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STRUCTURES OF MACROCALYXIN B, F, G AND H, AND MAOYERABDOSIN FROM *ISODON MACROCALYX*

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Key Word Index—*Isodon macrocalyx*; Labiatae; *ent*-kauranoid; macrocalyxin B; macrocalyxin F; macrocalyxin G; macrocalyxin H; maoyerabdosin.

Abstract—Four new diterpenoids, macrocalyxins B, F, G, and H, together with maoyerabdosin and the known rabdophyllin H, ponicidin, oridonin, and enmenol, were isolated from the leaves of *Iosdon macrocalyx* and their structures were elucidated from spectral and chemical evidence.

INTRODUCTION

In previous communications [1–3], we have reported on the isolation and structure determination of macrocalyxins A (**14**), C (**15**), D (**16**) and E (**17**) from *Isdodon macrocalyx* Kudo. Further investigation on the constituents of the same plant has led to the isolation of four new diterpene macrocalyxins, B (**2**), F (**1**), G (**5**) and H (**8**), in addition to maoyerabdosin [4]. This paper describes the isolation and structure elucidation of these four diterpenes together with the evidence for the revised structure (**9**) of maoyerabdosin, which was first isolated from *I. japonicus* (Burm.) Hara collected in Xin county, Henan, China.

RESULTS AND DISCUSSION

Dry leaves of *I. macrocalyx* collected in the Jiuhua Shan district, Anhui, China were extracted with ethanol. Silica gel column chromatography of the extract gave macrocalyxins B and F along with the known diterpenes macrocalyxins A, C, D and E.

A similar work up of dry leaves of *I. macrocalyx* collected in the Huang Shan district, Anhui, China yielded macrocalyxin G, macrocalyxin H and maoyerabdosin (**9**), as well as the known diterpenes rabdophyllin H (**6**), ponicidin (**10**), oridonin (**11**), and enmenol (**12**).

Macrocalyxin F (**1**), $C_{20}H_{26}O_6$, has a pentacyclic structure in which a ketone group is conjugated with an α-methylene group, as shown by the following spectral data: λ_{max} (EtOH) 223 nm (ε 8227); ν_{max} 1708 and 1640 cm^{-1}; ^1H NMR δ6.24 and 5.41 (each 1H, *br s*); ^{13}C NMR δ152.9 (*s*), 116.7 (*t*) (exo-methylene) and 208.2 (*s*) (ketone). The ^1H NMR spectrum of **1** showed the presence of three hydroxyl groups [δ8.24, 7.89 and 7.60 (each 1H, *s*)] of which the ^1H NMR signals at δ5.41 (*s*) and 4.95 (*dd*, $J = 4.3$, 8.4 Hz) coupled with the ^{13}C NMR signals at δ74.0 and 73.9 (each *d*) showed that two were secondary. This fact suggested that, of the three hydroxy groups in **1**, two are secondary and the third is tertiary, The ^1H NMR signals at δ9.36 (1H, *s*), 4.18 (1H, *d*, $J = 8.8$ Hz) and 4.12 (1H, *dd*, $J = 1.1$, 8.8 Hz), together with ^{13}C NMR signals at δ205.3 (*d*) and 69.3 (*t*) showed the presence of an aldehyde group and a $-CH_2-O$ group. The ^{13}C NMR spectrum of **1** showed the presence also of a methyl group, six methylenes, five methines, and four tetrasubstituted carbon atoms together with two olefinic, one aldehyde and one carbonyl carbon atom. These spectral data, coupled with a knowledge of the structures of the diterpenoids isolated so far from the genus *Isodon*, led to the assumption that macrocalyxin F had an *ent*-kaurane structure as its basic skeleton [5]. Acetylation of **1** with acetic anhydride and pyridine gave triacetyl macrocalyxin F (**3**). In the ^1H NMR spectrum of **3**, the signal of H-14 underwent a downfield shift to δ6.09 (*br s*), suggesting that it was assignable to H-14α, which is affected anisotropically by the 15-carbonyl group and has an angle of *ca* 90° to the C-13-proton. Treatment of **1** with acetone and anhydrous copper (II) sulphate gave the acetonide (**4**). This confirmed the presence of an α-oriented hydroxyl group at C-7 in macrocalyxin F (**1**).

Macrocalyxin F (**1**) is a pentacyclic compound as shown by the degree of unsaturation. From comparisons of the ^{13}C NMR spectra of **1** with those of other kaurene derivatives, it was assumed that no oxygenated group was present on the A-ring. The ^{13}C NMR signals of **1** at δ63.9 (*t*) and 103.7 (*s*) coupled the movement of the ^1H NMR signals of H-9β and H-12α to lower field at δ2.35 (1H, *s*)

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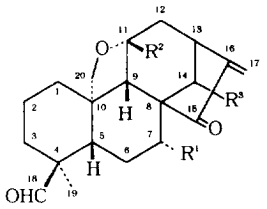
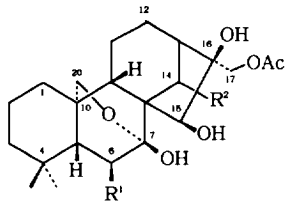
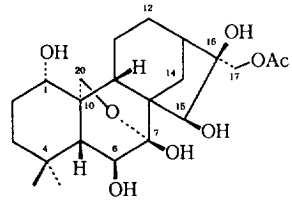


1 $R^1 = R^2 = R^3 = OH$
2 $R^1 = R^3 = OH$, $R^2 = OCH_3$
3 $R^1 = R^2 = R^3 = OAc$
4 $R^2 = OH$, $R^1, R^3 = -O-C(CH_3)_2-O-$



5 $R^1 = R^2 = OH$
6 $R^1 = OAc$, $R^2 = OH$
7 $R^1 = R^2 = OAc$



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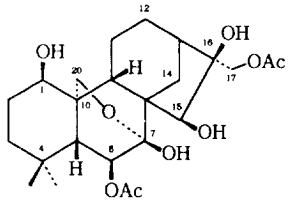

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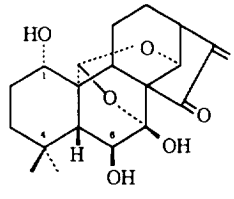

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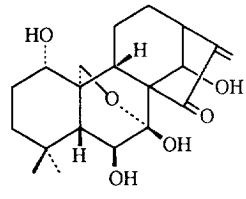

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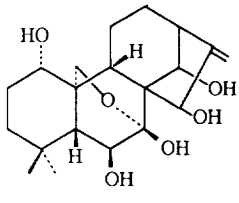

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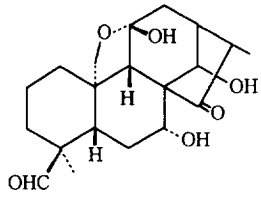

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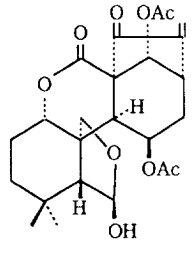

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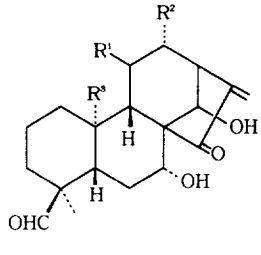
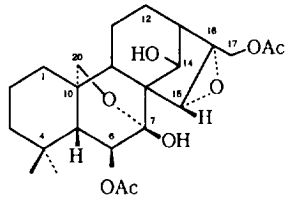


15 $R^1 = H$, $R^2 = OH$, $R^3 = CH_3$
16 $R^1 = R^2 = H$, $R^3 = CH_2OH$
17 $R^1 = = O$, $R^2 = OH$, $R^3 = CH_3$



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and 3.21 (1H, *dd*, $J = 9.0$, 14.1 Hz) and the movement of the ^{13}C NMR signals of C-9 and C-12 to lower field at δ62.1 (*d*) and 46.1 (*t*), respectively, suggested the presence of a hemiacetal ring attached to the C-11 position. In the NOESY spectrum of **1**, NOE cross peaks were observed for CH_2-20 and Me-4α, H-2α, H-6α and H-14α; H-9β and H-1β, H-5β and H-7β; CHO-4β and Me-4α, H-5β and H-3β, respectively. These results indicated not only the positions of the two secondary hydroxy groups and the hemi acetal ring, but also the presence of a Me group at the C-4α position and an aldehyde group at the C-4β position. Accordingly, macrocalyxin F has the structure (**1**), *ent*-7β, 11-α, 14-trihydroxy-18-aldehyde-11β-20-epoxy-kaur-16-en-15-one. It is the first example of 11α-20-epoxy *ent*-kauranoid from *Isodon* plants.

Macrocalyxin B (**2**), $C_{21}H_{28}O_6$, has a five membered ring system with a ketone conjugated group to an α-methylene group, as shown by the following spectral data: ν_{max} 1640 cm^{-1}; ^1H NMR δ6.24 and δ5.41 (each 1H, *br s*); ^{13}C NMR δ152.3 (*s*), δ117.4 (*t*) (exo-methylene) and δ207.6 (*s*) (ketone). The ^{13}C NMR data of macrocalyxin B (**2**) showed the presence of a methyl group, six methylenes five methines and four tetrasubstituted carbon atoms together with two olefinic, one aldehyde and one carbonyl carbon atom. The ^1H and ^{13}C NMR spectra of **2** were similar to those of macrocalyxin F (**1**). Macrocalyxin

B, however, has an extra signal for an –OMe group attached to the 11β-position, as shown by the following spectral data. In the ^{1}H NMR spectrum, the signal of H-1α of macrocalyxin B underwent an upfield shift by 0.71 ppm relative to the corresponding signal of **1** because of the space–steric effect of the –OMe group. On the other hand, in the ^{13}C NMR spectrum, the signals assignable to C-12 and C-9 of **2** underwent an upfield shift of 5.6 ppm and 0.6 ppm, respectively, and C-11 of **2** a downfield shift of 2.6 ppm compared to **1** because of the substituent effect due to the –OMe group [6]. Accordingly, macrocalyxin B has the structure **2**.

Macrocalyxin G (**5**), $C_{22}H_{34}O_8$. The IR spectrum of **5** did not show any absorption due to a double bond. The ^{1}H NMR spectrum of **5** showed the presence of two tertiary methyl groups [δ1.19 and 1.07 (each 3H, *s*)] and two methylene groups [δ4.10 (1H, *dd*, *J* = 1.0, 9.5 Hz) and 3.39 (1H, *d*, *J* = 9.5 Hz)] and [δ4.80, 4.58 (each 1H, *d*, *J* = 10.7 Hz)] located between an oxygen atom and a quaternary carbon. The ^{13}C NMR spectrum of **5** showed the presence of four methyl groups, five methylenes, six methines, four tetrasubstituted carbons, an acetal carbon [δ99.3 (*s*)] and two oxygenated methyl carbons [δ65.5 (*t*) and δ73.7 (*t*)]. A high resolution EIMS peak of macrocalyxin G at *m/z* 151, which is formed by the cleavage of the B-ring, indicated the presence of 7-20-epoxy-*ent*-kaurene structure [5]. The cumulative data suggested that macrocalyxin G had an *ent*-7α-hydroxy-7β-20-epoxy-kaurane skeleton which is typical of *Isodon* diterpenes [5].

The ^{1}H NMR spectrum of macrocalyxin G (**5**) showed the presence of five hydroxy groups [δ8.55, 7.93, 7.82, 7.08 and 4.92 (each 1H, disappeared on adding D_2O)] of which the ^{1}H NMR [δ4.11 (1H, *t*, *J* = 5.0 Hz), δ4.90 (1H, *s*) and δ5.03 (1H, *s*)] and ^{13}C NMR [δ73.2, 75.7, 72.0, (each *d*)] spectra showed that three are secondary. These data suggested that, of the five hydroxy groups in **5**, three are secondary, and two are tertiary. In the ^{1}H–^{1}H COSY spectrum of **5**, the following coupled cross peaks were observed: (i) for the signals at δ4.11 (1H, *t*, *J* = 5.0 Hz), 8.55 (1H, *d*, *J* = 4.5 Hz, OH) and 1.48 (1H, *dd*, *J* = 1.0, 5.2 Hz) due to the 5β-proton which is coupled by long-range interaction across the w-path with the signal of δ3.93 (1H, *dd*, *J* = 1.0, 9.5 Hz, Hb-20), (ii) for the signals at δ4.90 (1H, *s*), 7.92 (1H, *br s*, OH) and 2.36 (1H, *dd*, *J* = 1.0, 9.3 Hz) due to the 13α-proton which is coupled with the signal at δ1.83 (1H, *dd*, *J* = 9.3, 13.7 Hz, H-12α, and (iii) for the signals at δ5.03 (1H, *br s*), 7.08 (1H, *br s*, OH) and the 13α-proton [δ2.36 (1H, *dd*, *J* = 1.0, 9.3 Hz)] which is coupled by the long-range interaction across the w-path. These findings suggest that the signals at δ4.11, 4.90 and 5.03 are assignable to H-14α and -6α and -15α, respectively, while the signals at δ8.55, 7.92 and 7.08 are due to the hydroxyl groups attached to the 6β, 14β and 15β-positions, respectively. One of the two tertiary hydroxy groups was easily located to the 7β-position. The other was assigned to be at the 16α-position because the proton signal assigned to 12β was shifted downfield to δ2.71 (1H, *dd*, *J* = 9.2, 12.3 Hz). The ^{1}H NMR [δ1.91 (3H, *s*)] and ^{13}C NMR [δ171.2 (*s*), δ20.9 (*q*)] showed the presence of an acetyl group in **5**. The acetyl group was assigned to be at the 17-position because the proton signals assigned to the 17-position were shifted downfield to δ4.58 and 4.80 (each 1H, *d*, *J* = 10.7 Hz). These data suggested that macrocalyxin G has structure **5**. The presumed structure (**5**) was supported by the chemical reaction and NOESY spectra described below. Treatment of **5** with acetic anhydride and pyridine gave the 14-acetyl rabdophyllin H (**7**) [7]. In the NOESY spectra of macrocalyxin G (**5**), NOE cross peaks were observed for (i) Me-4α and H-6α, Ha-20, (ii) H-14α and H-11α, Hb-20, (iii) H-9β and H-5β, and (iv) H_2-17, H-13α and H-15α, respectively.

Macrocalyxin H (**8**), $C_{22}H_{34}O_8$, was found to contain two tertiary methyl groups [δH 1.22, 1.18 (each 3H, *s*), δC 33.4 (*q*), 23.1 (*q*)], two CH_2O-groups [δH 4.20, 4.07 (each 1H, *d*, *J* = 9.3 Hz), and 4.37, 4.32 (each 1H, *d*, *J* = 11.0 Hz), δC 65.5 (*t*) and 71.7 (*t*)], an acetyl group [δH 1.93 (3H, *s*), δC 171.1 (*s*), 20.9 (*q*)] and five hydroxy groups [ν_{max} 3440, 3350, 3320, 3250 cm^{-1}, δH 8.06, 7.81, 7.09, 5.69 and 4.83 (each 1H, disappeared on adding D_2O)]. The ^{13}C NMR spectrum of **8** showed the presence of three methyl groups, five methylenes, six methines, four tetrasubstituted carbons, an acetal carbon [δ97.2 (*s*)], two oxygenated methyl carbons [δ65.5 (*t*), and δ71.7 (*t*)] and an acetyl carbon [δ171.1 (*s*)]. The IR spectrum of **8** did not show any absorption due to a double bond. These spectral data suggest that macrocalyxin H has an *ent*-7α-hydroxy-7β-20-epoxy-kaurane skeleton which is typical of *Isodon* diterpenes [5].

The ^{1}H NMR signals at δ3.75 (1H, *t*, *J* = 3.0 Hz), 4.31 (1H, *t*, *J* = 5.0 Hz) and 4.57 (1H, *br s*) coupled with the ^{13}C NMR signals at δ65.3 (*d*), 74.7 (*d*) and 73.0 (*d*) indicate the presence of three secondary and two tertiary hydroxy groups in **8**. In the ^{1}H–^{1}H COSY spectra of **8**, the following coupled cross peaks were observed: (i) for the signals at δ3.75, 5.69 (1H, *br s*, OH), and 1.83 (2H, *m*) due to the 2-protons, (ii) for the signals at δ4.31 and 2.20 due to the 5β-proton which is coupled by long-range interaction along the w-path with the signal of δ4.20 (1H, *dd*, *J* = 1.0, 9.3 Hz, 20Hb), (iii) for the signals at δ4.57 (1H, *br s*) and 2.20 due to the 13 α-proton by long-range interaction along the w-path. Thus the signals at δ3.75, 4.31 and 4.57 were assigned to the H-1β, H-6α and H-15α, respectively. Accordingly, the three hydroxy groups are located at the 1α-, 6β-, and 15β-positions, respectively. One of the two tertiary hydroxy groups was easily located to the 7β-position. The other was assigned to be at the 16α-position because the proton signal assigned to C-12β was shifted downfield to δ2.60 (1H, *m*).

One of the two CH_2-O-groups [δH 4.20, 4.07 (each 1H, *dd*, *J* = 1.0, 9.3 Hz)] was easily assigned to lie between C-10 and C-7 because the two protons were coupled by long-range interaction across the w-path with the protons of C-5β and C-9β, respectively. Coupling cross peaks were observed for another oxygenated methyl group [δ4.37, 4.32 (each 1H, *d*, *J* = 11.0 Hz)] and the acetyl group [δ1.93 (3H, *s*)] in the ^{1}H–H COSY spectra of **8**. NOESY cross peaks were observed for the two protons of the oxygenated methyl group, H-13α- and H-15α in the NOESY spectrum of **8**. Thus the –CH_2–OAc group was

assigned to the 16α-position. Accordingly, it was concluded that macrocalyxin H had the structure **8**.

Maoyerabdosin (**9**), $C_{24}H_{36}O_9$. The IR spectrum did not show any absorption due to a double bond. The ^{1}H NMR spectrum showed the presence of two tertiary methyl groups [δ1.17, 0.92 (each 3H, *s*)] and two methylene groups [δ4.19, 4.08 (each 1H, *dd*, J = 1.0, 9.4 Hz) and δ4.49, 4.37 (each 1H, *d*, J = 11.3 Hz)] located between an oxygen atom and a quaternary carbon. The ^{13}C NMR spectrum of **9** showed the presence of two methyl groups, five methylenes, six methines, four tetra-substituted carbons, an acetalic carbon [δ96.0 (*s*)], two oxygenated methyl carbons [δ71.1 (*t*), 65.6 (*t*)] and two acetyl carbons [δ171.0 (*s*), 169.7 (*s*)]. On the other hand, EIMS peaks at *m/z* 167 and 149 which were formed by cleavage of the B-ring indicated the presence of the 7-20-epoxy-*ent*-kaurane structure [8]. The above data suggest that maoyerabdosin has an *ent*-7α-hydroxy-7β-20-epoxy kaurane skeleton [8] which is typical of *Isodon* diterpenes.

The ^{1}H NMR spectrum of maoyerabdosin (**9**) showed the presence of four hydroxyl groups [δ8.40, 5.80, 5.30 and 4.92 (each 1H, disappeared on adding D_2O)] of which the ^{1}H NMR [δ3.75 (1H, *d*, J = 3.1 Hz)] and ^{13}C NMR [δ65.0, 72.4 (each doublet)] spectra showed that two were secondary. These data suggest that, of the four hydroxyl groups in **9**, two are secondary and two are tertiary. In the ^{1}H–^{1}H COSY spectrum of **9**, the following coupling cross peaks were observed: (i) for the signals at δ3.75 (1H, *m*), 5.80 (1H, *d*, J = 3.9 Hz, OH) and 1.70 (2H, *m*, H_2-2, (ii) for the signals at δ4.42 (1H, *d*, J = 3.1 Hz) and 4.92 (1H, *d*, J = 3.1 Hz, OH). NOE cross peaks were observed (i) for the signal at δ3.75 and the signal at δ4.19 (1H, *d*, J = 1.0, 9.4 Hz, Hb-20, (ii) for the signal at δ4.42 and the signals at δ4.49 and 4.37 (each 1H, *d*, J = 11.3 Hz) H_2-17 in the NOESY spectrum of **9**. These data and the downfield shift of the signal due to H-9β, the signals at δ3.75 and 4.42 were assigned to H-1α and H-15α, respectively. Thus the two hydroxyl groups are located to the 1β- and 15β-positions, respectively. One of the two tertiary hydroxyl groups was easily located to the 7β-position. Another was assigned to be at the 16β-position because the signal assigned to the 12β proton was shifted downfield to δ2.47 (1H, *m*) and the ^{13}C signal uniquely upfield to δ19.8 (*t*). One of the two $-CH_2O-$ groups [δ4.19, 4.08 (each 1H, *dd*, J = 1.0, 9.4 Hz)] was easily assigned to the H_2-20 because the two protons were coupled by long-range interaction across the w-path with H-5β and H-9β, respectively, in the ^{1}H–^{1}H COSY spectrum of **9**. Another oxygenated methyl group [δ4.49, 4.37 (each 1H, *d*, J = 11.3 Hz)] was assigned to be at the 16α-position because NOESY cross peaks were observed between these two oxygenated methyl protons and both H-13α and H-15α in the NOESY spectrum of **9**.

Two acetyl groups at δ2.17 and 1.93 (each 3H, *s*) were assigned to the C6β- and C17- positions, because the proton signals of the C6α- and C17- position were shifted downfield to δ5.74 (1H, *d*, J = 5.2 Hz, H-6α) as well as to δ4.49 and 4.37 (each 1H, *d*, J = 11.3 Hz, H_2-17), respectively.

Accordingly, the structure of maoyerabdosin formerly **18** was revised to that depicted in **9**.

EXPERIMENTAL

General. Mps: uncorr.; IR: KBr disks; ^{1}H NMR: 200, 300 or 600 MHz, tetramethylsilane as int. standard; mass spectra: JEOL JMS-01SG-2 spectrometer; CC: silica gel G 60 (0.063–0.200 mm, Merck); TLC precoated silica gel plates F_{254} (0.25 and 0.5 mm in thickness). Extracts were dried over anhydrous Na_2SO_4.

Isolation of diterpenoids from dried leaves of the plant. The EtOH extract obtained from dried leaves of *Isodon macrocalyx* (10 kg) collected at Jiuha Shan, Anhui, China in late August, 1984, was concd under red. pres. to 10 l, and EtOH was added to the extract to make a 90% EtOH soln which was then treated with charcoal. After evapn of the solvent, the residue was dissolved in EtOAc. The soln was shaken with aq. Na_2CO_3 to remove the acidic substances, then the organic layer, after drying, was evapd under red. pres. to give a residue (180 g), which was chromatographed on a silica gel column developed with $CHCl_3$ containing increasing amounts of Me_2CO. Elution with $CHCl_3$ gave macrocalyxin A and oleanolic acid, Elution with $CHCl_3$–Me_2CO (9:1) gave macrocalyxin B and F. Elution with $CHCl_3$–Me_2CO (4:1) gave macrocalyxin C, D and E.

The EtOH extract obtained from the dried leaves of *Isodon macrocalyx* (10 kg) collected at Huang-Shan, Anhui, China in late August, 1986, was treated as above to give a residue (340 g) which was chromatographed on a silica gel column developed by stepwise elution with $CHCl_3$ containing increasing amounts of Me_2CO. Elution with $CHCl_3$ gave rabdophyllin H, macrocalyxin G and ponicidin. Elution with $CHCl_3$–Me_2CO (9:1) gave maoyerabdosin and macrocalyxin H. Elution with $CHCl_3$–Me_2CO (4:1) gave oridonin and enmenol. The yields, physical properties and spectral data of isolated compounds are as follows:

Macrocalyxin F (**1**). Needles (2g), mp 227–229° (from Me_2CO), $[\alpha]_D^{25}$ −127.9° (EtOH; *c* 0.5), UV λ_{max} (EtOH) 223 (ε 8227) nm. IR ν_{max} 3428, 3373, 3250, 2786, 2686, 1724, 1708, 1640 cm^{-1}; ^{1}H NMR (C_5D_5N): δ9.36 (1H, *s*, 4β-CHO), 8.24, 7.89, 7.60 (each 1H, H-14, H-11, OH-7), 6.24 (*s*, Ha-17), 5.41 (2H, *s*, H-14α, Hb-17), 4.95 (1H, *dd*, J = 4.3, 8.4 Hz, H-7β), 4.18 (1H, *d*, J = 8.8 Hz, Ha-20), 4.12 (1H, *dd*, J = 1.1, 8.8 Hz, Hb-20), 3.39 (1H, *ttd*, J = 4.2, 4.2, 13.6 Hz, H-1α), 3.27 (*d*, J = 9.1 Hz, H-13α), 3.21 (*dd*, J = 9.0, 14.1 Hz, H-12α), 2.35 (1H, *s*, H-9β), 2.21 (1H, *dd*, J = 1.3, 12.8 Hz, H-5β), 2.19 (1H, *dd*, J = 2.5, 14.1 Hz, H-12β), 2.15 (*ddd*, J = 12.2, 12.4, 12.5 Hz, H-6α), 1.72 (*dd*, J = 2.5, 12.0 Hz, H-6β), 1.59 (1H, *tttt*, J = 2.2, 3.5, 2.2, 13.8 Hz, H-2β), 1.50 (1H, *ttd*, J = 3.0, 14.1 Hz, H-2α), 1.41 (1H, *dddt*, J = 4.4, 4.4, 4.3, 12.2 Hz, H-3β), 1.18 (1H, *t*, J = 10.7, 13.5 Hz, H-1β), 1.10 (1H, *d*, J = 12.9 Hz, H-3α), 0.98 (3H, *s*, Me-4α); ^{13}C NMR (C_5D_5N): δ38.2 (*t*, C-1), 18.7 (*t*, C-2), 31.7 (*t*, C-3), 50.5 (*s*, C-4), 43.4 (*d*, C-5), 31.3 (*t*, C-6), 73.9 (*d*, C-7), 57.7 (*s*, C-8), 62.1 (*d*, C-9), 48.9 (*s*, C-10), 103.7 (*s*, C-11), 46.1 (*t*, C-12), 44.6 (*d*, C-13), 74.0 (*d*, C-14), 208.2 (*s*, C-15), 152.9 (*s*, C-16), 116.7 (*t*, C-17), 205.3 (*d*, C-18), 13.8 (*q*, C-19), 69.0 (*t*, C-20); HRMS *m/z* Found: 326.1729 $[M]^+$. $C_{20}H_{26}O_6$ requires: 362.1723. (Found: C, 63.30; H, 7.44. $C_{20}H_{26}O_6$ requires: C, 63.15; H, 7.37%).

Macrocalyxin B (**2**). Needles (0.1g), mp > 300° (from

Me_2CO), $[\alpha]_D^{22}$ −62.8° (MeOH; *c* 0.07). IR ν_{max} 3400, 1724, 1708, 1640 cm^{-1}; ^1H NMR (C_5D_5N): δ9.36 (1H, *s*, CHO-4β), 8.30, 7.55 (each 1H, H-14, OH-7), 6.25 (1H, *s*, Ha-17), 5.46 (1H, *s*, Hb-17), 5.21 (1H, *s*, H-14α), 4.90 (1H, *dd*, *J* = 4.0, 8.4 Hz, H-7β), 4.05 (1H, *dd*, *J* = 1.7, 8.8 Hz, Ha-20), 3.95 (1H, *d*, *J* = 8.8 Hz, Hb-20), 3.25 (1H, *d*, *J* = 8.9 Hz, H-13α), 3.14 (3H, *s*, –OMe), 2.90 (1H, *dd*, *J* = 9.0, 14.1 Hz, H-12α), 2.68 (1H, *ttd*, *J* = 4.2, 4.2, 13.6 Hz, H-1α), 2.16 (1H, *s*, H-9β), 2.13 (1H, *dd*, *J* = 1.8, 12.8 Hz, H-5β), 2.08 (1H, *ddd*, *J* = 12.2, 12.4, 12.5 Hz, H-6α), 1.80 (1H, *d*, *J* = 14.1 Hz, H-12β), 1.66 (1H, *dd*, *J* = 3.1, 12.4 Hz, H-6β), 1.55 (1H, *ttd*, *J* = 3.6, 3.6, 14.0 Hz, H-2β), 1.51 (1H, *ttd*, *J* = 3.0, 3.0, 14.0 Hz, H-2α), 1.38 (1H, *dddt*, *J* = 4.7, 4.6, 4.7, 11.3 Hz, H-3β), 1.08 (1H, *d*, *J* = 13.0 Hz, H-3α), 1.04 (1H, *t*, *J* = 13.9 Hz, H-1β), 0.95 (3H, *s*, Me-4α); ^{13}C NMR (C_5D_5N): δ38.1 (*t*, C-1), 18.5 (*t*, C-2), 31.5 (*t*, C-3), 50.5 (*s*, C-4), 43.5 (*d*, C-5), 31.2 (*t*, C-6), 73.7 (*d*, C-7), 57.4 (*s*, C-8), 61.5 (*d*, C-9), 48.6 (*s*, C-10), 106.3 (*s*, C-11), 40.5 (*t*, C-12), 44.5 (*d*, C-13), 73.5 (*d*, C-14), 207.6 (*s*, C-15), 152.3 (*s*, C-16), 117.4 (*t*, C-17), 205.1 (*d*, C-18), 13.6 (*q*, C-19), 69.5 (*t*, C-20), 47.3 (*q*, –OMe); HR-FAB-MS *m/z* found: 399.1758 $[M]^+$. $C_{21}H_{28}O_6Na$ requires 399.1788.

Macrocalyxin G (**5**). Needles (0.05g), mp 130–133°, $[\alpha]_D^{25}$ −38.66° (MeOH; *c* 0.45). IR ν_{max} 3300, 1740, 1240 cm^{-1}; ^1H NMR (C_5D_5N): δ8.55 (1H, *d*, *J* = 4.5 Hz, OH), 7.92, 7.82, 7.08, 4.92 (each 1H, *br s*, OH), 5.03 (1H, *br s*, H-15α), 4.90 (1H, *br s*, H-14α), 4.80, 4.58 (each 1H, *d*, *J* = 10.7 Hz, H_2-17), 4.11 (1H, *t*, *J* = 5.0 Hz, H-6α), 4.10 (1H, *dd*, *J* = 1.0, 9.5 Hz, Ha-20), 3.93 (1H, *dd*, *J* = 1.0, 9.5 Hz, Hb-20), 2.71 (1H, *dd*, *J* = 9.2, 12.3 Hz, H-12β), 2.52 (1H, *dd*, *J* = 6.0, 9.0 Hz, H-9β), 2.36 (1H, *dd*, *J* = 1.0, 9.3 Hz, H-13α), 1.91 (3H, *s*, OAc), 1.83 (1H, *dd*, *J* = 9.3, 13.7 Hz, H-12α), 1.48 (1H, *dd*, *J* = 1.0, 5.2 Hz, H-5β), 1.41 (2H, *m*, 3-H, H-11α), 1.31 (2H, *m*, H_2-2), 1.20 (3H, *m*, H-1, H-3, H-11β), 1.19 (3H, *s*, Me-4β), 1.07 (3H, *s*, Me-4α), 0.86 (1H, *m*, H-1); ^{13}C NMR (C_5D_5N): δ30.6 (*t*, C-1), 19.1 (*t*, C-2), 41.5 (*t*, C-3), 33.7 (*s*, C-4), 58.1 (*d*, C-5), 73.2 (*d*, C-6), 99.3 (*s*, C-7), 54.2 (*s*, C-8), 43.6 (*d*, C-9), 36.0 (*s*, C-10), 14.7 (*t*, C-11), 20.4 (*t*, C-12), 46.1 (*d*, C-13), 75.7 (*d*, C-14), 72.0 (*d*, C-15), 76.6 (*s*, C-16), 73.7 (*t*, C-17), 33.5 (*q*, C-18), 22.4 (*q*, C-19), 65.5 (*t*, C-20), 171.2, 20.9 (–OAc); HRMS *m/z* found: 426.2244 $[M]^+$. $C_{22}H_{34}O_8$ requires 426.2253.

Macrocalyxin H (**8**). Needles (0.07g), mp 230°, $[\alpha]_D^{25}$ −41.8° (MeOH; *c* 0.22). IR ν_{max} 3440, 3350, 3320, 3250, 1725, 1705, 1240, 1058 cm^{-1}; ^1H NMR (C_5D_5N): δ8.06, 7.81, 7.09, 5.69, 4.83 (each 1H, OH), 4.57 (1H, *br s*, H-15α), 4.37, 4.32 (each 1H, AB, *d*, *J* = 11.0 Hz, H_2-17), 4.31 (1H, *t*, *J* = 5.0 Hz, H-6α), 4.20, 4.07 (each 1H, *dd*, *J* = 1.0, 9.3 Hz, H_2-20), 3.75 (1H, *t*, *J* = 3.0 Hz, H-1α), 3.11 (1H, *ddd*, *J* = 1.0, 5.7, 10.9 Hz, H-9β), 2.60 (1H, *m*, H-12β), 2.20 (3H, *m*, H-3β, H-13α, H-5β), 2.10 (1H, *m*, H-11β), 1.99 (2H, *m*, H_2-14), 1.93 (3H, *s*, OAc), 1.83 (2H, *m*, H_2-2), 1.72 (1H, *m*, H-12α), 1.69 (1H, *m*, H-11α), 1.26 (1H, *m*, H-3α), 1.18, 1.22 (each 3H, *s*, Me_2-4); ^{13}C NMR (C_5D_5N): δ65.3 (*d*, C-1), 27.7 (*t*, C-2), 34.5 (*t*, C-3), 34.0 (*s*, C-4), 53.7 (*d*, C-5), 74.7 (*d*, C-6), 97.2 (*s*, C-7), 52.9 (*s*, C-8), 36.8 (*d*, C-9), 40.8 (*s*, C-10), 14.8 (*t*, C-11), 20.0 (*t*, C-12), 37.8 (*d*, C-13), 25.8 (*t*, C-14), 73.0 (*d*, C-15), 76.8 (*s*, C-16), 71.7 (*t*, C-17), 33.4 (*q*, C-18), 23.1 (*q*, C-19), 65.5 (*t*, C-20), 171.1, 20.9 (OAc); MS *m/z* 426 $[M]^+$. (Found C, 61.96; H, 8.23. $C_{22}H_{34}O_8$ requires: C, 61.97; H, 7.98%.)

Maoyerabdosin (**9**). Needles (0.1g), mp 243–245°, (from MeOH), $[\alpha]_D^{22}$ −30° (MeOH; *c* 0.1). IR ν_{max} 3550, 3490, 3440, 3280, 1715, 1360, 1220 cm^{-1}; ^1H NMR (C_5D_5N): δ8.40, 5.30 (each 1H, *br s*, OH), 5.80 (1H, *d*, *J* = 3.9 Hz, OH-1β), 5.74 (1H, *d*, *J* = 5.2 Hz, H-6α), 4.92 (1H, *d*, *J* = 3.1 Hz, OH-15β), 4.49, 4.37 (each 1H, AB, *d*, *J* = 11.3 Hz, H_2-17), 4.42 (1H, *d*, *J* = 3.1 Hz, H-15α), 4.19, 4.08 (each 1H, AB, *dd*, *J* = 1.0, 9.4 Hz, H_2-20), 3.75 (1H, *m*, H-1α), 3.22 (1H, *ddd*, *J* = 1.0, 5.5, 11.7 Hz, H-9β), 2.47 (1H, *m*, H-12β), 2.28 (2H, *m*, H-5β, H-13α), 2.17 (3H, *s*, OAc), 2.15 (1H, *m*, H-3β), 2.08 (1H, *dd*, *J* = 3.8, 12.8 Hz, H-14β), 2.06 (1H, *dd*, *J* = 6.5, 12.8 Hz, H-11β), 2.00 (1H, *d*, *J* = 12.9 Hz, 14α-H), 1.93 (1H, *s*, OAc), 1.70 (3H, *m*, H_2-2, H-12α), 1.60 (1H, *m*, H-11α), 1.20 (1H, *m*, H-3α), 1.17, 0.92 (each 3H, *s*, Me_2-4); ^{13}C NMR (C_5D_5N): δ65.0 (*d*, C-1), 27.4 (*t*, C-2), 34.1 (*t*, C-3), 33.9 (*s*, C-4), 50.9 (*d*, C-5), 75.4 (*d*, C-6), 96.0 (*s*, C-7), 52.8 (*s*, C-8), 36.8 (*d*, C-9), 40.8 (*s*, C-10), 14.8 (*t*, C-11), 19.8 (*t*, C-12), 36.5 (*d*, C-13), 25.9 (*t*, C-14), 72.4 (*d*, C-15), 77.6 (*s*, C-16), 71.1 (*t*, C-17), 32.2 (*q*, C-18), 22.8 (*q*, C-19), 65.6 (*t*, C-20), 171.0, 169.7, 21.4, 20.3 (2 × OAc); HRMS *m/z* found: 468.2357 $[M]^+$. $C_{24}H_{36}O_9$ requires: 468.2359. (Found: C, 61.41; H, 7.78. Calc. for $C_{24}H_{36}O_9$: C, 61.54; H, 7.69%.)

Rabdophyllin H (**6**). Needles (2 g), mp 220–222°, (from MeOH). IR ν_{max} 3449, 3350, 1750, 1740, 1720, 1380, 1240 cm^{-1}; ^1H NMR (C_5D_5N): δ8.31, 7.90 (each 1H, *s* OH), 5.76 (1H, *d*, *J* = 6.5 Hz, H-6α), 5.27 (1H, *s*, H-15α), 4.97 (1H, *s*, H-14α), 4.88, 4.67 (each 1H, *d*, *J* = 11.0 Hz, H_2-17), 4.16, 3.96 (each 1H, *d*, *J* = 9.2 Hz, H_2-20), 2.40 (1H, *br d*, *J* = 9.0 Hz, H-13α), 2.18, 1.95 (each 3H, *s*, 2 × OAc), 1.68 (1H, *d*, *J* = 6.5 Hz, H-5β), 1.14, 0.92 (each 3H, *s*, Me_2-4); ^{13}C NMR (C_5D_5N): δ31.1 (*t*, C-1), 18.9 (*t*, C-2), 41.2 (*t*, C-3), 33.7 (*s*, C-4), 54.8 (*d*, C-5), 75.4 (*d*, C-6), 98.1 (*s*, C-7), 53.9 (*s*, C-8), 44.9 (*d*, C-9), 36.0 (*s*, C-10), 14.6 (*t*, C-11), 21.4 (*t*, C-12), 44.0 (*d*, C-13), 71.5 (*d*, C-14), 73.5 (*d*, C-15), 77.5 (*s*, C-16), 73.5 (*t*, C-17), 32.5 (*q*, C-18), 21.5 (*q*, C-19), 66.1 (*t*, C-20), 171.1, 169.6, 20.8, 20.8 (2 × OAc); HRMS *m/z* found: 468.2352 $[M]^+$. $C_{24}H_{36}O_9$ requires: 468.2359..

Ponicidin (**10**). Needles (1 g), mp 240–242°. IR ν_{max} 3350, 1728, 1640, 1060 cm^{-1}; ^1H NMR (C_5D_5N): δ6.19 (1H, *s*, Ha-17), 5.91 (1H, *s*, H-20), 5.31 (1H, *s*, Hb-17), 5.04 (1H, *d*, *J* = 6.3 Hz, H-14β), 4.22 (1H, *d*, *J* = 1.1 Hz, H-6α), 3.83 (1H, *t*, *J* = 8.4 Hz, H-1β), 3.21 (1H, *m*, *H*-13α), 2.95 (1H, *d*, *J* = 7.0 Hz, H-9β), 2.93 (1H, *m*, H-12α), 2.34 (1H, *dd*, *J* = 7.0, 14.0 Hz, H-11α), 1.64 (1H, *d*, *J* = 1.2 Hz, H-5β), 1.05, 0.94 (each 3H, *s*, Me_2-4); HRMS *m/z* found: 362.1740 $[M]^+$, $C_{20}H_{26}O_6$ requires: 362.1729.

Oridonin (**11**). Needles (10 g), mp 247–249° (from MeOH). IR ν_{max} 3420, 3200, 1700, 1640, 1060 cm^{-1}; ^1H NMR (C_5D_5N): δ9.07, 7.40 (each 1H, *br s*, OH), 6.90 (1H, *d*, *J* = 10 Hz, OH-6β), 6.27, 5.51 (each 1H, *s*, H_2-17), 5.87 (1H, *br s*, OH), 5.51 (1H, *s*, H-14α), 4.77, 4.38 (each 1H, AB, *d*, *J* = 10 Hz, H_2-20), 4.24 (1H, *dd*, *J* = 7.0, 10.0 Hz, H-6α), 3.61 (1H, *t*, *J* = 7.0 Hz, H-1β), 3.20 (1H, *d*, *J* = 9.0 Hz, H-13α), 1.29, 1.14 (each 3H, *s*, Me_2-4); HRMS *m/z* found: 364.18766 $[M]^+$, $C_{20}H_{28}O_6$ requires: 364.1886.

Enmenol (**12**). Needles (2 g), mp 255–257°, (from MeOH). IR ν_{max} 3300, 3250, 1660, 1060 cm^{-1}; ^1H NMR (C_5D_5N): δ8.50 (1H, *br s*, OH), 7.85 (2H, *br s*, 2 × OH), 6.50 (1H, *br s*, OH), 5.75, 5.68 (each 1H, *s*, H_2-17), 5.36 (1H, *s*, H-15α), 5.16 (1H, *s*, H-14α), 4.86, 4.46 (each 1H, *d*, *J*

= 10.0 Hz, H_2-20), 4.28 (1H, *d*, *J* = 5.0 Hz, H-6α), 3.74 (1H, *t*, *J* = 8.0 Hz, H-1β), 2.91–2.87 (2H, *m*), 1.23, 1.19 (each 3H, *s*, Me_2-4); ^{13}C NMR (C_5D_5N): δ73.0 (*d*, C-1), 30.7 (*t*, C-2), 39.3 (*t*, C-3), 33.9 (*s*, C-4), 57.7 (*d*, C-5), 73.8 (*d*, C-6), 99.8 (*s*, C-7), 53.6 (*s*, C-8), 46.4 (*d*, C-9), 41.3 (*s*, C-10), 18.5 (*t*, C-11), 33.1 (*t*, C-12), 45.3 (*d*, C-13), 73.5 (*d*, C-14), 76.1 (*d*, C-15), 161.3 (*s*, C-16), 109.0 (*t*, C-17), 33.3 (*q*, C-18), 21.1 (*q*, C-19), 65.5 (*t*, C-20), HRMS *m/z* found: 366.204 $[M]^+$, $C_{20}H_{30}O_6$ requires: 366.2042.

7,11,14-*Triacetyl macrocalyxin F* (**3**). Macrocalyxin F (**1**) (30 mg) dissolved in a mixt. of Ac_2O and pyridine (1:1, 2 ml) was kept for 48 hr at room temp. Usual work-up and prep. TLC (CH_2Cl_2–Me_2CO, 9:1) of the crude product gave the triacetate **3** (15 mg), as needles mp 95–97°. IR ν_{max} 1740, 1727, 1705, 1645, 1249 cm^{-1}; ^{1}H NMR (C_5D_5N): δ9.38 (1H, *s*, CHO-4β), 6.26, 5.51 (each 1H, *s*, H_2-17), 6.09 (1H, *s*, H-14α), 5.67 (1H, *dd*, *J* = 6, 13 Hz, H-7β), 4.25, 4.22 (each 1H, *d*, *J* = 10 Hz, H_2-20), 2.94 (1H, *s*, H-9β), 2.09, 1.94, 1.83 (each 3H, *s*, 3 × OAc), 0.89 (3H, *s*, Me-4α); ^{13}C NMR (C_5D_5N): δ36.3 (*t*, C-1), 18.3 (*t*, C-2), 31.2 (*t*, C-3), 50.0 (*s*, C-4), 42.7 (*d*, C-5), 26.2 (*t*, C-6), 72.4 (*d*, C-7), 57.3 (*s*, C-8), 59.4 (*d*, C-9), 47.6 (*s*, C-10), 109.4 (*s*, C-11), 42.7 (*d*, C-12), 41.8 (*d*, C-13), 73.6 (*d*, C-14), 202.8 (*s*, C-15), 148.7 (*s*, C-16), 117.8 (*t*, C-17), 204.1 (*s*, C-18), 13.3 (*q*, C-19), 69.9 (*t*, C-20), 170.5, 169.8, 169.5, 21.9, 21.2, 20.9 (3 × OAc); MS *m/z*: 488 $[M]^+$, HRMS *m/z* found: 428.1833 $[M - HOAc]^+$. $C_{24}H_{28}O_7$ requires: 428.1834.

Macrocalyxin F 7-,14-*monoacetonide* (**4**). Macrocalyxin F (**1**) (20 mg) was dissolved in Me_2CO (20 ml) and anhydrous Cu_2SO_4 (2 g) was added to the soln. The reaction was refluxed gently for 3 days. The anhydrous $CuSO_4$ was filtered off and the solvent was removed under red. pres. to give the monoacetonide (20 mg). ^{1}H NMR (C_5D_5N): δ9.32 (1H, *s*, CHO-4β), 4.10, 3.80 (each 1H, *d*, *J* = 10 Hz, H_2-20), 4.00 (1H, *dd*, *J* = 4, 12 Hz, H-7β), 1.50, 1.30 (each 3H, $^{-O}_{-O}C^{Me}_{Me}$), 0.96 (3H, *s*, Me-4α).

Dihydromacrocalyxin F (**13**). Macrocalyxin F (**1**) (50 mg) was dissolved in MeOH (10 ml) and 10% Pd-C (15 mg) was added to the soln. The mixt. was hydrogenated for 1 hr. The catalyst was filtered off and the solvent was removed under red. pres. to give the dihydro compound (50 mg) as needles from MeOH, mp 254–256°. ^{1}H NMR (C_5D_5N): δ9.15 (1H, *s*, CHO-4β), 5.60 (1H, *d*, *J* = 1 Hz, H-14α), 4.80 (1H, *m*, H-7β), 4.00, 4.10 (each 1H, *d*, *J* = 10 Hz, H_2-20), 2.55 (1H, *d*, *J* = 3 Hz, H-13α), 3.38 (1H, *m*, H-16), 1.16 (3H, *d*, *J* = 9 Hz, Me-16), 0.90 (3H, *s*, Me-4α); MS *m/z*: 364 $[M]^+$; $\Delta\varepsilon_{307} - 0.77$ (MeOH).

7,14-*Diacetyl macrocalyxin G* (**7**). Macrocalyxin G (**5**) (15 mg) dissolved in a mixt. of Ac_2O and pyridine (1:1, 2 ml) was kept for 48 hr at room temp. Usual work-up and prep. TLC (CH_2Cl_2–Me_2CO, 9:1) of the crude product gave the diacetate **7** (8 mg), as needles mp 168–170°. IR ν_{max} 3500, 3440, 1745, 1735, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ5.34 (1H, *s*, H-14α), 5.30 (1H, *d*, *J* = 6.3 Hz, H-6α), 4.28 (2H, OH), 4.20 (1H, *s*, H-15α), 4.10, 3.83 (each 1H, *d*, *J* = 10 Hz, H_2-20), 4.05 (2H, *s*, H_2-17), 2.15, 2.10, 2.08 (each 3H, *s*, 3 × OAc), 1.13, 0.85 (each 3H, *s*, Me_2-4); ^{1}H NMR (C_5D_5N): δ5.98 (1H, *s*, H-14α), 5.59 (1H, *d*, *J* = 6.8 Hz, H-7α), 4.78 (1H, *d*, *J* = 3.9 Hz, H-15α), 4.65, 4.63 (each 1H, *d*, *J* = 10.0 Hz, H_2-17), 4.10, 3.97 (each 1H, *d*, *J* = 10.0 Hz, H_2-20), 2.15, 2.05, 1.95 (each 3H, *s*, 3 × OAc), 1.26, 1.03 (each 3H, *s*, Me_2-4); HRMS *m/z* found: 510.2474 $[M]^+$. $C_{26}H_{38}O_{10}$ requires: 510.2465.

Maoyerabdosin (**9**). Needles, mp 243–245°, (from MeOH), $[\alpha]_D^{25}$ −30° (MeOH; *c* 0.1). IR ν_{max} 3550, 3490, 3440, 3280, 1715, 1360, 1220 cm^{-1}; ^{1}H NMR (C_5D_5N): δ8.40, 5.30 (each 1H, *br s*, OH), 5.80 (1H, *d*, *J* = 3.9 Hz, OH-1β), 5.74 (1H, *d*, *J* = 5.2 Hz, H-6α), 4.92 (1H, *d*, *J* = 3.1 Hz, OH-15β), 4.49, 4.37 (each 1H, AB, *d*, *J* = 11.3 Hz, H_2-17), 4.42 (1H, *d*, *J* = 3.1 Hz, H-15α), 4.19, 4.08 (each 1H, AB, *dd*, *J* = 1.0, 9.4 Hz, H_2-20), 3.75 (1H, *m*, H-1α), 3.22 (1H, *ddd*, *J* = 1.0, 5.5, 11.7 Hz, H-9β), 2.47 (1H, *m*, H-12β), 2.28 (2H, *m*, H-5β, H-13α), 2.17 (3H, *s*, OAc), 2.15 (1H, *m*, H-3β), 2.08 (1H, *dd*, *J* = 3.8, 12.8 Hz, H-14β), 2.06 (1H, *dd*, *J* = 6.5, 12.8 Hz, H-11β), 2.00 (1H, *d*, *J* = 12.9 Hz, H-14α), 1.93 (3H, *s*, OAc), 1.70 (3H, *m*, H_2-2, H-12α), 1.60 (1H, *m*, H-11α), 1.20 (1H, *m*, H-3α), 1.17, 0.92 (each 3H, *s*, Me_2-4); ^{13}C NMR (C_5D_5N): δ65.0 (*d*, C-1), 27.4 (*t*, C-2), 34.1 (*t*, C-3), 33.9 (*s*, C-4), 50.9 (*d*, C-5), 75.4 (*d*, C-6), 96.0 (*s*, C-7), 52.8 (*s*, C-8), 36.8 (*d*, C-9), 40.8 (*s*, C-10), 14.8 (*t*, C-11), 19.8 (*t*, C-12), 36.5 (*d*, C-13), 25.9 (*t*, C-14), 72.4 (*d*, C-15), 77.6 (*s*, C-16), 71.1 (*t*, C-17), 32.2 (*q*, C-18), 22.8 (*q*, C-19), 65.6 (*t*, C-20), 171.0, 169.7, 21.4, 20.3 (2 × OAc); HRMS *m/z* found: 468.2357 $[M]^+$. Found C, 61.41; H, 7.78: $C_{24}H_{36}O_9$ requires: 468.2359. Found: C, 61.41; H, 7.78. $C_{24}H_{36}O_9$ requires: C, 61.54; H, 7.69%.

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