Caudatosides A−F: New Iridoid Glucosides from *Citharexylum caudatum*

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Six new iridoid glucosides, caudatosides A−F (**2**−**7**), and one known iridoid glucoside, 5-deoxypulchelloside I (**1**), were isolated from the fruits of *Citharexylum caudatum*. The structures of these compounds were elucidated by various one- and two-dimensional NMR techniques as well as high-resolution negative-ion ESIMS. Other plant parts were extracted on a small scale, and TLC of these extracts revealed the presence of the same iridoids.

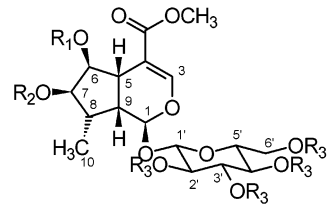
Citharexylum caudatum L. (Verbenaceae) is a large shrub originally found in the Caribbean, Mexico, and Central America. The plant was later introduced to Hawaii, where it has flourished and is considered a pest plant.[1] *C. caudatum* has been used as an emmenagogue, as an abortifacient, and as a pectoral in traditional medicine. The fruits have been used by natives to make beverages and are a food source for birds.[1] Recently, extracts of this plant were screened for activity against leishmania, and an extract from the fruits showed limited activity.

Iridoids are monoterpenes that are usually glucosylated and are widespread in Verbenaceae.[2] This class of compound has been shown to exhibit a wide range of biological activities[3] and has been found in other members of the *Citharexylum* genus, in *C. fruiticosum*[4,5] and, more recently, in *C. quadrangular*.[6] *C. fruiticosum* and *C. quadrangular* are apparently the only members of the genus that have been chemically investigated. The current work is the first investigation of *C. caudatum* and is also apparently the first investigation of the fruits of any member of the Verbenaceae family outside of the genus *Vitex*.

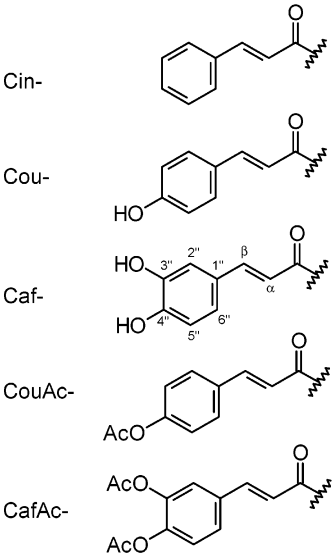
Results and Discussion

Dried, ground fruits of *C. caudatum* (1 kg) were sequentially extracted with petroleum ether, chloroform, acetone, and 95% ethanol. The acetone extract was fractionated initially by silica gel column chromatography, and further separation was carried out by reversed-phase (C_{18}) flash chromatography to give iridoid glucosides **1**−**5**. Preparative RP-TLC was used to isolate **6** and **7**.

The separation of **2** and **3** from each other, as well as separation of **6** and **7** from each other, proved difficult, presumably due to facile acyl transfer of the phenylpropanoid ester from the O-6 to the O-7 and vice versa, especially in aqueous conditions. (Interestingly, this phenomenon was not a problem in the separation of **4** and **5** from each other.) These pairs of compounds could not be separated from each other by normal-phase silica gel chromatography, except on a small scale by HPLC. Separation of **2**−**5** on a large scale was accomplished by rapid reversed-phase column chromatography to avoid acyl transfer facilitated by the aqueous conditions required for separation. To separate **6** from **7**, preparative RP-TLC was employed, with the eluting mobile phase modified with 0.1% trifluoroacetic acid. To avoid acyl transfer catalyzed by residual acid, $NaHCO_3$ was added to the scraped PTLC bands prior to adding the solvent used to extract the pure **6** and **7** from the silica gel.



	R_1	R_2	R_3
1	-H	-H	-H
2	-Cin	-H	-H
3	-H	-Cin	-H
4	-Cou	-H	-H
5	-H	-Cou	-H
6	-Caf	-H	-H
7	-H	-Caf	-H
8	-Ac	-Ac	-Ac
9	-Cin	-Ac	-Ac
10	-Ac	-Cin	-Ac
11	-CouAc	-Ac	-Ac
12	-Ac	-CouAc	-Ac
13	-CafAc	-Ac	-Ac
14	-Ac	-CafAc	-Ac



Compound **1** was determined to have the formula $C_{17}H_{26}O_{11}$ from the parent ion at *m/z* 405.14 $[M - H]^-$ in the negative ion low-resolution ESIMS and was determined to be an iridoid by the presence of diagnostic peaks in the ^1H NMR spectrum (Table 1). The structure of **1** was confirmed by comparison of the ^1H NMR data to data of known iridoids and determined to be 5-deoxypulchelloside I, first isolated from the leaves of *C. fruiticosum*.[5]

The ^1H NMR data of the remaining six compounds, **2**−**7**, were similar to the ^1H NMR data of **1** except for the

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Table 1. ^{1}H NMR Data for Compounds **1**−**7** (300 MHz, chemical shifts in δ, coupling constants in Hz, **1** in D_2O, **2**−**7** in acetone-d_6)

proton	**1**	**2**	**3**	**4**	**5**	**6**	**7**
1	5.60, d, $J_{1,9}$=1.5	5.58, d, $J_{1,9}$=3.3	5.61, d, $J_{1,9}$=2.1	5.58, d, $J_{1,9}$=3.0	5.60, d, $J_{1,9}$=2.4	5.57, d, $J_{1,9}$=3.0	5.59, d, $J_{1,9}$=2.1
3	7.47, d, $J_{3,5}$=0.9	7.42−7.45	7.42−7.45	7.42, d, $J_{3,5}$=1.2	7.44, d, $J_{3,5}$=0.6	7.41, d, $J_{3,5}$=1.5	7.44, d, $J_{3,5}$=0.9
5	2.90, ddd, $J_{5,3}$=0.9 $J_{5,6}$=0.9, $J_{5,9}$=9.3	3.01, ddd, $J_{5,3}$=obsc., $J_{5,6}$=2.4, $J_{5,9}$=8.9	2.96, ddd, $J_{5,3}$=obsc. $J_{5,6}$=1.5, $J_{5,9}$=9.0	2.99, ddd, $J_{5,3}$=1.2 $J_{5,6}$=2.4, $J_{5,9}$=9.3	2.94, ddd $J_{5,3}$=0.6 $J_{5,6}$=1.6, $J_{5,9}$=8.7	3.00, ddd, $J_{5,3}$=1.5 $J_{5,6}$=2.4, $J_{5,9}$=9.3	2.94, ddd $J_{5,3}$=0.9 $J_{5,6}$=1.8, $J_{5,9}$=9.0
6	4.02, dd, $J_{6,5}$=0.9 $J_{6,7}$=3.9	5.40, dd, $J_{6,5}$=2.4 $J_{6,7}$=4.6	4.34, dd, $J_{6,5}$=1.5 $J_{6,7}$=4.0	5.38, dd, $J_{6,5}$=2.4 $J_{6,7}$=4.3	4.32, dd, $J_{6,5}$=1.6 $J_{6,7}$=3.9	5.37, dd, $J_{6,5}$=2.4 $J_{6,7}$=4.2	4.32, dd, $J_{6,5}$=1.8 $J_{6,7}$=3.6
7	3.61, dd, $J_{7,6}$=3.9 $J_{7,8}$=9.3	3.81, dd, $J_{7,6}$=4.6 $J_{7,8}$=8.6	4.72, dd, $J_{7,6}$=4.0 $J_{7,8}$=9.2	3.79, dd, $J_{7,6}$=4.3 $J_{7,8}$=8.6	4.70, dd, $J_{7,6}$=3.9 $J_{7,8}$=9.3	3.77, dd, $J_{7,6}$=4.2 $J_{7,8}$=8.7	4.69, dd, $J_{7,6}$=3.6 $J_{7,8}$=9.0
8	2.31, ddq, $J_{8,7}$=9.3 $J_{8,9}$=9.3, $J_{8,10}$=7.5	2.35, ddq, $J_{8,7}$=8.6 $J_{8,9}$=8.9, $J_{8,10}$=7.2	2.67, ddq, $J_{8,7}$=9.2 $J_{8,9}$=9.0, $J_{8,10}$=7.2	2.34, ddq, $J_{8,7}$=8.6 $J_{8,9}$=9.3, $J_{8,10}$=7.5	2.65, ddq, $J_{8,7}$=9.3 $J_{8,9}$=8.7, $J_{8,10}$=7.2	2.32, ddq, $J_{8,7}$=8.7 $J_{8,9}$=9.3, $J_{8,10}$=7.5	2.64, ddq, $J_{8,7}$=9.0 $J_{8,9}$=9.0, $J_{8,10}$=7.2
9	2.86, ddd, $J_{9,1}$=1.5 $J_{9,5}$=9.3, $J_{9,8}$=9.3	2.82, ddd, $J_{9,1}$=3.3 $J_{9,5}$=8.9, $J_{9,8}$=8.9	2.88, ddd, $J_{9,1}$=2.1 $J_{9,5}$=9.0, $J_{9,8}$=9.0	2.81, ddd, $J_{9,1}$=3.0 $J_{9,5}$=9.3, $J_{9,8}$=9.3	2.85, ddd, $J_{9,1}$=2.4 $J_{9,5}$=8.7, $J_{9,8}$=8.7	2.81, ddd, $J_{9,1}$=3.0 $J_{9,5}$=9.3, $J_{9,8}$=9.3	2.85, ddd, $J_{9,1}$=2.1 $J_{9,5}$=9.0, $J_{9,8}$=9.0
10	1.07, d, $J_{10,8}$=7.5	1.13, d, $J_{10,8}$=7.2	1.11, d, $J_{10,8}$=7.2	1.12, d, $J_{10,8}$=7.5	1.10, d, $J_{10,8}$=7.2	1.12, d, $J_{10,8}$=7.5	1.09, d, $J_{10,8}$=7.2
1′	4.71, d, $J_{1',2'}$=8.4	4.67, d, $J_{1',2'}$=7.8	4.66, d, $J_{1',2'}$=7.8	4.66, d, $J_{1',2'}$=7.8	4.65, d, $J_{1',2'}$=8.1	4.65, d, $J_{1',2'}$=7.5	4.65, d, $J_{1',2'}$=8.1
2′	3.21, dd, $J_{2',1'}$=8.4 $J_{2',3'}$=9.3	3.21, dd, $J_{2',1'}$=7.8 $J_{2',3'}$=9.0	3.22, dd, $J_{2',1'}$=7.8 $J_{2',3'}$=9.0	3.20, dd, $J_{2',1'}$=7.8 $J_{2',3'}$=9.3	3.20, dd, $J_{2',1'}$=8.1 $J_{2',3'}$=9.0	3.22, dd, $J_{2',1'}$=7.5 $J_{2',3'}$=8.7	3.22, dd, $J_{2',1'}$=8.1 $J_{2',3'}$=8.7
3′,4′,5′	3.33−3.50	3.31−3.46	3.31−3.46	3.29−3.45	3.30−3.44	3.34−3.43	3.35−3.47
6′a	3.91, dd, $J_{6'a,5'}$=2.1 $J_{6'a,6'b}$=12.3	3.88, dd, $J_{6'a,5'}$=2.4 $J_{6'a,6'b}$=11.7	3.88, dd, $J_{6'a,5'}$=2.4 $J_{6'a,6'b}$=12.3	3.88, dd, $J_{6'a,5'}$=2.4 $J_{6'a,6'b}$=12.0	3.87, dd, $J_{6'a,5'}$=2.4 $J_{6'a,6'b}$=12.3	3.86, dd, $J_{6'a,5'}$=2.4 $J_{6'a,6'b}$=12.3	3.86, dd, $J_{6'a,5'}$=2.4 $J_{6'a,6'b}$=12.3
6′b	3.67−3.74 (obscured by $-CO_2CH_3$)	3.62−3.68 (obscured by $-CO_2CH_3$)	3.62−3.67 (obscured by $-CO_2CH_3$)	3.61−3.67 (obscured by $-CO_2CH_3$)	3.61−3.67 (obscured by $-CO_2CH_3$)	3.65−3.70 (obscured by $-CO_2CH_3$)	3.64−3.70 (obscured by $-CO_2CH_3$)
$-CO_2-CH_3$	3.74, s	3.64, s	3.69, s	3.63, s	3.68, s	3.64, s	3.68, s
α		6.59, d, $J_{\alpha,\beta}$=16.2	6.56, d, $J_{\alpha,\beta}$=15.9	6.37, d, $J_{\alpha,\beta}$=15.9	6.36, d, $J_{\alpha,\beta}$=15.9	6.31, d, $J_{\alpha,\beta}$=15.9	6.28, d, $J_{\alpha,\beta}$=16.2
β		7.72, d, $J_{\beta,\alpha}$=16.2	7.68, d, $J_{\beta,\alpha}$=15.9	7.64, d, $J_{\beta,\alpha}$=15.9	7.60, d, $J_{\beta,\alpha}$=15.9	7.57, d, $J_{\beta,\alpha}$=15.9	7.53, d, $J_{\beta,\alpha}$=16.2
2″		7.67−7.71	7.66−7.69	7.55, d, $J_{2'',3''}$=8.4	7.54, d, $J_{2'',3''}$=8.4	7.18, d, $J_{2'',6''}$=2.1	7.17, d, $J_{2'',6''}$=2.1
3″		7.42−7.45	7.42−7.45	6.89, d, $J_{3'',2''}$=8.4	6.89, d, $J_{3'',2''}$=8.4		
4″		7.42−7.45	7.42−7.45				
5″		7.42−7.45	7.42−7.45	6.89, d, $J_{5'',6''}$=8.4	6.89, d, $J_{5'',6''}$=8.4	6.87, d, $J_{5'',6''}$=7.8	6.86, d, $J_{5'',6''}$=8.4
6″		7.67−7.71	7.66−7.69	7.55, d, $J_{6'',5''}$=8.4	7.54, d, $J_{6'',5''}$=8.4	7.01, dd, $J_{6'',2''}$=2.1 $J_{6'',5''}$=7.8	7.01, dd, $J_{6'',2''}$=2.1 $J_{6'',5''}$=8.4

presence of new signals in the aromatic region consistent with a phenylpropanoid moiety, as well as a large downfield shift of either the H-6 or H-7, indicating esterification of the phenylpropanoid group at one of these positions.

Caudatoside A (**2**) was shown to have the molecular formula $C_{26}H_{32}O_{12}$ by analysis of the negative ion high-resolution ESIMS (*m*/*z* 571.1492 $[M + Cl]^-$). The ^{1}H NMR data of **2** (Table 1) were very similar to the ^{1}H NMR data of **1** except for new signals in the aromatic region and the large downfield shift of H-6 to δ 5.40, indicating esterification of O-6. The signals in the aromatic region are typical of a cinnamoyl ester, which was sited at C-6, due to the downfield shift of H-6. The glycosyl moiety at C-1 was confirmed as a glucopyranosyl moiety from the coupling constant data of the pentaacetate **9** (Table 2) prepared from **2**.

The stereochemistry of **2** was determined by comparison of chemical shifts and coupling constants to literature data and by analysis of the ROESY spectrum. The relationship of H-5 to H-9 was determined to be *cis* from the coupling constant (8.9 Hz), which is larger in *trans*-fused iridoids (∼12−13 Hz).[7,8] In most iridoids, the configuration of the 1-glucose, H-5, and H-9 is β, and the ^{13}C NMR chemical shifts of C-1 and C-1′ are typically δ 93−98 and 97−101, respectively. When the configuration at these three positions is α, the shifts of C-1 and C-1′ are, on average, 5−6 ppm further downfield.[9,10] The ^{13}C NMR data for all seven compounds reported here (Table 3) indicate the normal β stereochemistry for the 1-glucose, H-5, and H-9.

The stereochemistry at C-6, C-7, and C-8 was determined from the ROESY spectrum. Correlations (Figure 1) from the H-1 to CH_3-10, from CH_3-10 to H-7, and from H-7 to H-6 indicate that these protons are all on the same face of the molecule. The H-8 and H-9 correlate to one another, but H-8 did not correlate to H-7, indicating that H-8 and H-9 were on the opposite face of the molecule from H-1, H-6, H-7, and CH_3-10. The H-6 did not correlate to H-5, confirming that H-5 is on the same face as H-8 and H-9. From these data, compound **2** was determined to be 6-cinnamoyl-5-deoxypulchelloside I, named caudatoside A.

Caudatoside B (**3**) was shown to have the same molecular formula as **2**, $C_{26}H_{32}O_{12}$, by analysis of the negative ion high-resolution ESIMS (*m*/*z* 571.1522 $[M + Cl]^-$). The ^{1}H NMR data of **3** (Table 1) were similar to the ^{1}H NMR data of **2** except for the large upfield shift of H-6 and the downfield shift of H-7, indicating esterification at the O-7 instead of O-6. The aromatic regions of **2** and **3** were essentially identical. After acetylation of **3** to give **10**, the ^{1}H NMR spectrum of **10** (Table 2) again confirmed that the C-1 glycosyl moiety was a glucopyranosyl group. The stereochemistry of **3** was confirmed as described for **2**. From these data, compound **3** was determined to be 7-cinnamoyl-5-deoxypulchelloside I, named caudatoside B.

Caudatoside C (**4**) was shown to have the molecular formula $C_{26}H_{32}O_{13}$ by analysis of the negative ion high-resolution ESIMS (*m*/*z* 551.1723 $[M - H]^-$, 587.1544 $[M + Cl]^-$). The ^{1}H NMR data of **4** (Table 1) were essentially identical to the ^{1}H NMR data of **2** except for the aromatic region. The signals in the aromatic region clearly indicate the presence of a *p*-substituted phenylpropanoid. The HMBC spectrum showed a correlation between the methyl proton signal at δ 3.63 and the carbonyl carbon signal at δ 166.87, confirming that the methyl group was part of a methyl ester at C-4. Thus, the phenylpropanoid moiety was shown to be a *p*-coumaryl ester and not a *p*-methoxycinnamoyl ester. This ester was sited at C-6, on the basis of the chemical shift of H-6 (δ 5.38) in the ^{1}H NMR spectrum (Table 1). The glucopyranosyl moiety at C-1 was confirmed as described for **2** and **3**, as was the stereochemistry. From these data, compound **4** was determined to be 6-*p*-coumaryl-5-deoxypulchelloside I, named caudatoside C.

Caudatoside D (**5**) was shown to have the same molecular formula as **4**, $C_{26}H_{32}O_{13}$, by analysis of the negative ion high-resolution ESIMS (*m*/*z* 551.1797 $[M - H]^-$, 587.1612 $[M + Cl]^-$). The ^{1}H NMR data of **5** (Table 1) were essentially identical to the ^{1}H NMR data of **3** except for the aromatic region, indicating substitution at O-7. The resonances in the aromatic region were identical to those of **4**, confirming the presence of a *p*-coumaryl group. The

Table 2. ^{1}H NMR Data for Acetates **8**−**14** (300 MHz, chemical shifts in δ, coupling constants in Hz, $CDCl_3$)

proton	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	5.37, d, $J_{1,9}$=1.8	5.41, d, $J_{1,9}$=1.8	5.41, d, $J_{1,9}$=1.5	5.41, d, $J_{1,9}$=1.8	5.40, d, $J_{1,9}$=1.2	5.41, d, $J_{1,9}$=1.8	5.40, d, $J_{1,9}$=1.2
3	7.40, d, $J_{3,5}$=0.6	7.43, d, $J_{3,5}$=0.9	7.43, d, $J_{3,5}$=<0.6	7.43, d, $J_{3,5}$=1.2	7.42, d, $J_{3,5}$=0.9	7.44, d, (obscured by 2″)	7.42, d, $J_{3,5}$=<0.6
5	2.96, ddd, $J_{5,3}$=0.6	3.08, ddd, $J_{5,3}$=0.9	3.02, ddd, $J_{5,3}$=<0.6	3.07, ddd, $J_{5,3}$=1.2	3.01, ddd, $J_{5,3}$=0.6	3.07, ddd, $J_{5,3}$=1.5	3.01, ddd, $J_{5,3}$=0.9
	$J_{5,6}$=1.2, $J_{5,9}$=9.3	$J_{5,6}$=2.0, $J_{5,9}$=9.3	$J_{5,6}$=2.0, $J_{5,9}$=9.3	$J_{5,6}$=1.8, $J_{5,9}$=9.3	$J_{5,6}$=1.8, $J_{5,9}$=9.3	$J_{5,6}$=2.1, $J_{5,9}$=9.3	$J_{5,6}$=1.8, $J_{5,9}$=9.3
6	5.39, dd, $J_{6,5}$=1.2	5.53, dd, $J_{6,5}$=2.0	5.48, dd, $J_{6,5}$=2.0	5.53, dd, $J_{6,5}$=1.8	5.47, dd, $J_{6,5}$=1.8	5.52, dd, $J_{6,5}$=2.1	5.47, dd, $J_{6,5}$=1.8
	$J_{6,7}$=2.7	$J_{6,7}$=4.1	$J_{6,7}$=4.1	$J_{6,7}$=3.9	$J_{6,7}$=4.2	$J_{6,7}$=3.9	$J_{6,7}$=4.2
7	4.80, dd, $J_{7,6}$=2.7	4.88, dd, $J_{7,6}$=4.1	4.98, dd, $J_{7,6}$=4.1	4.88, dd, $J_{7,6}$=3.9	4.97, dd, $J_{7,6}$=4.2	4.88, dd, $J_{7,6}$=3.9	4.96, dd, $J_{7,6}$=4.2
	$J_{7,8}$=8.7	$J_{7,8}$=8.9	$J_{7,8}$=obsc.	$J_{7,8}$=8.7	$J_{7,8}$=obsc.	$J_{7,8}$=8.7	$J_{7,8}$=obsc.
8	2.48, ddq, $J_{8,7}$=8.7	2.57, ddq, $J_{8,7}$=8.9	2.58, ddq, $J_{8,7}$=obsc.	2.56, ddq, $J_{8,7}$=8.7	2.58, ddq, $J_{8,7}$=obsc.	2.54, ddq, $J_{8,7}$=8.7	2.57, ddq, $J_{8,7}$=obsc.
	$J_{8,9}$=9.6, $J_{8,10}$=7.5	$J_{8,9}$=9.3, $J_{8,10}$=7.2	$J_{8,9}$=9.3, $J_{8,10}$=7.2	$J_{8,9}$=9.6, $J_{8,10}$=7.2	$J_{8,9}$=9.3, $J_{8,10}$=7.2	$J_{8,9}$=9.3, $J_{8,10}$=7.2	$J_{8,9}$=9.3, $J_{8,10}$=7.5
9	2.91, ddd, $J_{9,1}$=1.8	3.00, ddd, $J_{9,1}$=1.8	2.97, ddd, $J_{9,1}$=1.5	2.99, ddd, $J_{9,1}$=1.8	2.97, ddd, $J_{9,1}$=1.2	2.98, ddd, $J_{9,1}$=1.8	2.97, ddd, $J_{9,1}$=1.2
	$J_{9,5}$=9.3, $J_{9,8}$=9.6	$J_{9,5}$=9.3, $J_{9,8}$=9.3	$J_{9,5}$=9.3, $J_{9,8}$=9.3	$J_{9,5}$=9.3, $J_{9,8}$=9.6	$J_{9,5}$=9.3, $J_{9,8}$=9.3	$J_{9,5}$=9.3, $J_{9,8}$=9.3	$J_{9,5}$=9.3, $J_{9,8}$=9.3
10	1.05, d, $J_{10,8}$=7.5	1.09, d, $J_{10,8}$=7.2	1.11, d, $J_{10,8}$=7.2	1.09, d, $J_{10,8}$=7.2	1.10, d, $J_{10,8}$=7.2	1.09, d, $J_{10,8}$=7.2	1.10, d, $J_{10,8}$=7.5
1′	4.80, d, $J_{1',2'}$=8.4	4.83, d, $J_{1',2'}$=8.4	4.84, d, $J_{1',2'}$=8.4	4.83, d, $J_{1',2'}$=8.4	4.83, d, $J_{1',2'}$=8.4	4.83, d, $J_{1',2'}$=8.4	4.83, d, $J_{1',2'}$=8.4
2′	4.95, dd, $J_{2',1'}$=8.4	4.97, dd, $J_{2',1'}$=8.4	4.98, dd, $J_{2',1'}$=8.4	4.97, dd, $J_{2',1'}$=8.4	4.98, dd, $J_{2',1'}$=8.4	4.98, dd, $J_{2',1'}$=8.4	4.98, dd, $J_{2',1'}$=8.4
	$J_{2',3'}$=9.6	$J_{2',3'}$=9.6	$J_{2',3'}$=obsc.	$J_{2',3'}$=9.6	$J_{2',3'}$=obsc.	$J_{2',3'}$=9.6	$J_{2',3'}$=obsc.
3′	5.20, dd, $J_{3',2'}$=9.6	5.22, dd, $J_{3',2'}$=9.6	5.22, dd, $J_{3',2'}$=9.6	5.22, dd, $J_{3',2'}$=9.6	5.22, dd, $J_{3',2'}$=9.6	5.22, dd, $J_{3',2'}$=9.6	5.22, dd, $J_{3',2'}$=9.6
	$J_{3',4'}$=9.6	$J_{3',4'}$=9.6	$J_{3',4'}$=9.6	$J_{3',4'}$=9.6	$J_{3',4'}$=9.6	$J_{3',4'}$=9.6	$J_{3',4'}$=9.6
4′	5.08, dd, $J_{4',3'}$=9.6	5.10, dd, $J_{4',3'}$=9.6	5.10, dd, $J_{4',3'}$=9.6	5.10, dd, $J_{4',3'}$=9.6	5.10, dd, $J_{4',3'}$=9.6	5.10, dd, $J_{4',3'}$=9.6	5.10, dd, $J_{4',3'}$=9.6
	$J_{4',5'}$=9.6	$J_{4',5'}$=9.6	$J_{4',5'}$=9.6	$J_{4',5'}$=9.6	$J_{4',5'}$=9.6	$J_{4',5'}$=9.6	$J_{4',5'}$=9.6
5′	3.74, ddd, $J_{5',4'}$=9.6	3.76, ddd, $J_{5',4'}$=9.6	3.76, ddd, $J_{5',4'}$=9.6	3.76, ddd, $J_{5',4'}$=9.6	3.76, ddd, $J_{5',4'}$=9.6	3.77, ddd, $J_{5',4'}$=9.6	3.76, ddd, $J_{5',4'}$=9.6
	$J_{5',6'a}$=2.4, $J_{5',6'b}$=4.5	$J_{5',6'a}$=2.1, $J_{5',6'b}$=4.2	$J_{5',6'a}$=2.1, $J_{5',6'b}$=4.4	$J_{5',6'a}$=2.1, $J_{5',6'b}$=4.4	$J_{5',6'a}$=2.1, $J_{5',6'b}$=4.5	$J_{5',6'a}$=1.8, $J_{5',6'b}$=4.5	$J_{5',6'a}$=1.8, $J_{5',6'b}$=4.2
6′a	4.14, dd, $J_{6'a,5'}$=2.4	4.16, dd, $J_{6'a,5'}$=2.1	4.15, dd, $J_{6'a,5'}$=2.1	4.16, dd, $J_{6'a,5'}$=2.1	4.15, dd, $J_{6'a,5'}$=2.1	4.16, dd, $J_{6'a,5'}$=1.8	4.15, dd, $J_{6'a,5'}$=1.8
	$J_{6'a,6'b}$=12.3	$J_{6'a,6'b}$=12.3	$J_{6'a,6'b}$=12.3	$J_{6'a,6'b}$=12.3	$J_{6'a,6'b}$=12.3	$J_{6'a,6'b}$=12.3	$J_{6'a,6'b}$=12.3
6′b	4.29, dd, $J_{6'b,5'}$=4.5	4.30, dd, $J_{6'b,5'}$=4.2	4.30, dd, $J_{6'b,5'}$=4.4	4.30, dd, $J_{6'b,5'}$=4.4	4.30, dd, $J_{6'b,5'}$=4.5	4.31, dd, $J_{6'b,5'}$=4.5	4.30, dd, $J_{6'b,5'}$=4.2
	$J_{6'b,6'a}$=12.3	$J_{6'b,6'a}$=12.3	$J_{6'b,6'a}$=12.3	$J_{6'b,6'a}$=12.3	$J_{6'b,6'a}$=12.3	$J_{6'b,6'a}$=12.3	$J_{6'b,6'a}$=12.3
$-CO_2-CH_3$	3.70, s	3.71, s	3.71, s	3.71, s	3.71, s	3.71, s	3.71, s
a		6.44, d, $J_{\alpha,\beta}$=15.9	6.38, d, $J_{\alpha,\beta}$=15.9	6.39, d, $J_{\alpha,\beta}$=15.9	6.33, d, $J_{\alpha,\beta}$=15.9	6.39, d, $J_{\alpha,\beta}$=15.9	6.32, d, $J_{\alpha,\beta}$=15.9
b		7.68, d, $J_{\beta,\alpha}$=15.9	7.65, d, $J_{\beta,\alpha}$=15.9	7.66, d, $J_{\beta,\alpha}$=15.9	7.62, d, $J_{\beta,\alpha}$=15.9	7.62, d, $J_{\beta,\alpha}$=15.9	7.58, d, $J_{\beta,\alpha}$=15.9
2″		7.52−7.56	7.50−7.53	7.55, d, $J_{2'',3''}$=8.4	7.53, d, $J_{2'',3''}$=8.4	7.38, d, $J_{2'',6''}$=2.1	7.35, d, $J_{2'',6''}$=2.1
3″		7.38−7.40	7.37−7.40	7.13, d, $J_{3'',2''}$=8.4	7.12, d, $J_{3'',2''}$=8.4		
4″		7.38−7.40	7.37−7.40				
5″		7.38−7.40	7.37−7.40	7.13, d, $J_{5'',6''}$=8.4	7.12, d, $J_{5'',6''}$=8.4	7.24, d, $J_{5'',6''}$=8.4	7.22, d, $J_{5'',6''}$=8.4
6″		7.52−7.56	7.37−7.53	7.55, d, $J_{6'',5''}$=8.4	7.53, d, $J_{6'',5''}$=8.4	7.42, dd, $J_{6'',2''}$=2.1 $J_{6'',5''}$=8.4	7.40, dd, $J_{6'',2''}$=2.1 $J_{6'',5''}$=8.4
ace-tates	1.88, 1.99	1.90, 1.99	1.90, 2.00	1.90, 1.99	1.90, 2.00	1.90, 1.99	1.90, 2.01
	1.99, 2.02	2.00, 2.03	2.03, 2.07	2.00, 2.04	2.03, 2.06	2.01, 2.04	2.04, 2.06
	2.06, 2.09	2.11	2.10	2.11, 2.32	2.10, 2.31	2.11, 2.31 2.32	2.10, 2.30 2.31

glucopyranosyl moiety at C-1 was confirmed as described for **2** and **3**, as was the stereochemistry. Compound **5** was therefore determined to be 7-*p*-coumaryl-5-deoxypulchelloside I, named caudatoside D.

Caudatoside E (**6**) was shown to have the molecular formula $C_{26}H_{32}O_{14}$ by analysis of the negative ion high-resolution ESIMS (*m*/*z* 567.1683 [M − H]$^-$). The ^{1}H NMR data of **6** (Table 1) were similar to the ^{1}H NMR data of **2** and **4** except for the aromatic region, which clearly showed the presence of either a caffeoyl or a feruloyl phenylpropanoid group sited at the O-6. HMBC was used to show that the methyl signal at δ 3.64 was due to a methyl ester at C-4, as described above for **4**, thus making the phenylpropanoid moiety a caffeoyl group. The glucopyranosyl moiety at C-1 was confirmed as described for **2** and **3**, as was the stereochemistry. From these data, compound **6** was determined to be 6-caffeoyl-5-deoxypulchelloside I, named caudatoside E.

Caudatoside F (**7**) was shown to have the same molecular formula as **6**, $C_{26}H_{32}O_{14}$, by analysis of the negative ion high-resolution ESIMS (*m*/*z* 567.1464 [M − H]$^-$). The ^{1}H NMR data of **7** were very similar to the ^{1}H NMR data of **5** (Table 1) except for the aromatic region, again indicating 7-substitution. The presence of a caffeoyl group was proven as for **6**. The glucopyranosyl moiety at C-1 was confirmed as described for **2** and **3**, as was the stereochemistry. From these data, compound **7** was determined to be 7-caffeoyl-5-deoxypulchelloside I, named caudatoside F.

Other plant parts of *C. caudatum* were collected along with the fruits. All parts were collected from Hawaii except one sample of stemwood, which was collected from Panama. Other Hawaiian samples include stems, stemwood, fruits/inflorescence, and leaves. These five samples were extracted separately on a small scale with 95% ethanol for 24 h. These extracts were subjected to silica gel TLC as well as RP-TLC (C_{18}) along with the pure iridoids that were

Table 3. ^{13}C NMR Data for Compounds **1**−**14**[a] (75 MHz, chemical shifts in δ, **1** in D_2O, **2**−**7** in Acetone-d_6, and **8**−**14** in $CDCl_3$)

carbon	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	95.52	94.96	94.96	94.96	94.96	94.94	94.95	93.72	93.80	93.80	93.79	93.80	93.76	93.75
3	153.04	152.90	152.86	152.84	152.81	152.89	152.81	151.69	151.67	151.46	151.65	151.46	151.68	151.47
4	109.92	109.66	110.17	109.76	110.25	109.74	110.26	109.56	109.52	109.74	109.51	109.74	109.44	109.70
5	36.79	36.75	39.02	36.75	39.04	36.65	38.98	35.10	35.39	35.26	35.39	35.25	35.35	35.19
6	76.15	78.76	74.62	78.50	74.69	78.51	74.69	75.48	75.64	75.70	75.71	75.70	75.80	75.63
7	78.34	78.14	81.64	78.23	81.38	78.22	81.34	78.04	78.12	78.23	78.12	78.30	78.06	78.40
8	36.94	39.76	36.24	39.76	36.26	39.68	36.24	35.66	35.88	36.51	35.91	36.51	35.90	36.44
9	38.78	40.00	39.24	40.01	39.30	39.95	39.28	38.45	38.59	38.77	38.60	38.78	38.57	38.72
10	12.82	13.99	13.88	14.01	13.89	13.98	13.89	13.09	13.22	13.32	13.22	13.32	13.22	13.31
1′	98.34	99.18	99.25	99.18	99.30	99.14	99.28	95.43	95.48	95.44	95.48	95.44	95.45	95.40
2′	72.66	74.33	74.21	74.34	74.29	74.22	74.19	70.41	70.43	70.44	70.44	70.44	70.41	70.40
3′	76.42	77.78	77.61	77.64	77.69	77.49	77.56	72.32	72.35	72.35	72.36	72.36	72.34	72.32
4′	69.67	71.41	71.28	71.43	71.38	71.30	71.28	67.98	68.02	68.02	68.03	68.02	67.98	67.96
5′	75.67	77.62	77.69	77.78	77.76	77.79	77.79	72.12	72.15	72.15	72.16	72.16	72.13	72.12
6′	60.80	62.82	62.69	62.84	62.76	62.66	62.63	61.56	61.62	61.60	61.62	61.60	61.60	61.57
$-CO_2CH_3$	52.07	51.29	51.40	51.28	51.36	51.31	51.35	51.52	51.62	51.56	51.62	51.57	51.65	51.58
$-CO_2CH_3$	169.29	166.86	167.45	166.87	167.40	166.92	167.42	166.03	165.93	165.97	165.93	165.97	165.92	165.95
−OCOAcyl		166.00	166.64	166.44	167.00	166.60	167.04		165.34	165.97	165.23	165.84	164.96	165.57
a		119.39	118.93	115.96	115.52	115.68	115.30		117.56	117.27	117.74	117.46	118.74	118.48
b		144.70	144.95	144.82	145.04	145.40	145.55		145.03	145.25	143.89	144.10	143.08	143.25
1″		135.29	135.12	126.90	126.78	127.27	127.18		134.15	134.09	131.90	131.84	133.04	132.97
2″		128.73	128.76	130.64	130.69	115.04	115.12		128.02	128.05	129.16	129.19	122.72	122.68
									6.02					
3″		129.56	129.55	116.47	116.49	146.24	146.24		128.78	128.75	122.05	122.02	142.26	142.22
4″		130.82	130.90	160.17	160.25	148.73	148.79		130.27	130.30	151.97	151.99	143.38	143.38
5″		129.56	129.55	116.47	116.49	116.30	116.33		128.78	128.75	122.05	122.02	123.85	123.81
6″		128.73	128.76	130.64	130.69	122.19	122.21		128.02	128.05	129.16	129.19	126.37	126.41
$-OCOCH_3$								20.08	20.19	20.19	20.19	20.19	20.20	20.19
								20.57(2)	20.67(2)	20.67(2)	20.67(2)	20.67(2)	20.69(2)	20.68(2)
								20.75(2)	20.83	20.83	20.84	20.83	20.73	20.71
								20.86	20.89	20.97	20.88	20.96	20.77	20.75
											21.23	21.22	20.86	20.84
													20.89	20.98
$-OCOCH_3$								169.04	168.91	168.92	168.91	168.92	167.85	167.82
								169.35	169.21	169.21	168.97	168.95	167.95	167.92
								169.62	169.97	169.34	169.21	169.21	168.92	168.93
								170.11	170.21	169.97	169.97	169.34	169.23	169.22
								170.31	170.42	170.42	170.19	169.97	170.00	169.35
								170.56			170.43	170.42	170.22	169.99
													170.46	170.44

[a] Assignments were confirmed by HSQC and HMBC spectra at 300 MHz.

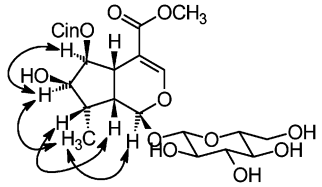

Figure 1. ROESY correlations observed for compound **2**.

isolated as described above. All samples of *C. caudatum* showed the presence of these iridoids. The leaf and fruit/inflorescence samples showed particularly strong bands corresponding to caudatosides A and B, and the Hawaiian stemwood sample showed a very strong band corresponding to 5-deoxypulchelloside I.

Caudatosides A−F are very similar to iridoids isolated from *N. arbortristis*. The basic *N. arbortristis* iridoid structure has the opposite stereochemistry at the 8-position and sometimes includes a hydroxyl on C-10.[11−17] *N. arbortristis* extracts have been shown to exhibit many types of biological activity.[18−24] The acetone extract of *C. caudatum* showed weak activity against a cutaneous *Leishmania* axenic amastigote screen, but the chloroform extract showed somewhat better activity, suggesting that any antileishmanial activity may not be due to the iridoids. However, the pure iridoids have not yet been screened.

Experimental Section

General Experimental Procedures. Melting points were obtained on a Fisher-John melting point apparatus and are uncorrected. Specific rotations were measured on a Jasco DIP-1000 digital polarimeter using a Na lamp at 28 °C. IR spectra were obtained on a Nicolet Nexus 670 FT-IR spectrometer as films on a NaCl disk. NMR spectra were obtained on a Varian Mercury 300 MHz spectrometer equipped with a Sun Microsystems Ultra 5 processor and VNMR version 5.1b software. UV spectra were run on a Hewlett-Packard 8453 UV−visible spectrophotometer with data obtained via Hewlett-Packard UV−visible ChemStation software. Low- and high-resolution mass spectra were conducted in the negative ion mode on a Micromass (Beverly, MA) quadrupole time-of-flight (Q-ToF2) mass spectrometer with a modified dual micro-electrospray source for internal calibration. All high-resolution spectra were calibrated with poly(ethylene glycol) with an average mass of 600 Da. Samples **1**−**7** were electrosprayed from 1:1 methanol/water, and samples **8**−**14** were electrosprayed from 9:1 methanol/chloroform (first dissolved in chloroform). Column chromatography was performed with 60−200 mesh silica gel (J.T. Baker), and flash reversed-phase column chromatography was performed with 40 μm C_{18} adsorbent (J.T. Baker). Preparative TLC was performed on J.T. Baker Si-C_{18}F reversed-phase TLC plates (20 × 20 cm, 200 μm thickness). The compounds were visualized on TLC plates by short (254 nm) and long (366 nm) wavelength UV light and by spraying with 1% vanillin/H_2SO_4 followed by heating on a hot plate for 5 min. Solvents were reagent grade and used as purchased. Screens for activity against *Leishmania* amastigotes were conducted at the Walter Reed Army Institute of Research.

Plant Material. Samples of *Citharexylum caudatum* L. were collected in Maui, Hawaii, in 1970 by Dr. Yoneo Sagawa of the University of Hawaii at Manoa, where voucher specimens (UH-619) are kept.

Extraction and Isolation. Dried, ground fruits of *C. caudatum* (1 kg) were extracted three times with petroleum ether (4 L each extraction), then three times with chloroform (4 L each), followed by four extractions with acetone (4 L each) and 95% ethanol (4 L each). The combined acetone extracts were concentrated in vacuo to give a light brown powder (56.1

g). This extract was subjected to column chromatography on silica gel using CH_2Cl_2 followed by increasing amounts of MeOH in CH_2Cl_2. Eighteen fractions were collected. Fractions 10 and 11 were combined (3.4 g, eluting with 12.5−15% MeOH in CH_2Cl_2), fractions 12 and 13 were combined (18.4 g, eluting with 15−17.5% MeOH in CH_2Cl_2), and fractions 14 and 15 were combined (17.8 g, eluting with 17.5−20% MeOH in CH_2Cl_2). Combined fractions 10/11 were subjected to flash RP-CC using a gradient from 85:7.5:7.5 H_2O/MeOH/AcCN to 0:50:50 H_2O/MeOH/AcCN. This column yielded **2** (477 mg, eluting with 50:25:25 H_2O/MeOH/AcCN) and **3** (644 mg, eluting with 40:30:30 H_2O/MeOH/AcCN).

A portion of combined fractions 12/13 (1.8 g) was subjected to flash RP-CC using the same gradient as for combined fractions 10/11. This column yielded **4** (521 mg, eluting with 65:17.5:17.5 H_2O/MeOH/AcCN) and **5** (725 mg, eluting with 55:22.5:22.5 H_2O/MeOH/AcCN).

A portion of combined fractions 14/15 (2.0 g) was subjected to flash RP-CC using a gradient from 93:7 H_2O/MeOH to 100% MeOH. This column yielded **1** (1.34 g, nonretained) and a mixture of **6** and **7** (484 mg, eluting from 19% to 60% MeOH). A portion of this mixture of **6** and **7** (103 mg) was subjected to preparative RP-TLC using 60:25:15:0.1 H_2O/MeOH/AcCN/trifluoroacetic acid. The bands were immediately marked and scraped after development and transferred into a flask containing acetonitrile, a small amount of $NaHCO_3$, and anhydrous Na_2SO_4 to avoid acyl transfer. After filtration and evaporation of the relevant fractions, pure **6** (29 mg) and **7** (46 mg) were obtained.

5-Deoxypulchelloside I (1): white crystalline solid (1.34 g); mp 94−97 °C; $[\alpha]^{28}_D$ −112.7° (*c* 0.0116, 4:1 CH_3CN/CH_3OH); UV (CH_3OH) λ_{max} (log ϵ): 237 (4.41), 328 nm (3.21); IR (film, NaCl), ν_{max} 3372 (OH), 2921, 1693, 1640, 1440, 1303, 1184, 1076 cm^{-1}; ^1H NMR (D_2O, 300 MHz) (Table 1); ^{13}C NMR (D_2O, 75 MHz) (Table 3); low-resolution ESIMS *m*/*z* 441.10 $[M + Cl]^-$.

Caudatoside A (2): tan solid (477 mg); mp 105−108 °C; $[\alpha]^{28}_D$ −75.2° (*c* 0.0108, 4:1 CH_3CN/CH_3OH); UV (CH_3OH) λ_{max} (log ϵ) 278 nm (4.27); IR (film, NaCl), ν_{max} 3385 (OH), 2949, 1704, 1637, 1450, 1440, 1364, 1310, 1287, 1184, 1075 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) (Table 1); ^{13}C NMR (acetone-d_6, 75 MHz) (Table 3); high-resolution ESIMS *m*/*z* 571.1492 $[M + Cl]^-$ (calcd for $C_{26}H_{32}O_{12}$+Cl, 571.1583).

Caudatoside B (3): tan solid (644 mg); mp 112−115 °C; $[\alpha]^{28}_D$ −80.4° (*c* 0.0108, 4:1 CH_3CN/CH_3OH); UV (CH_3OH) λ_{max} (log ϵ) 278 nm (4.21); IR (film, NaCl), ν_{max} 3388 (OH), 2936, 1702, 1638, 1440, 1286, 1182, 1075 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) (Table 1); ^{13}C NMR (acetone-d_6, 75 MHz) (Table 3); high-resolution ESIMS *m*/*z* 571.1522 $[M + Cl]^-$ (calcd for $C_{26}H_{32}O_{12}$+Cl, 571.1583).

Caudatoside C (4): light tan solid (521 mg); mp 111−114 °C; $[\alpha]^{28}_D$ −88.7° (*c* 0.0096, 4:1 CH_3CN/CH_3OH); UV (CH_3OH) λ_{max} (log ϵ) 233 (4.08), 313 nm (4.22); IR (film, NaCl), ν_{max} 3377 (OH), 2951, 1697, 1635, 1605, 1515, 1440, 1366, 1290, 1170, 1075 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) (Table 1); ^{13}C NMR (acetone-d_6, 75 MHz) (Table 3); high-resolution ESIMS *m*/*z* 587.1544 $[M + Cl]^-$ (calcd for $C_{26}H_{32}O_{13}$+Cl, 587.1532); 551.1723 $[M - H]^-$ (calcd for $C_{26}H_{31}O_{13}$, 551.1765).

Caudatoside D (5): light tan solid (725 mg); mp 124−127 °C; $[\alpha]^{28}_D$ −74.1° (*c* 0.0096, 4:1 CH_3CN/CH_3OH); UV (CH_3OH) λ_{max} (log ϵ) 232 (4.05), 314 nm (4.22); IR (film, NaCl), ν_{max} 3377 (OH), 2951, 1696, 1635, 1605, 1515, 1440, 1367, 1289, 1170, 1075 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) (Table 1); ^{13}C NMR (acetone-d_6, 75 MHz) (Table 3); high-resolution ESIMS *m*/*z* 587.1612 $[M + Cl]^-$ (calcd for $C_{26}H_{32}O_{13}$+Cl, 587.1532); 551.1797 $[M - H]^-$ (calcd for $C_{26}H_{31}O_{13}$, 551.1765).

Caudatoside E (6): light tan solid (29 mg); mp 72−75 °C; $[\alpha]^{28}_D$ −41.6° (*c* 0.0084, 4:1 CH_3CN/CH_3OH); UV (4:1 CH_3CN/CH_3OH) λ_{max} (log ϵ) 221 (4.16), 235 (4.15), 297 (4.00), 325 nm (4.06); IR (film, NaCl), ν_{max} 3381 (OH), 2938, 1689, 1636, 1601, 1525, 1442, 1376, 1288, 1185, 1076, 988 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) (Table 1); ^{13}C NMR (acetone-d_6, 75 MHz) (Table 3); high-resolution ESIMS *m*/*z* 603.1373 $[M + Cl]^-$ (calcd for $C_{26}H_{32}O_{14}$+Cl, 603.1481); 567.1683 $[M - H]^-$ (calcd for $C_{26}H_{31}O_{14}$, 567.1714).

Caudatoside F (7): light tan solid (46 mg); mp 76−79 °C; $[\alpha]^{28}_D$ −57.3° (*c* 0.0084, 4:1 CH_3CN/CH_3OH); UV (4:1 CH_3CN/CH_3OH) λ_{max} (log ϵ) 222 (4.19), 235 (4.19), 298 (4.04), 324 nm (4.12); IR (film, NaCl), ν_{max} 3388 (OH), 2939, 1686, 1636, 1602, 1524, 1442, 1374, 1287, 1184, 1077, 989 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) (Table 1); ^{13}C NMR (acetone-d_6, 75 MHz) (Table 3); high-resolution ESIMS *m*/*z* 603.1353 $[M + Cl]^-$ (calcd for $C_{26}H_{32}O_{14}$+Cl 603.1481); 567.1464 $[M - H]^-$ (calcd for $C_{26}H_{31}O_{14}$, 567.1713).

Acetylation of Compounds 1−7. Compounds **1**−**7** (20 mg, except compound **6**, 13 mg) were each treated with Ac_2O (1 mL) and pyridine (1 mL) at room temperature for 24 h. The reaction mixture was suspended in 10 mL of H_2O, then subsequently extracted three times with $CHCl_3$ (10 mL each). The combined $CHCl_3$ layers were extracted twice with 1 N HCl (10 mL each), once with 5% $NaHCO_3$ (10 mL), and finally once with saturated NaCl (10 mL). Each $CHCl_3$ layer was dried over Na_2SO_4 and filtered to give compounds **8**−**14**, respectively.

5-Deoxypulchelloside I hexaacetate (8): colorless amorphous solid (29 mg); UV (CH_2Cl_2) λ_{max} (log ϵ) 233 (4.06), 281 nm (2.99); IR (film, NaCl), ν_{max} 2955, 1751, 1713, 1643, 1437, 1369, 1228, 1080, 1040, 910, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (Table 2); ^{13}C NMR ($CDCl_3$, 75 MHz) (Table 3); low-resolution ESIMS *m*/*z* 693.25 $[M + Cl]^-$.

Caudatoside A pentaacetate (9): colorless amorphous solid (27 mg); UV (CH_2Cl_2) λ_{max} (log ϵ) 281 nm (4.16); IR (film, NaCl), ν_{max} 2954, 1757, 1715, 1639, 1368, 1229, 1166, 1078, 1039, 912, 732 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (Table 2); ^{13}C NMR ($CDCl_3$, 75 MHz) (Table 3); ESIMS *m*/*z* 781.31 $[M + Cl]^-$.

Caudatoside B pentaacetate (10): colorless amorphous solid (29 mg); UV (CH_2Cl_2) λ_{max} (log ϵ) 281 nm (4.09); IR (film, NaCl), ν_{max} 2954, 1755, 1714, 1639, 1368, 1229, 1165, 1078, 1040, 913, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (Table 2); ^{13}C NMR ($CDCl_3$, 75 MHz) (Table 3); ESIMS *m*/*z* 781.31 $[M + Cl]^-$.

Caudatoside C hexaacetate (11): colorless amorphous solid (25 mg); UV (CH_2Cl_2) λ_{max} (log ϵ) 285 nm (3.98); IR (film, NaCl), ν_{max} 2954, 1758, 1715, 1640, 1508, 1369, 1228, 1165, 1079, 1039, 912, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (Table 2); ^{13}C NMR ($CDCl_3$, 75 MHz) (Table 3); ESIMS *m*/*z* 839.31 $[M + Cl]^-$.

Caudatoside D hexaacetate (12): colorless amorphous solid (25 mg); UV (CH_2Cl_2) λ_{max} (log ϵ) 285 nm (3.99); IR (film, NaCl), ν_{max} 2953, 1755, 1714, 1639, 1508, 1370, 1228, 1164, 1079, 1040, 913, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (Table 2); ^{13}C NMR ($CDCl_3$, 75 MHz) (Table 3); ESIMS *m*/*z* 839.31 $[M + Cl]^-$.

Caudatoside E heptaacetate (13): colorless amorphous solid (15 mg); UV (CH_2Cl_2) λ_{max} (log ϵ) 284 nm (4.07); IR (film, NaCl), ν_{max} 2956, 1756, 1714, 1641, 1505, 1435, 1371, 1228, 1180, 1040, 991, 906, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (Table 2); ^{13}C NMR ($CDCl_3$, 75 MHz) (Table 3); ESIMS *m*/*z* 897.34 $[M + Cl]^-$.

Caudatoside F heptaacetate (14): colorless amorphous solid (24 mg); UV (CH_2Cl_2) λ_{max} (log ϵ) 282 nm (4.18); IR (film, NaCl), ν_{max} 2954, 1756, 1714, 1640, 1505, 1436, 1371, 1218, 1180, 1111, 1078, 1040, 991, 905, 872 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (Table 2); ^{13}C NMR ($CDCl_3$, 75 MHz) (Table 3); ESIMS *m*/*z* 897.31 $[M + Cl]^-$.

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