Diterpenoids from *Isodon adenantha*

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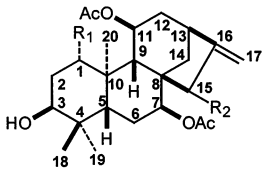
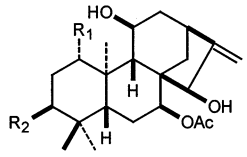
Eleven new diterpenoids, adenanthins B−L (**1**−**11**), together with five known analogues, calcicolin B (**12**), adenanthin (**13**), weisiensin A (**14**), nervosanin (**15**), and forrestin C (**16**), were isolated from the aerial parts of *Isodon adenantha*. The structures of **1**−**11** were elucidated on the basis of spectral methods, as well as the X-ray crystallographic analysis of **11**. Compounds **2**, **5**, and **14** showed significant inhibitory activities against K562 cells, with IC_{50} values less than 4.0 μg/mL, respectively.

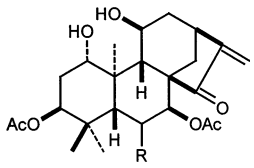
Isodon species are rich in *ent*-kaurane diterpenoids, some of which have antitumor, antibacterial, and antiinflammatory activities.[1−3] As a medicinal herb used to treat enteritis and dysentery in folk medicine in Yunnan Province,[1] *Isodon adenantha* (Diels) Hara has been investigated phytochemically several times since 1987, leading to the isolation of three *ent*-kaurane diterpenoids.[4−6] As part of a research program on the bioactive constituents of *Isodon* species, we have investigated *I. adenantha* collected from Dali, Yunnan Province. As a result, 11 new diterpenoids, adenanthins B−L (**1**−**11**), together with five known analogues, calcicolin B (**12**), adenanthin (**13**), weisiensin A (**14**), nervosanin (**15**), and forrestin C (**16**), were isolated from the EtOAc extract of the leaves. Some of those compounds were evaluated for their cytotoxicity against K562 cells. In this paper, we wish to report the structural elucidation of these new compounds and the results of bioactivity testing toward the K562 tumor cell line.



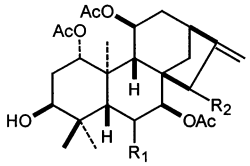
1 R_1 = AcO R_2 = β-OH
2 R_1 = AcO R_2 = =O
3 R_1 = AcO R_2 = β-AcO
6 R_1 = OH R_2 = =O



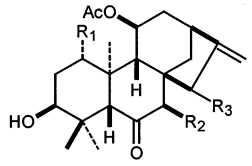
4 R_1 = OH R_2 = AcO
7 R_1 = AcO R_2 = OH



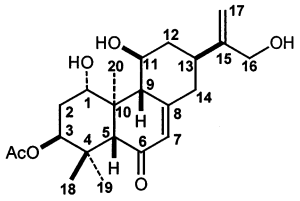
5 R = H
8 R = α-OH



9 R_1 = =O R_2 = β-OH
13 R_1 = =O R_2 = =O
14 R_1 = α-OH R_2 = =O
15 R_1 = =O R_2 = β-AcO
16 R_1 = α-OH R_2 = β-OH



10 R_1 = AcO R_2 = OH R_3= β-AcO
12 R_1 = OH R_2 = OAc R_3= =O



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Results and Discussion

The 70% aqueous acetone extract prepared from the leaves of *I. adenantha* was partitioned between EtOAc and H_2O and then *n*-BuOH and H_2O. Repeated column chromatography of the EtOAc layer on silica gel and RP-8 yielded adenanthins B−L (**1**−**11**) and five known *ent*-kauranoids (**12**−**16**).

Adenanthin B (**1**), obtained as colorless crystals, was shown to possess a molecular formula of $C_{26}H_{38}O_8$ from the HREIMS molecular ion peak observed at *m*/*z* 478.2605, combined with an analysis of its ^1H and ^{13}C NMR spectral data. The IR, MS, and NMR data of **1** indicated the presence of three acetoxyl groups, three methyl groups, five methylenes (including one exomethylene group), eight methines (including five oxygenated methines), and four quaternary carbons. Considering the structural type of the diterpenoids isolated from *I. adenantha* previously,[4−6] **1** was tentatively assigned as an *ent*-kauranoid, which was further verified by 2D NMR experiments. From its $^1H-^1H$ COSY and HMQC spectra were revealed the following partial structures: $-CHCH_2CH-$ (C-1 to C-3), $-CHCH_2-CH-$ (C-5 to C-7), and $-CHCHCH_2CHCH_2-$ (C-9, C-11 to C-14). In the HMBC spectrum, the partial structures were correlated to constitute an *ent*-kauranoid because of the observation of the correlations between Me-20 (δ 1.28, 3H, s) (with C-1, C-5, C-9, and C-10), H-5 (δ 2.58, 1H, dd, J = 1.8, 12.4 Hz) (with C-3, C-4, C-6, C-7, C-10, and Me-18, 19), H-11 (δ 5.90, 1H, t, J = 3.8 Hz) (with C-8, C-10, C-12, and C-13), and H-15 (δ 4.43, 1H, dd, J = 2.5, 11.1 Hz) (with

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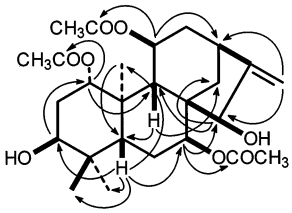

Figure 1. Selected HMBC correlations of **1**.

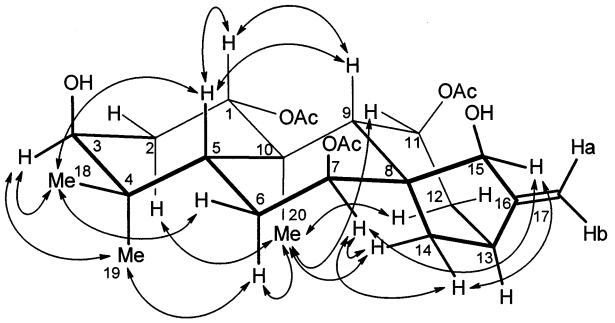

Figure 2. Key ROESY correlations of **1**.

C-7, C-14, and C-16). According to the cross-peaks in the HMBC spectrum and the analysis of MS and NMR spectra of **1**, three acetoxyl groups were placed at C-1, C-7, and C-11 and two hydroxyl groups at C-3 and C-15, respectively (Figure 1).

The relative configurations of the substituents were revealed by the analysis of the ROESY spectrum of **1**, and correlations of H-1β with H-5β and -9β, H-3α with Me-18 and -19, H-7α with H-14α, H-11α with Me-20, and H-15α with H-14β could be clearly observed from the spectrum (Figure 2), suggesting that the substituents at C-1, C-3, C-7, C-11, and C-15 possess an α-, β-, β-, β-, and β-orientation, respectively. Thus, **1** was elucidated as 3β,15β-dihydroxy-1α,7β,11β-triacetoxy-*ent*-kaur-16-ene.

Adenanthin C (**2**) was obtained as colorless cubes and gave *m/z* 476.2347 $[M]^+$ for $C_{26}H_{36}O_8$ by HREIMS. A general analysis of all the spectra obtained revealed **2** to be an *ent*-kauranoid also, and its structure was quite similar to that of **1** except for the moiety at C-15. A carbonyl group at the C-15 position was evident for **2** instead of a hydroxyl group at the same position in **1**. The carbonyl group was conjugated with an exocyclic methylene in **2**, as suggested by the following spectral data: UV (MeOH) λ_{max} (log ϵ) 238 (3.97) nm; ^{1}H NMR δ 5.87 and 5.10 (each 1H, s); ^{13}C NMR δ 112.6 (t), 151.6 (s), and 204.7 (s). Moreover, the cross-peaks in the ROESY spectrum of **2** indicated that the other substituents in **2** had the same orientations as those in **1**. Therefore, **2** was determined as 3β-hydroxy-1α,7β,1β-triacetoxy-*ent*-kaur-16-en-15-one.

HREIMS of adenanthin D (**3**) indicated it has a molecular formula of $C_{28}H_{40}O_9$ (*m/z* 520.2621). Comparison of the IR, MS, and 1D and 2D NMR spectral data of **3** with those of **1** clearly revealed that the structure of **3** was very similar to that of **1**. The only difference between these two compounds was the group at the C-15 position, and there was an acetoxyl group at the C-15 in **3** instead of a hydroxyl group at this position in **1**. Also, it was evident from the ROESY spectrum of **3** that all substituents possess the same orientations as those of **1**. Accordingly, **3** was finally deduced as 3β-hydroxy-1α,7β,11β,15β-tetraacetoxy-*ent*-kaur-16-ene.

Inspection of the IR, MS, and 1D and 2D NMR spectral data led to the conclusion that adenanthin E (**4**) is composed of a basic skeleton as an *ent*-kaurene diterpenoid having five substituents (three hydroxyl groups and two acetoxyl groups). According to the cross-peaks appearing in the HMBC spectrum, the acetoxyl groups could be located at C-3 and C-7, respectively, while the hydroxyl groups were connected to C-1, C-11, and C-15. These substituents were determined to be 1α-, 3β-, 7β-, 11β-, and 15β-oriented based on an analysis of the ROESY spectrum. Therefore, **4** was elucidated as 1α,11β,15β-trihydroxy-3β,7β-diacetoxy-*ent*-kaur-16-ene.

Its IR, MS, and NMR spectra indicated that adenanthin F (**5**) is also a polysubstituted *ent*-kaurene diterpenoid. Due to the UV absorption at 240 nm (log ϵ 3.82) and the IR spectral bands at 1705 and 1645 cm^{-1}, as well as the ^{1}H NMR δ 5.88 and 5.16 (each 1H, s) and ^{13}C NMR δ 110.7 (t), 152.6 (s), and 205.5 (s) signals, it was determined that an exomethylene group and a keto group were conjugated. A comparison of all the spectra of **5** with those of **4** clearly showed that the two compounds were similar apart from the C-15 position. Therefore, **5** was characterized as 1α,11β-dihydroxy-3β,7β-diacetoxy-*ent*-kaur-16-en-15-one.

Compound **6** was obtained as an amorphous powder, possessing a molecular formula of $C_{24}H_{34}O_7$ by HREIMS (*m/z* 434.2269). A careful analysis of its IR, MS, 1D NMR, and 2D NMR spectral data enabled the conclusion to be reached that the structure of adenanthin G (**6**) is closely comparable to that of **2**. The only difference between these two compounds is that a hydroxyl group, rather than an acetoxyl group, could be located at the C-1α position in **6**. Adenanthin G (**6**) was therefore concluded to be 1α,3β-dihydroxy-7β,11β-diacetoxy-*ent*-kaur-16-en-15-one.

Adenanthin H (**7**) was determined to possess the same molecular formula and to have the same substituents on the same basic skeleton as adenanthin E (**4**) as deduced by comparing their spectral data. The two compounds differed only in the nature of the substituents at C-1 and C-3. The hydroxyl group at C-1 and the acetoxyl group at C-3 in compound **4** were transposed in **7**, which was confirmed by the observation of the correlations between H-1 with OAc in the HMBC spectrum and H-3 with OH in the ^{1}H$-^1$H COSY spectrum. Thus, **7** was elucidated as 3β,11β,15β-trihydroxy-1α,7β-diacetoxy-*ent*-kaur-16-ene.

Compounds **1**$-$**7** are all the *ent*-kaurene diterpenoids lacking any substituent at C-6 while possessing a substituent at C-7. Characteristically, these compounds exhibit a ^{13}C NMR signal (t, C-6) at the region δ 24.1$-$25.1 (Table 1). However, this characteristic signal disappeared for adenanthin I (**8**). Compound **8** was obtained as colorless crystals, having a molecular formula of $C_{24}H_{34}O_8$ by HREIMS (*m/z* 450.2270, calcd 450.2254) and possessing one more oxygen atom than adenanthin F (**5**). Comparison of the NMR spectral data of **8** with those of **5** indicated similarities in most of their structures apart from the C-6 substituents. Due to the absence of any characteristic signal at δ 24.1$-$25.1 in the ^{13}C NMR spectrum of **8**, this compound could be assigned as the 6-hydroxy derivative of **5**, which was verified by the signal at δ 69.5 (d, C-6) in the ^{13}C NMR spectrum and correlations of H-6 (δ 4.39, 1H, br s) with OH (δ 6.92, 1H, d, J = 4.44 Hz), H-6 with H-5 (δ 2.17, 1H, s), and H-6 with H-7 (δ 5.62, 1H, d, J = 3.64 Hz) in the ^{1}H$-^1$H COSY and HMQC NMR spectra. Unambiguous assignments of the stereochemistry of **8** were obtained from a ROESY experiment. From the correlations observed, it could be concluded that the substituents were of the same orientation as those of **5** except for the C-6 substituent. From the correlations of H-6β with H-5β and H-6β with Me-18, OH-6 could be assigned with the α-orientation.

Table 1. ^{13}C NMR Spectral Data for Compounds **1**−**7** (C_5D_5N, 100.6 MHz, δ in ppm)

carbon	1	2	3[a]	4	5	6[a]	7
1	80.3 d	80.5 d	80.3 d	76.7 d	76.2 d	75.7 d	81.4 d
2	33.7 t	33.6 t	33.6 t	34.4 t	34.0 t	37.6 t	33.8 t
3	75.2 d	75.6 d	75.1 d	78.9 d	79.0 d	75.8 d	75.6 d
4	37.7 s	38.0 s	37.6 s	36.6 s	36.6 s	37.6 s	38.0 s
5	39.1 d	39.5 d	39.1 d	40.7 d	40.9 d	39.3 d	39.7 d
6	24.8 t	25.0 t	24.2 t	25.0 t	25.1 t	25.0 t	25.0 t
7	78.7 d	73.0 d	79.5 d	79.4 d	73.2 d	73.0 d	79.8 d
8	48.0 s	51.0 s	47.1 s	48.6 s	51.1 s	51.0 s	48.6 s
9	50.2 d	56.3 d	51.5 d	53.9 d	61.1 d	57.3 d	53.1 d
10	43.0 s	44.0 s	43.0s	43.8 s	44.8 s	44.8 s	43.0 s
11	70.6 d	70.2 d	69.0 d	66.1 d	66.6 d	71.6 d	66.3 d
12	40.2 t	39.3 t	40.3 t	43.0 t	41.4 t	38.3 t	43.6 t
13	38.6 d	37.0 d	38.9d	39.8 d	37.5 d	36.8 d	39.8 d
14	35.4 t	36.3 t	36.0 t	36.0 t	36.3 t	35.9 t	36.5 t
15	81.4 d	204.7 s	79.9 d	81.0 d	205.5 s	205.2 s	81.0 d
16	158.3 s	151.6 s	153.1 s	159.4 s	152.6 s	151.7 s	159.2 s
17	105.7 t	112.6 t	106.2 t	106.0 t	110.7 t	111.7 t	106.6 t
18	28.8 q	29.3 q	28.8 q	27.7 q	27.7 q	29.0 q	28.9 q
19	22.2 q	22.5 q	22.1 q	21.7 q	21.8 q	22.3 q	22.7 q
20	14.2 q	15.1 q	14.2 q	13.9 q	14.3 q	14.3 q	14.5 q
OAc	170.7 s	170.7 s	170.8 s	170.9 s	170.5 s	170.4 s	171.7 s
	170.4 s	170.5 s	170.4 s	170.5 s	170.4 s	169.7 s	170.8 s
	169.0 s	169.6 s	170.0 s	21.8 q	21.8 q	21.6 q	21.9 q
	21.9 q	22.2 q	169.9 s	21.0 q	21.0 q	21.3 q	21.8 q
	21.5 q	21.9 q	22.1 q				
	21.3 q	21.4 q	21.4 q				
			21.2 q				
			21.1 q				

[a] Recorded at 125.8 MHz.

Therefore, **8** was characterized as 1α,6α,11β-trihydroxy-3β,7β-diacetoxy-*ent*-kaur-16-en-15-one.

Adenanthin J (**9**), an amorphous powder, was found to possess the molecular formula $C_{26}H_{36}O_9$ from the HREIMS molecular ion peak at *m/z* 492.2374 (calcd 492.2359). Its IR, MS, and 1D and 2D NMR spectral data suggested **9** to be a polysubstituted *ent*-kaurene diterpenoid, with the ketone and exomethylene functionalities being unconjugated due to a lack of any significant absorption in the UV spectrum. Analysis of the 2D NMR spectral data led to the conclusion that the ketone was at C-6 on the basis of the correlations of H-5 (δ 4.05, 1H, s) with C-6 (δ 207.7, s) and H-7 (δ 4.97, 1H, overlap) with C-6. Moreover, the C-1, C-7, and C-11 positions were each substituted by an acetoxyl group, while C-3 and C-15 were hydroxylated on the basis of a detailed spectral analysis. The relative stereochemistry of all substituents of **9** was assigned on the basis of ROESY NMR correlations. Thus, the structure of **9** was deduced as 3β,15β-dihydroxy-1α,7β,11β-triacetoxy-*ent*-kaur-16-en-6-one.

Adenanthin K (**10**) was also assigned the molecular formula of $C_{26}H_{36}O_9$ (found *m/z* 492.2382; calcd 492.2359). Inspection of its MS and 1D and 2D NMR spectra suggested that not only the basic skeleton of **10** but also the substituents were the same as adenanthin J (**9**). The ketone and exomethylene functionalities were also unconjugated, on the basis of the UV spectrum. The differences between the two compounds were in the substituents at C-7 and C-15. Unlike the structure of adenanthin J (**9**), there was a hydroxyl group at C-7 and an acetoxyl group at C-15 in **10**, which was confirmed by the following evidence: the upfield shift of C-7 (δ 84.9), C-15 (δ 80.0), and C-16 (δ 153.4) and the downfield shift of C-6 (δ 213.7) in the ^{13}C NMR spectrum, as well as the observation of the correlations between H-15 with OAc in the HMBC spectrum and H-7 with OH in the $^1H-^1H$ COSY spectrum. The relative configurations of the substituents were indicated from a ROESY experiment. Thus, **10** was elucidated as 3β,7β-dihydroxy-1α,11β,15β-triacetoxy-*ent*-kaur-16-en-6-one. Adenanthin K (**10**) is the first *ent*-kaurene diterpenoid to be isolated from the *Isodon* genus in which a hydroxyl group is located at C-7 with a ketone at C-6.

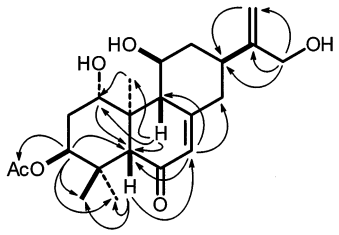

Figure 3. Selected HMBC correlations of **11**.

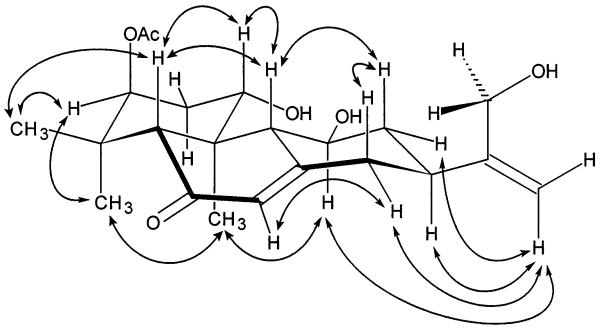

Figure 4. ROESY correlations of **11**.

Adenanthin L (**11**), obtained as colorless crystals, was assigned a molecular formula of $C_{22}H_{32}O_6$, as deduced by HREIMS (obsd *m/z* 392.2199, calcd 392.2223) and analysis of its ^{13}C NMR spectrum. It contained an acetoxyl group as determined from the EIMS fragment ion peak at *m/z* 332 $[M - AcOH]^+$ and the ^{13}C NMR signals at δ 170.15 (s) and 20.93 (q). Also revealed in the ^{13}C NMR spectrum of **11** were two double bonds including an exomethylene group (δ 128.0 d, 157.8 s; 153.6 s, and 108.2 t) and a ketone (δ 199.3 s). Due to the absorption in the UV spectrum at 243 nm (log ϵ 4.06), one of the olefinic bonds was concluded to be conjugated with the ketone. According to the carbon number for the basic skeleton and the characteristic signals in the NMR spectra, **11** was assigned as a diterpenoid constituted by three rings. The $^1H-^1H$ COSY and HMQC spectra of **11** revealed the following partial structures: a substituted cyclohexane attached with two olefinic bonds (ring C) and $-CHCH_2CH-$ (C-1 to C-3). These were connected to form a tricycloditerpene based on the HMBC spectral correlations of H-3 (with C-5, Me-18, -19, and OAc), H-5 (with C-1, C-7, Me-18, -19, and -20), H-9 (with C-1, C-5, C-12, and Me-20), and H-16 (with C-13, C-15, and C-17) (Figure 3). Moreover, because of the correlations of H-5 with Me-18, H-5 with H-1, H-5 with H-9, Me-20 with H-11, and Me-19 with Me-20 in the ROESY spectrum of **11** (Figure 4), combined with the biogenetic analogy between **11** and the other diterpenoids (**1**−**10**, **12**−**16**) isolated from the same plant, **11** was deduced as an *ent*-abietane diterpenoid with the substituents at C-1, C-3, and C-11 being in the α-, β-, and β-orientation, respectively. The structure and relative stereochemistry were also supported by the results of single-crystal X-ray crystallographic analysis for compound **11** (Figure 5). Thus, **11** was determined as 1α,11β,16-trihydroxy-3β-acetoxy-*ent*-abieta-7,15(17)-dien-6-one.

Five known diterpenoids isolated from *I. adenantha* were identified as calcicolin B (**12**),[7] adenanthin (**13**),[4] weisiensin A (**14**),[8] nervosanin (**15**),[9] and forrestin C (**16**),[10] respectively, by comparing their spectral data with those reported in the literature. Compounds **12**, **15**, and **16** were obtained from this plant for the first time.

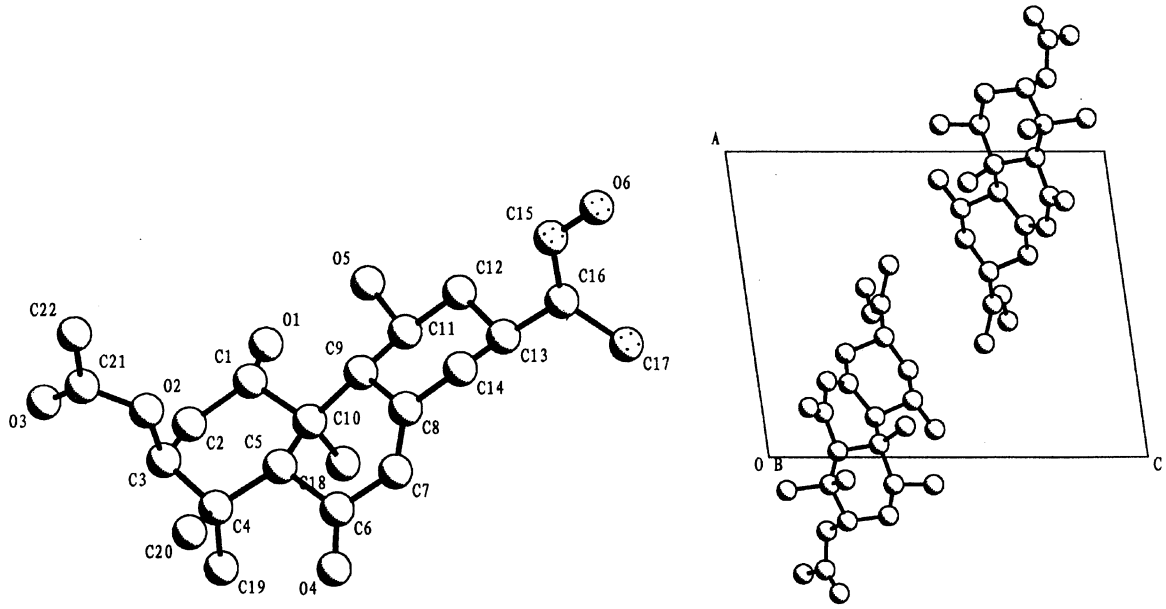

Figure 5. Crystal structure of **11**.

Selected diterpenoids (**1**−**5**, **7**, **8**, **11**, **13**−**15**) were tested for their ability to inhibit human tumor K562 cells, using a previously described method,[3] with *cis*-platinum as a positive reference substance. Compounds **2**, **5**, and **14** showed significant inhibitory activities against K562 cells with IC_{50} = 3.3, 3.6, and 3.3 μg/mL, respectively (*cis*-platinum: IC_{50} = 1.9 μg/mL).

Experimental Section

General Experimental Procedures. Melting points (uncorrected) were obtained on an XRC-1 apparatus. Optical rotations were taken on a JASCO DIP-370 digital polarimeter. UV spectra were obtained on a UV 210A spectrometer. IR spectra were measured on a Bio-Rad FTS-135 spectrometer with KBr pellets. 1D and 2D NMR spectra were run on Bruker AM-400 and DRX-500 instruments with TMS as internal standard. MS were recorded on a VG Auto Spec-3000 spectrometer. Si gel (200−300 mesh) for column chromatography and TLC were obtained from Qingdao Marine Chemical Factory, Qingdao, People's Republic of China.

Plant Material. The aerial parts of *Isodon adenantha* were collected in Dali, Yunnan Province, People's Republic of China, in July 1997, and were air-dried. The identity of the plant material was verified by Prof. Xi-Wen Li, and a voucher specimen (KIB 97-07-88 Li) has been deposited in the Laboratory of Phytochemistry, Kunming Institute of Botany.

Extraction and Isolation. The dried and powdered leaves (7.43 kg) were extracted with 70% Me_2CO (3 × 30 L) and filtered. The filtrate was concentrated in vacuo and extracted with EtOAc and *n*-BuOH, successively. The EtOAc extract (200 g) was subjected to column chromatography on a silica gel (200−300 mesh, 2.3 kg) column eluting with a $CHCl_3$−Me_2CO (1:0−0:1) gradient system to yield fractions I−V. Fraction II (39.1 g) was further purified by repeated column chromatography over silica gel developing with petroleum ether−2-propanol (25:1) and RP-8 (MeOH−H_2O, 5.5:4.5) to afford **1** (2.45 g), **2** (15.10 g), and **13** (1.10 g). Fraction III (29.9 g) was subjected to column chromatography over Si gel and RP-8 eluting with $CHCl_3$−MeOH (50:1), cyclohexane−2-propanol (10:1), and MeOH−H_2O (5.5:4.5), respectively, to yield **3** (722 mg), **5** (667 mg), **6** (27 mg), **9** (183 mg), **10** (73 mg), **12** (43 mg), **14** (132 mg), **15** (131 mg), and **16** (54 mg). Fractions IV−V (17.0 g) were subjected to column chromatography on Si gel (cyclohexane−2-propanol, 20:1−5:1; $CHCl_3$−MeOH, 10:1) to provide **11** (687 mg) and then on RP-8 (MeOH−H_2O, 4.5:5.5−6:4) and MCI-gel CHP-20P (MeOH−H_2O, 8:2) to give **4** (231 mg), **7** (43 mg), and **8** (88 mg).

Adenanthin B (1): colorless cubes (acetone); mp 210.5−212.5 °C; $[\alpha]_D^{22}$ 0° (*c* 0.25, $CHCl_3$); UV (MeOH) λ_{max} end absorption; IR (KBr) ν_{max} 3561, 3507, 3000−2873, 1723, 1481, 1435, 1370, 1244, 1222, 1130, 1068, 1032, 1006, 949 cm^{-1}; ^1H NMR (C_5D_5N, 400.13 MHz) δ 6.45 (1H, br s, OH-3), 5.90 (1H, t, J = 3.8 Hz, H-11α), 5.83 (1H, dd, J = 5.1, 10.6 Hz, H-1β), 5.23 (1H, s, H-17a), 5.18 (1H, br s, H-7α), 4.95 (1H, d, J = 2.5 Hz, H-17b), 4.43 (1H, dd, J = 2.5, 11.1 Hz, H-15α), 3.71 (1H, t, J = 2.5 Hz, H-3α), 3.37 (1H, d, J = 11.1 Hz, OH-15), 2.62 (1H, br s, H-9β), 2.58 (1H, dd, J = 1.8, 12.4 Hz, H-5β), 2.50 (1H, m, H-13α), 2.12 (2H, overlap, H_2-2), 1.98 (2H, overlap, H_2-12), 1.75 (1H, overlap, H-14α), 1.72 and 1.75 (each 1H, overlap, H-6α and -6β), 1.28, 1.12, and 0.90 (each 3H, s, Me-20, -18, -19), 1.21 (1H, dd, J = 4.4, 11.9 Hz, H-14β), 2.19, 2.10, and 1.84 (each 3H, s, 3 × OAc); ^{13}C NMR (C_5D_5N, 100 MHz) spectral data, see Table 1; FABMS (+) *m/z* 479 $[M + 1]^+$; EIMS *m/z* 478 $[M]^+$ (6), 461 (25), 436 (1), 418 (1), 400 (1), 376 (1), 358 (13), 340 (4), 330 (2), 316 (5), 298 (100), 280 (31), 270 (5); HREIMS *m/z* 478.2605 (calcd for $C_{26}H_{38}O_8$, 478.2567).

Adenanthin C (2): colorless cubes (acetone); mp 228−229 °C; $[\alpha]_D^{22.5}$ −23.2° (*c* 0.42, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 238 (3.97) nm; IR (KBr) ν_{max} 3400, 2910, 1730, 1230, 1032 cm^{-1}; ^1H NMR (C_5D_5N, 400.13 MHz) δ 6.46 (1H, br s, OH-3), 5.92 (1H, t, J = 4.3 Hz, H-11α), 5.77 (1H, dd, J = 4.4, 11.0 Hz, H-1β), 5.87 (1H, s, H-17a), 5.42 (1H, br s, H-7α), 5.10 (1H, s, H-17b), 3.69 (1H, br s, H-3α), 2.59 (1H, s, H-9β), 2.73 (1H, dd, J = 5.2, 9.3 Hz, H-5β), 2.88 (1H, m, H-13α), 2.29 (2H, overlap, H_2-2), 2.11 (2H, overlap, H_2-12), 2.15 (1H, overlap, H-14α), 2.18 (2H, overlap, H_2-6), 1.35, 1.11, and 0.89 (each 3H, s, Me-20, -18, -19), 1.55 (1H, br d, J = 10.6 Hz, H-14β), 2.15, 2.15, and 1.69 (each 3H, s, 3 × OAc); ^{13}C NMR (C_5D_5N, 100 MHz) spectral data, see Table 1; FABMS(+) *m/z* 477 $[M + 1]^+$; HREIMS *m/z* 476.2347 (calcd for $C_{26}H_{36}O_8$, 476.2410).

Adenanthin D (3): colorless crystals (acetone); mp 147−148 °C; $[\alpha]_D^{27}$ +14.4° (*c* 0.18, MeOH); UV (MeOH) λ_{max} end absorption; IR (KBr) ν_{max} 3600−3300, 2990−2800, 1740, 1434, 1375, 1270, 1159, 1132, 1070, 1037, 997, 965, 932, 912, 888 cm^{-1}; ^1H NMR (C_5D_5N, 500.13 MHz) δ 6.38 (1H, d, J = 3.25 Hz, OH-3), 5.88 (1H, br d, J = 3.15 Hz, H-11α), 5.87 (1H, dd, J = 4.68, 11.08 Hz, H-1β), 5.75 (1H, s, H-15α), 5.00 (1H, br s, H-7α), 4.92−4.90 (2H, overlap, H_2-17), 3.67 (1H, br s, H-3α), 2.71 (1H, br s, H-9β), 2.52 (1H, br s, H-13α), 2.40 (1H, br d, J = 12.22 Hz, H-5β), 2.17 (1H, overlap, H-2β), 2.10 (1H, overlap, H-2α), 2.00−1.93 (2H, overlap, H_2-12), 1.93 (1H, overlap, H-6β), 1.79 (1H, d, J = 12.10 Hz, H-14α), 1.62 (1H, br t, J = 12.22 Hz, H-6α), 1.28 (3H, s, Me-20), 1.26 (1H, overlap, H-14β), 1.07 (3H, s, Me-18), 0.87 (3H, s, Me-19), 2.22, 2.03, 1.95, and 1.95 (each 3H, s, 4 × OAc); ^{13}C NMR (C_5D_5N, 125.8 MHz) spectral

Table 2. ^{13}C NMR Spectral Data for Compounds **8**−**11** (C_5D_5N, 100.6 MHz, δ in ppm)

carbon	8	9	10	11	carbon	8	9	10	11
1	77.6 d	79.6 d	80.0 d	71.6 d	14	37.4 t	33.7 t	35.0 t	41.9 t
2	34.0 t	33.3 t	33.4 t	32.1 t	15	206.6 s	81.5 d	80.0 d	153.6 s
3	80.1 d	75.1 d	75.6 d	79.5 d	16	152.4 s	157.3 s	153.4 s	64.5 t
4	37.4 s	37.1 s	37.1 s	36.1 s	17	110.0 t	106.4 t	106.4 t	108.2 t
5	43.3 d	51.3 d	49.9 d	57.4 d	18	28.4 q	27.4 q	27.3 q	27.6 q
6	69.5 d	207.7 s	213.7 s	199.3 s	19	24.2 q	22.9 q	23.1 q	22.2 q
7	76.4 d	86.1 d	84.9 d	128.0 d	20	15.3 q	15.0 q	15.7 q	10.9 q
8	49.4 s	51.8 s	51.8 s	157.8 s	OAc	170.4 s	170.3 s	171.1 s	170.2 s
9	60.8 d	50.0 d	51.0 d	61.2 d		170.4 s	170.3 s	170.4 s	20.9 q
10	44.6 s	49.0 s	48.2 s	47.4 s		21.6 q	169.0 s	170.1 s	
11	67.1 d	69.6 d	68.8 d	69.2 d		20.9 q	21.8 q	22.0 q	
12	41.3 t	39.8 t	40.4 t	42.0 t			21.3 q	21.5 q	
13	38.1 d	38.1 d	38.9 d	37.1 d			20.9 q	21.5 q	

data, see Table 1; EIMS *m/z* 520 $[M]^+$ (1), 478 (1), 460 (22), 442 (1), 418 (9), 400 (30), 382 (2), 358 (73), 340 (59), 322 (15), 298 (100), 280 (75), 265 (28), 255 (16), 237 (15), 225 (16), 213 (23), 185 (22), 171 (20), 155 (24); HREIMS *m/z* 520.2621 (calcd for $C_{28}H_{40}O_9$, 520.2672).

Adenanthin E (4): amorphous powder; $[\alpha]_D^{27}$ +33.0° (*c* 0.27, MeOH); UV (MeOH) λ_{max} end absorption; IR (KBr) ν_{max} 3600−3200, 2972, 2950, 2934, 1729, 1706, 1466.9, 1372, 1262, 1248, 1226, 1192, 1176, 1129, 1109, 1070, 1036 cm^{-1}; ^1H NMR (C_5D_5N, 500.13 MHz) δ 6.02 (1H, d, J = 9.26 Hz, OH-15), 5.88 (1H, br s, H-11α), 5.30 (1H, s, H-17a), 5.16 (1H, br s, H-7α), 5.13 (1H, s, H-17b), 4.96 (1H, t, J = 2.80 Hz, H-3α), 4.45 (1H, d, J = 9.26 Hz, H-15α), 4.33 (1H, dd, J = 4.38, 10.92 Hz, H-1*β*), 2.78 (1H, s, H-9*β*), 2.63 (1H, d, J = 3.25 Hz, H-13α), 2.28 (1H, overlap, H-2α), 2.20 (1H, overlap, H-5*β*), 2.12 (1H, overlap, H-2*β*), 2.10 (2H, overlap, H_2-12), 1.94 (1H, d, J = 11.60 Hz, H-14α), 1.74 (2H, overlap, H_2-6), 1.30 (3H, s, Me-20), 1.28 (1H, overlap, H-14*β*), 0.91 (3H, s, Me-19), 0.86 (3H, s, Me-18), 2.23 and 1.98 (each 3H, s, 2 × OAc); ^{13}C NMR (C_5D_5N, 100.6 MHz) spectral data, see Table 1; EIMS *m/z* 436 $[M]^+$ (1), 418 (2), 376 (11), 358 (14), 340 (2), 332 (6), 316 (10), 298 (61), 280 (66), 269 (15), 225 (14), 200 (22), 187 (27), 157 (26), 133 (23), 101 (66), 84 (100); HREIMS *m/z* 436.2418 (calcd for $C_{24}H_{36}O_7$, 436.2461).

Adenanthin F (5): colorless crystals; mp 121−122 °C; $[\alpha]_D^{26}$ −9.2° (*c* 0.33, MeOH); UV (MeOH) λ_{max} (log ϵ) 239.5 (3.82) nm; IR (KBr) ν_{max} 3600−3200, 2963, 2871, 1727, 1705, 1645, 1468, 1438, 1376, 1267, 1243, 1197, 1163, 1028, 991, 933 cm^{-1}; ^1H NMR (C_5D_5N, 500.13 MHz) δ 6.31 (1H, d, J = 4.20 Hz, OH-1α), 5.96 (1H, br s, OH-11*β*), 5.88 (1H, s, H-17a), 5.87 (1H, br s, H-11α), 5.45 (1H, br s, H-7α), 5.16 (1H, s, H-17b), 4.94 (1H, br s, H-3α), 4.18 (1H, br d, J = 10.95 Hz, H-1*β*), 2.99 (1H, d, J = 3.25 Hz, H-13α), 2.79 (1H, br s, H-9*β*), 2.34 (1H, overlap, H-14α), 2.32 (1H, overlap, H-5*β*), 2.28 (1H, overlap, H-2α), 2.16 (2H, overlap, H_2-12), 2.10 (1H, overlap, H-2*β*), 1.69 (2H, overlap, H_2-6), 1.54 (1H, dd, J = 3.40, 11.88 Hz, H-14*β*), 1.36 (3H, s, Me-20), 0.87 (3H, s, Me-19), 0.84 (3H, s, Me-18), 2.27 and 1.95 (each 3H, s, 2 × OAc); ^{13}C NMR (C_5D_5N, 100.6 MHz) spectral data, see Table 1; EIMS *m/z* 434 $[M]^+$ (2), 374 (62), 314 (62), 296 (98), 281 (61), 270 (53), 253 (29), 243 (52), 227 (41), 216 (100), 199 (60), 171 (63), 159 (43), 137 (72), 105 (81); HREIMS *m/z* 434.2253 (calcd for $C_{24}H_{34}O_7$, 434.2304).

Adenanthin G (6): amorphous powder; $[\alpha]_D^{26}$ −30.7° (*c* 0.49, MeOH); UV (MeOH) λ_{max} (log ϵ) 237 (3.67) nm; IR (KBr) ν_{max} 3600−3200, 2925, 2860, 1731, 1647, 1461, 1375, 1256, 1128, 1068, 1032, 988, 935 cm^{-1}; ^1H NMR (C_5D_5N, 500.13 MHz) δ 6.83 (1H, br s, H-11α), 5.89 (1H, s, H-17a), 5.46 (1H, br s, H-7α), 5.12 (1H, s, H-17b), 4.63 (1H, dd, J = 5.05, 10.45 Hz, H-1*β*), 3.76 (1H, br s, H-3α), 2.91 (1H, br s, H-13α), 2.66 (1H, overlap, H-5*β*), 2.64 (1H, overlap, H-9*β*), 2.37 (1H, overlap, H-2α), 2.36 (1H, d, J = 11.80 Hz, H-14α), 2.22 (1H, overlap, H-2*β*), 2.18 (1H, overlap, H-12α), 2.05 (1H, m, H-2*β*), 1.72 (2H, overlap, H_2-6), 1.71 (3H, s, Me-20), 1.57 (1H, dd, J = 3.64, 11.80 Hz, H-14*β*), 1.14 (3H, s, Me-18), 0.92 (3H, s, Me-19), 2.15 and 1.73 (each 3H, s, 2 × OAc); ^{13}C NMR (C_5D_5N, 125.8 MHz) spectral data, see Table 1; EIMS *m/z* 434 $[M]^+$ (2), 416 (1), 391 (3), 374 (5), 362 (32), 332 (62), 314 (50), 296 (43), 286 (20), 270 (12), 260 (25), 242 (100), 225 (30), 214 (15), 199 (91), 185 (18), 171 (34), 155 (35), 143 (43), 129 (32), 109 (51); HREIMS *m/z* 434.2269 (calcd for $C_{24}H_{34}O_7$, 434.2304).

Adenanthin H (7): colorless crystals; mp 188−190 °C; $[\alpha]_D^{27}$ −33.3° (*c* 0.15, MeOH); UV (MeOH) λ_{max} end absorption; IR (KBr) ν_{max} 3592−3202, 2990−2884, 1709, 1437, 1374, 1256, 1172, 1132, 1032, 996 cm^{-1}; ^1H NMR (C_5D_5N, 500.13 MHz) δ 6.42 (1H, br s, OH-3*β*), 6.37 (1H, br s, OH-11*β*), 6.06 (1H, d, J = 9.28 Hz, OH-15*β*), 5.94 (1H, dd, J = 4.40, 10.80 Hz, H-1*β*), 5.30 (1H, s, H-17a), 5.15 (1H, br s, H-7α), 5.13 (1H, s, H-17b), 4.91 (1H, br s, H-11α), 4.45 (1H, d, J = 9.28 Hz, H-15α), 3.79 (1H, br s, H-3α), 2.82 (1H, s, H-9*β*), 2.63 (1H, d, J = 2.80 Hz, H-13α), 2.54 (1H, d, J = 13.22 Hz, H-5*β*), 2.23 (1H, overlap, H-2*β*), 2.20−2.10 (2H, overlap, H_2-12), 2.13 (1H, overlap, H-2α), 1.88 (1H, overlap, H-14α), 1.84 (1H, overlap, H-6*β*), 1.72 (1H, d, J = 13.22 Hz, H-6α), 1.31 (3H, s, Me-20), 1.25 (1H, br d, J = 12.28 Hz, H-14*β*), 1.14 (3H, s, Me-18), 0.94 (3H, s, Me-19), 2.10 and 2.08 (each 3H, s, 2 × OAc); ^{13}C NMR (C_5D_5N, 100.6 MHz) spectral data, see Table 1; EIMS *m/z* 436 $[M]^+$ (1), 376 (17), 358 (22), 332 (5), 316 (43), 298 (100), 288 (10), 280 (36), 255 (16), 231 (15), 213 (27), 204 (20), 187 (23), 105 (45), 91 (52); HREIMS *m/z* 436.2429 (calcd for $C_{24}H_{36}O_7$, 436.2461).

Adenanthin I (8): colorless needles; mp 215−217 °C; $[\alpha]_D^{26}$ −4.0° (*c* 0.46, MeOH); UV (MeOH) λ_{max} (log ϵ) 240 (3.83) nm; IR (KBr) ν_{max} 3600−3200, 2990−2840, 1719, 1645, 1377, 1315, 1266, 1162, 1117, 1059, 1041, 1029, 986, 939 cm^{-1}; ^1H NMR (C_5D_5N, 400.13 MHz) δ 6.92 (1H, d, J = 4.44 Hz, OH-6α), 6.26 (1H, d, J = 5.66 Hz, OH-1α), 6.09 (1H, d, J = 3.12 Hz, H-11α), 5.97 (1H, br s, OH-11*β*), 5.91 (1H, s, H-17a), 5.62 (1H, d, J = 3.64 Hz, H-7α), 5.15 (1H, s, H-17b), 4.93 (1H, br s, H-3α), 4.39 (1H, br s, H-6*β*), 4.22 (1H, dd, J = 5.66, 9.12 Hz, H-1*β*), 3.28 (1H, d, J = 12.50 Hz, H-14α), 3.02 (1H, d, J = 3.12 Hz, H-13α), 2.98 (1H, s, H-9*β*), 2.48 (1H, overlap, H-2α), 2.45 (1H, overlap, H-12α), 2.22 (1H, overlap, H-12*β*), 2.17 (1H, s, H-5*β*), 2.13 (1H, overlap, H-2*β*), 1.94 (3H, s, Me-20), 1.84 (1H, dd, J = 3.92, 12.50 Hz, H-14*β*), 1.52 (3H, s, Me-19), 1.00 (3H, s, Me-18), 2.25 and 1.98 (each 3H, s, 2 × OAc); ^{13}C NMR (C_5D_5N, 100.6 MHz) spectral data, see Table 2; EIMS *m/z* 450 $[M]^+$ (1), 390 (50), 372 (13), 348 (1), 330 (53), 312 (54), 297 (31), 286 (44), 269 (25), 259 (20), 243 (17), 233 (20), 225 (26), 215 (33), 193 (38), 175 (44), 159 (44), 147 (36), 137 (54), 121 (86), 109 (71); HREIMS *m/z* 450.2270 (calcd for $C_{24}H_{34}O_8$, 450.2254).

Adenanthin J (9): amorphous powder; $[\alpha]_D^{27}$ −7.9° (*c* 0.71, MeOH); UV (MeOH) λ_{max} end absorption; IR (KBr) ν_{max} 3608−3322, 2942, 2880, 1740, 1546, 1438, 1373, 1235, 1119, 1071, 1032, 952 cm^{-1}; ^1H NMR (C_5D_5N, 400.13 MHz) δ 6.72 (1H, br s, OH-3*β*), 5.96 (1H, dd, J = 4.56, 11.04 Hz, H-1*β*), 5.82 (1H, br s, H-11α), 5.23 (1H, s, H-17a), 4.98 (1H, overlap, H-17b), 4.97 (1H, overlap, H-7α), 4.48 (1H, d, J = 9.68 Hz, H-15α), 4.05 (1H, s, H-5*β*), 3.92 (1H, d, J = 9.68 Hz, OH-15*β*), 3.55 (1H, br s, H-3α), 3.03 (1H, br s, H-9*β*), 2.51 (1H, br s, H-13α), 2.14 (1H, overlap, H-2*β*), 2.04 (1H, overlap, H-2α), 1.95 (2H, overlap, H_2-12), 1.68 (1H, dd, J = 5.60, 12.20 Hz, H-14α), 1.47 (3H, s, Me-19), 1.32 (1H, overlap, H-14*β*), 1.29 (3H, s, Me-20), 1.20 (3H, s, Me-18), 2.17, 2.11, and 1.89 (each 3H, s, 3 × OAc); ^{13}C NMR (C_5D_5N, 100.6 MHz) spectral data, see Table 2; EIMS *m/z* 492 $[M]^+$ (1), 432 (27), 414 (1), 390 (9), 372 (73), 354 (67), 330 (20), 312 (100), 294 (39), 279 (25), 241 (18), 227 (34), 214

(76), 200 (24), 187 (22), 175 (41), 164 (35), 138 (36), 123 (33), 109 (45); HREIMS *m/z* 492.2374 (calcd for $C_{26}H_{36}O_9$, 492.2359).

Adenanthin K (10): amorphous powder; $[\alpha]_D^{26}$ −170.5° (*c* 0.21, MeOH); UV (MeOH) λ_{max} end absorption; IR (KBr) ν_{max} 3600−3250, 2990−2800, 1724, 1546, 1436, 1373, 1252, 1116, 1076, 1034, 1005, 957 cm^{-1}; ^1H NMR (C_5D_5N, 400.13 MHz) δ 8.13 (1H, br s, OH-7β), 6.08 (1H, dd, J = 4.48, 11.24 Hz, H-1β), 6.04 (1H, s, H-15α), 5.92 (1H, br s, H-11α), 5.05 (1H, s, H-17a), 4.98 (1H, s, H-17b), 4.64 (1H, s, H-5β), 3.89 (1H, s, H-7α), 3.59 (1H, br s, H-3α), 3.30 (1H, s, H-9β), 2.56 (1H, br s, H-13α), 2.29 (1H, overlap, H-2β), 2.03 (1H, overlap, H-2α), 2.02 (2H, overlap, H_2-12), 1.76 (1H, d, J = 12.26 Hz, H-14α), 1.54 (3H, s, Me-19), 1.37 (1H, overlap, H-14β), 1.37 (3H, s, Me-20), 1.28 (3H, s, Me-18), 2.25, 2.03, and 1.99 (3H each, s, 3 × OAc); ^{13}C NMR (C_5D_5N, 100.6 MHz) spectral data, see Table 2; EIMS *m/z* 492 $[M]^+$ (3), 474 (3), 450 (3), 432 (30), 414 (9), 390 (50), 372 (78), 354 (35), 344 (10), 330 (80), 312 (100), 294 (59), 283 (40), 266 (27), 249 (31), 225 (30), 207 (64); HREIMS *m/z* 492.2382 (calcd for $C_{26}H_{36}O_9$, 492.2359).

Adenanthin L (11): colorless crystals; mp 272−273 °C; $[\alpha]_D^{17}$ +28.5° (*c* 0.44, MeOH); UV (MeOH) λ_{max} (log ϵ) 243 (4.06) nm; IR (KBr) ν_{max} 3526 (br s), 3142, 2934, 1734, 1671, 1459, 1352, 1247, 1222, 1187, 1068, 1041, 1005 cm^{-1}; ^1H NMR (C_5D_5N, 400.13 MHz) δ 8.25, 7.79 (each 1H, br s, 2 × OH), 6.59 (1H, br s, OH-16), 5.99 (1H, s, H-7), 5.45 (1H, s, H-17a), 5.08 (1H, s, H-17b), 4.92 (1H, br s, H-3α), 4.49 (1H, overlap, H-1β), 4.45 (2H, overlap, H_2-16), 4.00 (1H, m, H-11α), 2.86 (1H, s, H-5β), 2.71 (1H, d, J = 8.80 Hz, H-9β), 2.62 (1H, overlap, H-14α), 2.60 (1H, overlap, H-12α), 2.39−2.20 (2H, overlap, H_2-2), 2.37 (1H, overlap, H-13α), 2.28 (1H, overlap, H-14β), 1.90 (1H, q, J = 11.92 Hz, H-12β), 1.45 (3H, s, Me-19), 1.30 (3H, s, Me-18), 1.26 (3H, s, Me-20), 2.06 (3H, s, OAc); ^{13}C NMR (C_5D_5N, 100.6 MHz) spectral data, see Table 2; EIMS *m/z* 392 $[M]^+$ (9), 374 (21), 356 (6), 332 (10), 314 (100), 296 (24), 278 (11), 270 (23), 252 (12), 243 (18), 225 (17), 217 (28), 199 (68), 185 (31), 173 (39), 159 (71); HREIMS *m/z* 392.2199 (calcd for $C_{22}H_{32}O_6$, 392.2223).

X-ray Crystallographic Analysis of Adenanthin L (11).[11] A colorless crystal of $C_{22}H_{32}O_6$ having approximate dimensions 0.20 × 0.50 × 1.00 mm was mounted on a glass fiber. All measurements were made on a MAC DIP-2030K imaging plate area detector with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXS86) and expanded using Fourier techniques. Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions a = 10.849(1) Å, b = 7.360(1) Å, c = 13.401(1) Å, β = 98.273(2)°, V = 1058.9(1) Å^3. For Z = 2 and fw = 392.49, the calculated density is 1.23 g/cm^3. The space group was determined to be $P2_12_12_1$. A total of 1838 reflections were collected, and 1828 were observable and useful reflections ($|F|^2 \geq 8\sigma|F|^2$). The final R-factor is 0.070 with R_w = 0.069 ($w = 1/\sigma^2|F|$), s = 8.772, $(\Delta/\sigma)_{max}$ = 0.378, $(\Delta\rho)_{min}$ = −0.230 e/Å^3, and $(\Delta\rho)_{max}$ = 0.280 e/Å^3.

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Supporting Information Available: Atomic coordinates of the crystal structure of adenanthin L (**11**). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(11) Crystallographic data for adenanthin L (**11**) have been deposited at the Cambridge Crystallographic Data Center. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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