Tetrahedron Vol. 48, No. 23, pp. 4725-4732, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

UNUSUAL CASSANES FROM A *CHAMAECRISTA* SPECIES

Bertha Barba, Jésus G. Diaz, Virgil L. Goedken, Werner Herz*†

Department of Chemistry, The Florida State University, Tallahassee, FL 32306, U.S.A.

Xorge A. Dominguez

Departamento de Química Organica, ITESM, Suc. Correos "J", Monterrey, N. L. 64849, México

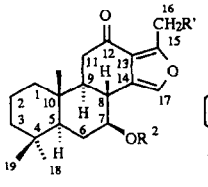
(*Received in USA* 15 *November* 1991)

Key Words. Cassanes; Diterpenes; Chamaecrista flexuosa *var.* texana*; Leguminosae*

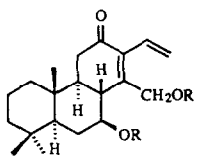
Abstract. Isolation and structure determination of four unusual cassanes, one containing an ethynyl group, and one *bis*-norcassane from *Chamaecrista flexuosa* var. *texana* (syn. *Cassia texana*) is reported.

Introduction

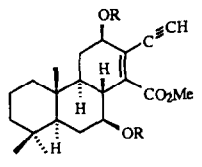
The cassanes comprise a relatively rare group of rearranged diterpenes whose biogenesis involves the migration of a methyl group from C-13 to C-14 of the pimarane skeleton[1]. Their occurrence seems to be limited to certain subgroups within the family Leguminosae. In the present article we report the isolation and structure determination of four unusual cassanes 1a, 1c, 2a and 3a and one *bis*-nor cassane 4 from the roots of *Chamaecrista flexuosa* (L.) Greene var. *texana* (Buckley) Irwin and Barneby (syn. *Cassia texana* Buckley)[3]. This taxon is endemic to southeastern Texas and adjacent areas of Mexico and is a member of subfamily Caesalpinioideae, tribe Cassiae, a tribe from which no cassanes have so far been reported. Piceatannol (3,4,3',5'-tetrahydroxystilbene)[4,5] and several commonly encountered phenol derivatives were also found.



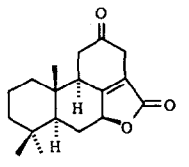
1a R^1,R^2=H
b R^1=H,R^2=Ac
c R^1=OH, R^2=H
d R^1=OAc, R^2=Ac



2 a R=H
b R=Ac



3 a R=H
b R=Ac



4

Results and Discussion

Since the new cassanes 1a, 1c, 2a, 3a and 4 which we have named chamaetexanes A, B, C, D and E were obtained in small amounts only, their structure determination depended almost entirely on spectroscopic techniques and X-ray diffraction. The mass, ^{1}H-

† Dedicated to Professor Gabor Fodor on the occasion of his 75th birthday.

and ^{13}C-NMR spectra (Tables 1 and 2) of chamaetexane A, $C_{20}H_{28}O_3$, mp. 175-178°, and the mass and ^{1}H-NMR spectra of its monoacetate **1b** indicated that chamaetexane A was a tetracyclic diterpene with an A ring corresponding to the A ring of pimaranes and abietanes (three methyl singlets, carbon signals corresponding to C-1 through C-4, C-10, C-18, C-19, C-19 and C-20) and an equatorial secondary - OH evidenced by an appropriately split multiplet at δ3.61 moving to δ4.75 after acetylation. One of the protons adjacent to the -CH-OH group whose signal appeared at δ1.98 was clearly part of a methylene unit and coupled to a methine hydrogen at δ0.98, the signal of the other methylene proton being buried in a complex of several signals near δ1.6. A third proton adjacent to the -CHOH group was a methine hydrogen (*ddd* at δ2.61) further coupled vicinally to a proton in the δ1.6 complex and allylically (J=1.5Hz) to a vinylic proton at δ7.51 whose chemical shift indicated the presence of extended conjugation. Finally the ^{13}C-NMR spectrum revealed the presence of a conjugated ketone (C-Signal at δ196.08) apparently flanked on the one hand by a methylene unit (two *dd*'s at δ2.52 and 2.20 mutually coupled by 16.5 Hz and adjacent to a methine in the δ1.6 complex) and on the other by one of two olefinic bonds. One of these was tri- and the other tetrasubstituted because of the presence of three singlets and one doublet in the sp^2 region of the ^{13}C-NMR spectrum. The trisubstituted double bond carried the proton responsible for the signal at δ7.51, the tetrasubstituted double bond carried a methyl (sharp singlet at δ2.56) whose chemical shift indicated that it was strongly deshielded, possibly by the carbonyl group. The nature of the fourth oxygen was at first unclear, but since the ^{13}C-NMR spectrum exhibited only one signal in the C-O region, that of a doublet at δ75.62 due to the secondary hydroxyl, the fourth oxygen had to be that of an ether linking the tri- and tetrasubstituted double bonds.

To eliminate further speculation, the structure was solved by X-ray crystallography. Fig. 1 is a stereoscopic view of the molecule which demonstrates formula **1a** for chamaetexanin A. Crystal data are given in the Experimental section; lists of torsion angles, bond distances, bond angles, refined positional coordinates with anisotropic thermal parameters and observed and calculated structure factors are deposited in the Cambridge Crystallographic Centre.

After structure elucidation of **1a** and **1b**, the results of NOE difference spectrometry in Table 3 permitted us to assign the multiplets arising from H-1, H-2 and H-3 and the singlets arising from H-18, H-19 and H-20 all of which remained essentially unchanged throughout the series.

Chamaetexanin B which formed a diacetate and whose ^{1}H-NMR spectrum (Table 1) differed from that of chamaetexanin A only in replacement of the vinylic methyl signal by signals characteristic of -CH_2OH was therefore **1c**.

Chamaetexanin C, $C_{20}H_{30}O_3$, was non-crystalline and also formed a diacetate. The ^{1}H-NMR spectra of these two substances (Table 1) and the ^{13}C-NMR spectrum of the diacetate (Table 2) indicated that the nature and substitution pattern of rings A and B were the same as in chamaetexanins A and B. In these two instances sequential decoupling from C-5 through C-11 was possible and established the location of the carbonyl group, which was again conjugated (singlet at δ198.69), on C-12. The conjugated double bond carried a -CH_2OH group (AB system centered at δ4.57 which moved downfield on acetylation) and a vinyl group represented by an ABX system (A at δ5.49, B at δ5.24 and X at δ6.43). Since the X proton was homoallylically coupled to H-8 (J=2 Hz), the vinyl group was attached to C-13 and the -CH_2OH group was attached to C-14 of the tricyclic nucleus, thus leading to the cassane structures **2a** and **2b** as proper representations for chamaetoxin C and its diacetate[6].

Structure elucidation of chamaetexanin D, $C_{21}H_{30}O_4$, mp 183-185°, is best discussed in terms of structure **3a** which we derived with some difficulty. Rings A and B, with an equatorial hydroxyl group at C-7, corresponded to those of chamaetexanins A-C, but the conjugated ketone group was missing and replaced by another secondary hydroxyl. This was initially placed on C-14, thus negating the presence of a cassane nucleus, because H-8 was coupled not only to H-7 and H-9, but also (J=3.5 Hz) to the proton under the second hydroxyl at δ4.21. The latter experienced the expected paramagnetic shift to δ5.48 on conversion to a diacetate and was

Table 1. ^{1}H-NMR Spectra of Compounds **1a-d, 2a,b, 3a,b and 4** ($CDCl_3$, 500 MHz)*

H	1a	1b	1c	1d	2a	2b	3a	3b	4
1α	0.89*dt*	0.93	0.92	0.93	0.89	0.88	0.86	0.91	0.92
1β	1.71*brd*	1.72	1.71	1.72	1.64	1.67	1.73	1.69	1.87
2α	1.50*dquint*	1.50	1.50	1.50	1.50	1.50	1.40	1.51	~1.53*m*
2β	1.60*tq*	1.59	1.58	1.58	1.57	1.58	1.60	1.56	1.53*m*
3α	1.15*dt*	1.19	1.16	1.17	1.13	1.16	1.14	1.17	1.11
3β	1.45*brd*	1.42	1.45	1.45	1.44	1.44	1.43	1.43	~1.53*m*
5	0.98*dd*	1.05	1.00	1.04	0.98	1.03	0.92	1.01	1.17
6α	1.98*ddd*	2.15	1.99	2.17	2.01	2.21	1.95	2.11	2.51
6β	1.50*ddd*	1.45	1.52	1.51	1.60	1.39	1.36	1.32	1.28
7	3.61*dddd*	4.75*ddd*	3.62*dddd*	4.76*ddd*	3.72*dddd*	4.89*ddd*	3.46	4.60	4.85*dddd*
8	2.61*ddd*	2.90	2.64	2.94	2.71*brt*	2.79*ddd*	3.52	2.80	-
9	~1.55*m*	1.60*ddd*	~1.55*m*	~1.50*m*	1.43*m*	1.39*ddd*	1.06	1.22*ddd*	2.68*brd*
11α	2.52*dd*	2.55	2.61	2.61	2.48	2.59	2.18*ddd*	2.16*ddd*	2.63*brdd*
11β	2.20*dd*	2.20	2.27	2.26	2.13	2.17	1.22*ddd*	1.55*m*	2.59*ddd*
12	-	-	-	-	-	-	4.21*ddd*	5.48	-
13	-	-	-	-	-	-	-	-	3.11*ddd*
									3.05*brd*
15	-	-	-	-	6.43*ddd*	6.40	-	-	-
16	2.56*s*†	2.55†	4.78*dd*	5.36*d*	5.49*dd*	5.46*dd*	3.22*s*	3.07*s*	-
			4.75*dd*	5.33*d*	5.24*dd*	5.31*dd*			
17	7.51*d*	6.98	7.59	7.16	4.65*brd*	4.87	3.79*s*†	3.78*s*†	-
					4.49*d*	4.73	(OMe)	(OMe)	
18†	0.90*s*	0.90	0.90	0.90	0.90	0.85	0.89	0.90	0.97
19†	0.87*s*	0.87	0.89	0.86	0.87	0.89	0.85	0.86	0.84
20†	0.96*s*	0.99	0.98	0.98	0.85	0.96	0.83	0.81	0.68
Ac†		2.165		2.16		2.06		2.09	
				2.09		2.02		2.01	
OH	1.60*d*		4.98*t*						
			1.63*d*						

J (Hz): Compounds **1a-d-4a,b**, 1α,1β=1α,2β=2α,2β=2β,3α=13.5;1α,2α=1β,2α=1β,2β=2α,3α=2α,3β=2β,3β=3.5; Compounds **1a-d-3a,b**, 5,6α=2.5; 5,6β=6α,6β=13; 6α,7=5; 6β,7=11; 7,8=10.5; compounds **1a-d**, 8,9=11.5; 8,15=1.5, 9,11α=3; 11β=13.5; 11α,11β=16.5; compounds **1a,c**, 7, OH=6; compound **1c**, 17, OH=6; compounds **2a,b** 8,9=11.5; 8,15=2; 9,11a=2.5, 9,11b=14; 11a, 11b=15.5; compounds **3a,b** 8,9= 10.5; 9,11α=2; 9,11β=12; 11α,11β=12; 11α,12=6; 11β,12=10.5; compound **4**, 5,6α; 5,6β=6α,6β=12.5; 6α,7=7.5, 6β,7=10.5; 7,9=1; 7,13α=2.5; J9, 13α=2.5; 9,11α=2; 9,11β=9; 11α, 11β=16.5; 13α,13β=21.

* Signal splittings are not repeated if identical with splittings in preceeding column

† Intensity three protons

also coupled to the two protons on C-11 (*J*'s=10.5 and 6 Hz). However, this did not allow for placement of a carbomethoxy group whose presence was evident from the ^{1}H- and ^{13}C-NMR spectra and accounted for the extra carbon atom; neither could it be reconciled with the three additional unsaturations evident from the empirical formula.

Initially the ^{13}C-NMR spectrum of **3a** was equally confusing since it exhibited only two singlets in the δ120-160 region characteristic of sp^2 carbon and four signals in the C-O region, two doublets clearly associated with the two -CHOH groups, one relatively weak signal at δ78.52 which appeared to be a singlet and one stronger one at δ84.16 whose multiplicity initially remained

obscure. However, solution of the puzzle became possible when examination of the fully coupled ^{13}C-NMR spectrum revealed that the signal at δ84.16 exhibited a coupling of 254 Hz, i.e. that it was the signal of an acetylenic CH, also responsible for a relatively weak singlet at δ3.07 in the ^{1}H-NMR spectrum, which was also present in the ^{1}H-NMR spectrum of 3b and was originally attributed to a persistent impurity. The acetylenic carbon partner of the doublet at δ84.16 was therefore responsible for the weak singlet at δ78.52; therefore chametexanin D incorporated an ethynyl group.

Table 2. ^{13}C-NMR spectra of compounds **1a**, **2b**, **3a** and **4a** (67.89 MHz, $CDCl_3$)*

C	1a	2b	3a	4a
1	38.70*t*	38.32*t*[a]	38.35*t*	37.46*t*
2	18.54*t*	18.54*t*	18.71*t*	18.51*t*
3	41.69*t*	41.66*t*	41.83*t*	41.72*r*
4	33.12*s*	32.98*s*	33.09*s*	33.72*s*
5	52.18*d*[a]	50.83*d*[b]	52.59*d*	50.08*d*[a]
6	32.17*t*	28.20*t*	32.49*t*	31.02*t*
7	75.62*d*	75.13*d*	73.23*d*	79.73*d*
8	40.42*d*	43.64*d*	46.15*d*[a]	162.98*s*
9	52.04*d*[a]	50.46*d*[b]	48.53*d*[a]	49.22*d*[a]
10	36.48*s*	36.02*s*	36.17*s*	not seen
11	39.88*t*	38.32*t*[a]	29.96*t*	39.24*t*
12	196.08*s*	198.69*s*	68.86*d*	205.48*s*
13	127.70*s*	140.46*s*	143.68*s*	34.61*t*
14	117.69*s*	150.01*s*	123.68*s*	121.83*s*
15	156.42*s*	130.08*d*	78.52*s*	171.49*s*
16	13.74*q*	122.46*t*	84.16*d* (254Hz)	-
17	137.24*d*	64.00*t*	170.40*s*	-
18	33.32*q*	33.06*q*	33.09*q*	33.52*q*
19	21.70*q*	21.50*q*	21.39*q*	21.76*q*
20	14.08*q*	14.37*q*	14.17*q*	14.17*q*
		170.63*s*, 170.05*s*		
		21.39*q*, 20.33*q*		

* Multiplicity by DEPT pulse sequence. Assignments by comparison with related compounds in the literature.
[a,b] Assignments with the same letter in the same column may be interchanged.

Table 3. NOE Difference Spectrum of **1b** (500 MHz, $CDCl_3$)

Irradiated	Observed (%)
H-1β	H-1α (25)
H-3α	H-3β (24), H-18 (4.5)
H-5α	H-1α (9.9), H-3α (2.3), H-62 (2.7), H-18 (5.1)
H-7α	H-5α (5.0), H-6α (5.6), H-9α (4.6), H-17 (4.7)
H-8β	H-6β (2.8), H-11β (3.9), H-20 (7.9)
H-11α	H-1β (4.4), H-9α (2.2), H-11β (13.6)
H-11β	H-1β (2.4), H-6β (5.4), H-8β (2.4), H-11α (8.7), H-20 (2.2)
H-17	H-7α (2.6), H-8β (1.4), Ac (2.8)
H-18	H-1β (3.2), H-2β (1.2), H-3α (2.3), H-5α (2.9), H-6α (3.6)
H-19	H-2β (6.4), H-3β (7.2), H-20 (5.5)
H-20	H-1β (1.8), H-2β (2.3), H-3β (2.8), H-8β (5.1), H-11β (3.1), H-19 (2.4).

If, by analogy with **1a**, **1c** and **2a**, chamaetexane D were a cassane, placement of the carbomethoxy group on C-14 and placement of the ethynyl group on C-13 as in **3a** would follow. In this case the extra 3.5 Hz coupling exhibited by the H-8 signal would have to be attributed to homoallylic coupling with an α-orientated proton on C-12 carrying the second hydroxyl group. Reversal of the two substituents on C-13 and C-14 would produce a cleistanthane, an alternative which, although unlikely in view of the structures of **1a**, **1c** and **2a**, could not be dismissed out of hand.

To remove this faint doubt the proposed structure was verified by X-ray crystallography. Fig. 2 is a stereoscopic view of the molecule which shows that formula **3a** for chamaetexanin D is correct. Ring C is a slightly distorted half-chair as seen from the torsion angles of ring C^7. The distortion brings H-12α closer to the 90° angle (relative to the plane of the double bond) for maximum allylic or homoallylic coupling and probably accounts for the 3.5 Hz value for $J_{8\alpha,\ 12\alpha}$. Crystal data are given in the Experimental section; lists of torsion and bond angles, refined positional coordinates and observed and calculated structure factors are deposited with the Cambridge Crystallographic Centre.

Finally we consider chamaetexanin E, $C_{18}H_{24}O_3$, mp 215-218°. The empirical formula and the ^{13}C-NMR spectrum (Table 2) suggested the presence of a *bis*-norcassane. Rings A and B were intact but the oxygen function on C-7 was modified as evidenced by the paramagnetic shift of the H-7 signal to δ4.85. Furthermore the usual large coupling involving H-7 and H-8 (J~10.5 Hz) was replaced by two small couplings which indicated that C-8 might be involved in a double bond whose presence was revealed by two C-singlets at δ121.83 and 162.98. The two small couplings constants might then be due to allylic, homoallylic or W-type coupling.

The ^{13}C-NMR spectrum also exhibited two singlets at δ171.49 and 205.48. The former indicated the presence of an α,β-unsaturated lactone, thus accounting for the appearance of one of the olefinic signals, that of the β-carbon, at very low field; the second indicated the presence of a ketone. This was flanked by two methylenes. One, H-13a,b was represented by an AB system centered at δ3.08 which exhibited the characteristically large *gem*-coupling of 21 Hz. The A component was responsible for a 2.5 Hz coupling to H-7 and also for a small coupling to a signal at δ2.68. The second methylene was represented by an AB system centered at δ2.59 (H-11α,β, $J_{\alpha,\beta}$=16.5 Hz) each of whose components was also coupled to the signal at δ2.68 by 9 and approximately 2 Hz, respectively. This permitted expansion of the structural formula to **4**, a *bis*-norcassane, where H-13a is homoallylically coupled to H-7 and H-9 and where H-7 is also long range coupled to H-9. Since C-13 is not functionalized the loss of the two carbon side chain is easiest to explain in terms of the cleavage of a β-diketone formed from the tricyclic precursor of **1a** by isomerization of a $\Delta^{14(17)}$-enol to a $\Delta^{8(14)}$-enal and further oxidation of the aldehyde to a carboxylic acid and subsequent lactonization, although stepwise degradation of the side chain on C-13 to a β-ketoaldehyde or β-ketoacid followed by loss of formaldehyde or CO_2 cannot be excluded.

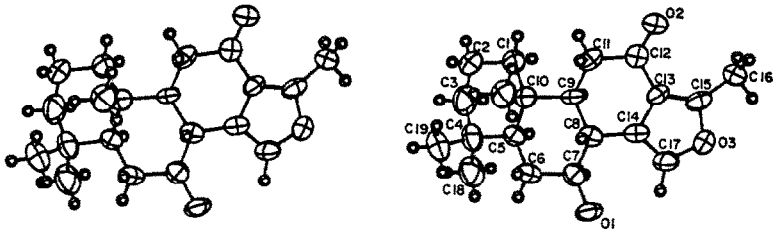


Figure 1. Stereoscopic view of **1a**

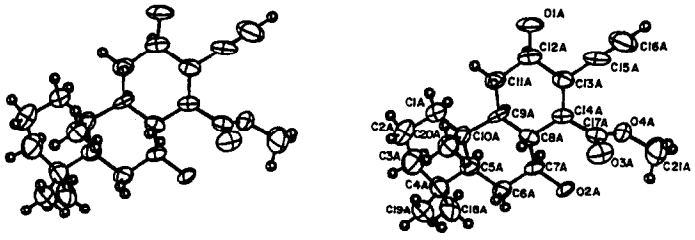


Figure 2. Steroscopic view **3a**

To the best of our knowledge chamaetexanin D is unique among naturally-occurring diterpenes in incorporating an acetylenic bond and, more specifically, an ethynyl group. It is interesting that the **2a** and **3a** can be related by invoking a transfer of two hydrogens from the vinyl group on C-13 to the carbonyl group on C-12, but this can scarcely be the biogenetic pathway leading to **3a**.

Experimental

Isolation of Constituents. Roots (1.9 kg) of *Chamaecrysta flexuosa* var. *texana* collected in November 1988 in Apodaca, Nueva Leon, Mexico (voucher 8246 CTR in the herbarium of ITESM, Monterrey) were macerated and extracted with MeOH in a Soxhlet apparatus for seven days. Evaporation of the extract at reduced pressure gave 50.2 g of residue which was subjected to flash chromatography over a column of silica gel 60 (230-400 mesh), using hexane, benzene, benzene-EtOAc 3:1 and 1:1 EtOAc and MeOH). The hexane fractions contained 2.5 g of a hydrocarbon mixture which was not investigated further. The benzene fractions contained 3.0 g of material which was chromatographed over Sephadex LH-20 (eluent hexane - $CHCl_3$-MeOH, 3:1:1) to give 12.4 mg of vanillin and a mixture of fatty acids which was not investigated further. The benzene-EtOAc (1:1) fractions (10.2 g) were rechromatographed over Si-gel using benzene-EtOAc (1:1) and then over Sephadex LH-20 using hexane - $CHCl_3$ - MeOH (1:1:1) to give 180.2 mg of piceatannol (3,4,3',5'-tetrahydroxystilbene), mp. 230-234°, identified by MS, ^{1}H- and ^{13}C-NMR spectrometry. The residues from this fraction, from the EtOAc fraction (8.2 g) and from the MeOH fractions (14.5 g) consisted of polar mixtures which failed to yielded homogeneous material when further purification was attempted.

The benzene - EtOAc (3:1) fractions were rechromatographed over Sephadex LH-20 (hexane - $CHCl_3$ - MeOH, 1:1:1, 26 fractions of 40 ml each), the eluate being monitored by TLC. Frs. 1-5 (0.3 g) on further purification over Sephadex LH-20 (hexane-$CHCl_3$-MeOH, 3:1:1) yielded 7.5 mg of an impure yellow anthraquinone. Fraction 6 and 7 (0.65 g) on rechromatography over silica gel (diethyl ether-hexane, 7:3) gave in subfractions 3-15 8.1 mg of pyrrogallol 2-methyl ether and in subfractions 20-35 11.4 mg of vanillyl alcohol. Fractions 8-12 (2.61 g) on rechromatography over Sephadex LH 20 (hexane - $CHCl_3$ - MeOH, 3:1:1) yielded from subfractions 3-8 35.3 mg of **1a** after further chromatographic purification (silica gel, diethyl ether-hexane, 9:1), from subfractions 10-15 12.1 mg of **2a** after further chromatographic purification (silica gel, ether-hexane, 4:1) and from subfractions 7-23 14.0 mg of **4** after final purification by chromatography (silica gel, ether-hexane, 4:1). Fractions 13-21 (1.22 g) on rechromatography over Sephadex LH-20 (hexane - $CHCl_3$ - MeOH, 3:1:1) gave from subfractions 10-18 9.2 mg of **1c** after further chromatography (silica gel, ether-hexane, 7:3) and from subfractions 19-27 after further chromatography (silica gel, ether-hexane, 7:3) 14.8 mg of **3a**. Fractions 22-25

(0.62 g) on rechromatography over Sephadex LH-20 (hexane - $CHCl_3$-MeOH) afforded from subfractions 7-14 after further chromatography (silica gel, benzene-acetone, 9:1) 8.4 mg of 3-hydroxy-4-methoxysalicylaldehyde and from subfractions 20-25 after further chromatography (Sephadex LH-20, hexane - $CHCl_3$ - MeOH, 1:1:1) 17.2 mg of *p*-hydroxybenzaldehyde.

Chamaetexanin A (15,17-epoxy-7β-hydroxy-12-oxocassa-13 (15), 14 (17)-diene) (1a). Colorless needles, mp 175-178 °C, (hexane-ethyl acetate 1:1); $C_{20}H_{28}O_3$ (316), MS EI m/z (rel. int.) 316 (100); ^{1}H- and ^{13}C-NMR spectra in Tables 1 and 2. The monoacetate was prepared in the usual fashion with acetic anhydride - pyridine as colorless crystals, mp 110 °C, $C_{22}H_{30}O_4$ (358), MS CI (isobutane) m/z (rel. int.) 359 (M^++1, 100), 299 (53); ^{1}H-NMR spectrum in Table 2.

Chamaetexanin B (7β, 16-dihydroxy-15, 17-epoxy-12-oxo-cassa-13 (15), 14 (17)-diene) (1c). Amorphous solid; mp 153-155 °C (hexane; $C_{20}H_{28}O_4$ (332); MS CI (isobutane) m/z (rel. int.) 333 (M^++1, 100), 315 (26), 273 (26); ^{1}H-NMR spectrum in Table 1. The diacetate 1d was prepared in the usual fashion as a gum; $C_{24}H_{32}O_6$ (416); MS CI (isobutane) m/z (rel. int.) 417 (M^++1, 24), 357 (100); ^{1}H-NMR spectrum in Table 1.

Chamaetexanin C (7β, 16-dihydroxy-12-oxo-cassa-13,15-diene) (2a). Gum; $C_{20}H_{30}O_3$ (318); MS EI m/z (rel. int.) 318 (69) 300 (23), 289 (100) 271 (41) ^{1}H-NMR in Table 1. Diacetate 2b prepared in the usual fashion was also non-crystalline; $C_{24}H_{34}O_5$ (402); MS CI (isobutane) m/z (rel. int.) 403 (M^++1, 36), 343 (100), 342 (57), 283 (75); ^{1}H- and ^{13}C-NMR spectra in Tables 1 and 2.

Chamaetexanin D (Methyl 7β, 12β-dihydroxycass-13-en-15-yn-17-oate (3a). Transparent white crystals, mp 183-185 °C (hexane-acetone); $C_{21}H_{30}O_4$ (346); MS CI (isobutane) m/z (rel. int.) 347 (M^+, 53), 329 (100); ^{1}H- and ^{13}C-NMR spectra in Tables 1 and 2. The diacetate 3b was a colorless solid (mp not taken because of smallness of sample) whose MS did not exhibit the molecular ion even under chemical ionization conditions due to loss of acetic acid; $C_{25}H_{34}O_6$ (430); MS CI (isobutane) m/z (rel. int.) 371 (M^++1 - AcOH, 100), 311 (61); ^{1}H-NMR spectrum in Table 1.

*Chamaetexanin E (15,16-*Bis-*nor-12oxocassan-8αH,17-olide)* (4). Colorless crystals, mp 215-218 °C (hexane); $C_{18}H_{24}O_3$ (288); MS EI m/z (rel. int.) 288 (M^+, 100), 269 (23); ^{1}H- and ^{13}C-NMR spectrum in Tables 1 and 2.

X-Ray analysis of 1a. Single crystals were grown by slow evaporation from ethyl acetate solution. The crystals were orthorhombic, space group $P2_12_12_1$ with a = 6.229(4), b = 11.452(4), c = 24.288(9) Å and d_{calcd} = 1.21g cm^{-3} for Z = 4 (Mγ = 316.44). The intensity data were measured on a CAD4 Enraf Nonius Diffractometer (Mo radiation, monochromated, Θ-2Θ scans). The size of the crystal used for collection was approximately 0.04 x 0.08 x 0.30 mm^3. No absorption correction was necessary (μ = 0.744). A total of 1660 reflections were measured for Θ ≤ 50°, of which 885 were considered to be observed [I ≥ 2σ(I)]. The structure was solved by direct methods using MULTAN 78[8] and refined by full-matrix least-squares methods. In the final refinement anisotropic thermal parameters were used for nonhydrogen atoms. Methyl hydrogen atoms were located from a difference Fourier map; the remaining hydrogen atom parameters were calculated assuming idealized geometry. Hydrogen atom contributions were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices were R = 5.9 and R_W = 6.1 for the 885 observed reflections. The final difference Fourier map was essentially featureless with no peaks greater than 0.3 e A^{-3}.

X-Ray analysis of 3a. Single crystals were grown by slow evaporation from a hexane-ethyl acetate solution. The crystals were monoclinic, space group $P2_1$ with a = 7.677(3), b = 26.344(4), c = 9.995(2) Å and d_{calcd} = 1.179 g cm^{-3} for Z = 4 (Mγ = 346.47). The size of the crystal used for collection was approximately 0.1 x 0.15 x 0.4 mm^3. No absorption correction was necessary (μ = 0.748). A total of 3797 reflections were measured for Θ ≤ 50°, of which 1930 were considered to be observed [I ≥ 2σ(I)]. The structure was solved by direct methods using MULTAN 78[22] and refined as described in the preceding paragraph. The final discrepancy

indices were R = 6.4 and R_w = 6.1% for the 1930 observed reflections. The final difference Fourier map was essentially featureless with no peaks greater than 0.3 e A^{-3}.

Acknowledgment. J.G.D. thanks the Dirección General de Investigación, Cientifica y Tecnica of Spain for a fellowship.

References and Notes

1. The name cassane derives from the native name "cassa" for *Erythrophleum guineense*, the first source of a crystalline *Erythophleum* alkaloid[2] the nature of whose carbon skeleton was not established until considerably later.
2. Dalma, *Helv. Chim. Acta* **1939**, *22*, 1497-1512.
3. In botanical nomenclature we follow H. S. Irwin and R. C. Barneby. The American Cassiinae - A Synoptical Revision of Leguminosae, Caesalpinioideae, tribe Cassieae, subtribe Cassiinae in the New World, Memoirs New York Bot. Garden **1982**, *35*, 1-918.
4. J. Cunningham, E. Haslam and R. D. Haworth, *J. Chem. Soc.* **1963**, 2875.
5. Y. Kashiwasa, G.-I. Nonaka and I. Nishioka, *Chem. Pharm. Bull.* **1984**, *32*, 3501.
6. After completion of our work, isolation of a related compound, 3,12-dioxocassa-13,15-diene, from *Eragrostis ferruginea* (Gramineae) was described; K. Nishiya, T. Kimura, K. Takeya, H. Itokawa and S. R. Lee, *Phytochemistry* **1991**, *30*, 2410. This is the first report of a cassane from a plant family other than Leguminosae.
7. Although there were two independent molecules per unit cell, there were no chemically significant differences between the two.
8. P. Main "Multan 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data", Department of Physics, University of York, York, England.