467 (21,9), 405/407 (100,32), 345/347 (40,14), 329 (26), 309 (33), 281 (19), 205 (16).

Juncin C [4].—[α]²⁵_D -79° (c = 0.02, CHCl₃); hreims *m/e* 640.2304 for C₃₁H₄₁ClO₁₂ (required 640.2287); ir (CHCl₃) 3520, 1760, 1740, cm⁻¹; cims (CH₄) *m/z* (rel. int.) [MH]⁺ 641/643 (11,5), 581/583 (13,8), 521/523 (19,7), 461/463 (18,6), 443 (16), 419 (41), 401 (31), 383 (43), 358 (79), 341 (100), 323 (74), 305 (40), 217 (31), 205 (12), 103 (37).

Juncin D [5].—[α]²⁵_D -68° (c = 0.007, CHCl₃); ir (CHCl₃) 3540, 1770, 1710 cm⁻¹; cims (CH₄) *m/z* (rel. int.) [MH]⁺ 599/601 (4,1), 539/541 (3,1), 479/481 (5,2), 419/421 (14,4), 401 (7), 359/361 (23,9), 341 (25), 323 (22), 279 (37), 205 (70), 149 (100), 99 (22).

Juncin E [6].—[α]²⁵_D -66° (c = 0.02, CHCl₃); ir (CHCl₃) 3540, 1780, 1750, 1740, 1720 cm⁻¹; cims (CH₄) *m/z* (rel. int.) [MH]⁺ 657/659 (45,16), 597/599 (77,29), 537 (20), 477 (16), 417 (20), 357 (30), 339 (37), 281 (57), 279 (100), 205 (77), 149 (59).

Juncin F [7].—[α]²⁵_D -7° (c = 0.004, CHCl₃); ir (CHCl₃) 3490, 1790, 1740, 1730 cm⁻¹; cims (CH₄) *m/z* (rel. int.) [MH]⁺ 629/631 (21,7), 569/571 (9,2), 541/543 (60,20), 481 (27), 421/423 (60,21), 361/363 (100,41), 343 (43), 325 (43), 307 (21), 279 (26), 205 (34), 149 (50).

9-Deacetyl juncin C [8].—Juncin C (2 mg) dissolved in a solution of 0.1% K₂CO₃ in MeOH (1 ml) was stirred at room temperature for 20 h. The reaction mixture was neutralized with HOAc-MeOH (1:10). CHCl₃ (5 ml) and H₂O (5 ml) were added, the two phases were separated, and the organic layer was dried over MgSO₄. The residue after evaporation of the solvents afforded 9-deacetyl juncin C: C₂₉H₃₉ClO₁₁; *m/z* [MH]⁺ 599/601 (22,7); ¹H nmr (360) MHz, (CDCl₃) 6.26 (1H, d, *J* = 10.3, H-2), 5.98 (1H, d, *J* = 11.9, H-4), 5.76 (1H, dd, *J* = 10.3, 11.9, H-3), 5.62 (1H, m, H-16), 5.51 (1H, s, H-16'), 5.45 (1H, t, H-14), 5.10 (1H, d, *J* = 1.7, H-6), 5.07 (1H, t, *J* = 3, H-12), 4.84 (1H, d, *J* = 1.7, H-7), 4.00 (1H, s, 9-OH), 3.64 (1H, m, H-10), 3.40 (1H, m, H-9), 2.90 (1H, q, *J* = 7, H-17), 2.79 (1H, d, *J* = 3.5, H-20a), 2.70 (1H, s, 8-OH), 2.41 (1H, d, *J* = 3.5, H-20b), 2.16 (3H, s, OAc), 2.00 (3H, s, OAc), 1.42 (3H, d, *J* = 7, Me-18), 1.09 (3H, d, *J* = 6.4, Me-24), 1.01 (3H, d, *J* = 6.4, Me-25).

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