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DITERPENES FROM *ZUELANIA GUIDONIA*

MAMUNUR R. KHAN,* ALEXANDER I. GRAY, DAVID R. REED,† IAN H. SADLER† and PETER G. WATERMAN

Phytochemistry Research Laboratories, Department of Pharmacy, University of Strathclyde, Glasgow G1 1XW, Scotland, U.K., †Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland, U.K.

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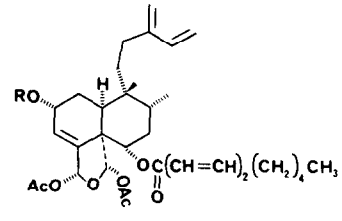
Key Word Index—*Zuelania guidonia*; Flacourtiaceae; stem bark; clerodane diterpenes; zuelanin skeleton; (*rel*)-18β,19α-diacetoxy-10β,17β,19β,20α-clerod-12,14-dien-18,19-oxide; isozuelanin skeleton; (*rel*)-18β,19α-diacetoxy-10β,17β,19β,20α-clerod-13(16),14-dien-18,19-oxide.

Abstract—Four novel diterpenes have been isolated from the stem bark of *Zuelania guidonia*. These compounds are based on two novel derivations of the clerodane nucleus, the zuelanin skeleton [(*rel*)-18β,19α-diacetoxy-10β,17β,19β,20α-clerod-3,12,14-trien-18,19-oxide] and the isozuelanin skeleton [(*rel*)-18β,19α-diacetoxy-10β,17β,19β,20α-clerod-3,12,14-trien-18,19-oxide]. On the basis of spectroscopic studies and some chemical modifications the four new compounds have been identified as 2α-hydroxyzuelanin-6β-cinnamate, 6β-hydroxyzuelanin-2α-cinnamate, 2β-hydroxyzuelanin-6β-cinnamate and 2β-acetoxyisozuelanin-6β-cinnamate.

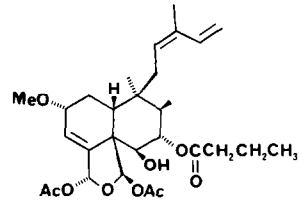
INTRODUCTION

Zuelania guidonia (Sw.) Britton et Millsp. is a shrub or small tree found in Guanacaste Province, Costa Rica [1]. The leaves have been reported [2] to contain large quantities of condensed tannins but no other phytochemical data is available on this species. We have now undertaken an investigation of the stem bark. This has proved to be a rich source of diterpenes based on the clerodane-18,19-acetal nucleus recently reported for the first time from *Casearia pitumba* [3] (e.g. pitumbin, **1**) and *Casearia sylvestris* [4] (e.g. **2**). In this paper we report the identification of the four major diterpenes of a sample of stem bark. We have assigned to these compounds the trivial names 2α-hydroxyzuelanin-6β-cinnamate (**3**), 6β-hydroxyzuelanin-2α-cinnamate (**4**), 2β-hydroxy-zuelanin-6β-cinnamate (**5**) and 2β-acetoxyisozuelanin-6β-cinnamate (**6**). These names are based on the so far theoretical parent compounds zuelanin (**7**) and isozuelanin (**8**) in which C-2 and C-6 are unsubstituted.



1 R=H

14 R=Ac



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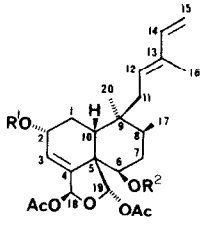
RESULTS AND DISCUSSION

Column chromatography of a petrol extract of the stem bark of *Z. guidonia* over silica gel, eluting with petrol containing increasing amounts of ethyl acetate, gave numerous bands, four of which yielded pure compounds; labelled A–D and isolated with 8, 20, 30 and 33% ethyl acetate, respectively.

The major compound (C), has been characterized as (*rel*)-2α-hydroxyzuelanin-6β-cinnamate (**3**). It was optically active and a UV maximum at 275 nm suggested an extended aromatic chromophore. The IR spectrum revealed bands for the occurrence of hydroxyl, three carbonyl moieties (1710, 1750 cm^{-1} esters, 1640 cm^{-1} α,β-unsaturated ester), and an *exo*-methylene (3080 cm^{-1}). EIMS revealed a highest mass ion at *m/z* 546 which solved for $C_{33}H_{38}O_7$ but the ^{13}C NMR spectrum showed 33 carbons associated with 39 hydrogens. This suggested that, with the addition of an hydroxyl proton, the correct hydrogen count should be 40 and that the empirical formula would be $C_{33}H_{40}O_8$. Thus the compound must undergo facile elimination of the elements of water on EIMS.

^1H and ^{13}C NMR spectra are recorded in Tables 1 and 2, respectively. ^1H–^{13}C correlations were determined by a 2D ^1H–^{13}C one-bond heteronuclear correlation set up to

*Present address: Department of Chemistry, University of Utah, Salt Lake City, UT 84112, U.S.A.

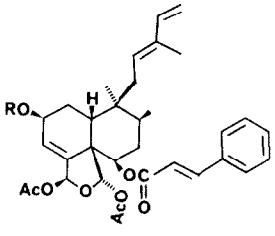


3 R^1 = H, R^2 = cinnamoyl

11 R^1 = Ac, R^2 = cinnamoyl

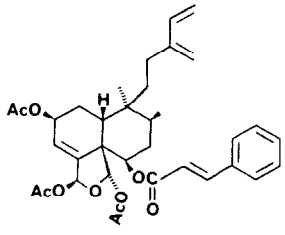
4 R^1 = cinnamoyl, R^2 = H

12 R^1 = cinnamoyl, R^2 = Ac



5 R = H

13 R = Ac



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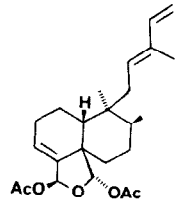

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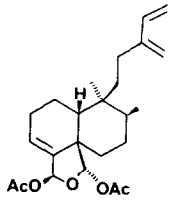

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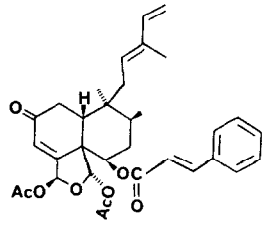

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remove all ^1H–^1H couplings, except those between non-equivalent methylene protons [5]. The spectra revealed the presence of two acetoxy and one cinnamoyl substituents, features which were confirmed by major EIMS fragments at *m/z* 131 $[C_9H_7O]^+$ and *m/z* 43. Subtraction of these esterifying groups leaves a nucleus $C_{20}H_{30}O_5$, suggesting that **3** was a diterpene. The ^1H NMR spectrum revealed a series of signals which could be interpreted, with the aid of decoupling experiments, as $-CH_2-CH=C(Me)-CH=CH_2$, an hypothesis substantiated by the occurrence of a fragment at *m/z* 81 $[C_6H_9]^+$ in the EIMS. This is identical to the side-chain found in the diterpenes from *Casearia sylvestris* (e.g. **2**).

The NMR spectra showed the remaining 14 carbons to consist of two methyls (one tertiary, one secondary), seven methines (two oxymethine, two acetal, one olefinic), two saturated methylenes, and three quaternary carbons. The occurrence of a 2,6-oxygenated kolavane nucleus in which an acetal had formed between Me-18 and Me-19 was established by three chemical modifications. Firstly, oxidation with Jones' reagent yielded the 2-oxokolavane-18,19-oxide (**9**) in which H-1 and H-10 were observed as a clear ABX system with H-10 *trans*-diaxial with a C-1 proton. Secondly, saponification removed the three acylating groups at C-6, C-18 and C-19 and opened the acetal ring to give the 2,6-dihydroxyclerodane-18,19-dial (**10**). Thirdly, acetylation of **3** gave the 2-acetoxy derivative (**11**) in which H-2 showed deshielding of 1.09 ppm. ^1H and ^{13}C NMR spectra of **9**–**11** are given in Tables 1 and 2, respectively.

There remained the problem of resolving stereochemistry at C-2, C-5, C-6, C-8, C-9, C-10, C-18 and C-19. This was achieved by a combination of chemical shift, coupling and NOE studies. The presence of a *cis* A/B ring junction was indicated from the deshielded ^{13}C resonance for C-20 (δ25.0) [3, 4, 6]. The oxymethine proton H-2 showed numerous couplings which could not be individually resolved but its broad nature ($W_{1/2}$ = 20 Hz) contrasted with the relatively sharp signal reported for **1** [3] in which H-2 is pseudoequatorial and with comparable pseudoequatorial H-2 oxymethine signals in other compounds in the zeulanin series (see below). On this evidence the 2-hydroxyl substituent was assigned the pseudoequatorial conformation in **3**. The situation with respect to the C-6 substituent was more simply resolved; H-6 showed distinct axial–axial coupling (12.1 Hz) so requiring the cinnamate ester to be equatorial. Further, spin–spin decoupling experiments allowed $H\text{-}7_{ax}$ to be identified. This proton revealed three large coupling interactions (*gem*, $H\text{-}6_{ax}$, $H\text{-}8_{ax}$) so requiring Me-17 to be equatorial.

The relative stereochemistry was examined through an extensive series of NOE experiments, the significant results of which are shown in Fig. 1. These may be summarised as follows: (i) in the zuelanin ring system the equatorial conformation of Me-20 was established by its irradiation causing enhancements of $H\text{-}1_{eq}$ and H-10. The axial nature of H-2 was supported by an interaction with

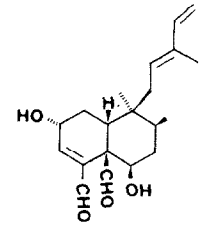

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Table 1. ^{1}H NMR chemical shift values for isolated diterpenes, derivatives and allied compounds

H	3	9	10	11	4	12	5	13	6
1	2.25 *m*	2.91 *dd* (13.3, 7.0)	2.19 *m*						
	1.73 *m*	2.61 *m*							
2	4.51 *m* ($W_{1/2}=20$)	—	4.53 *m* ($W_{1/2}=20$)	5.60 *m* ($W_{1/2}=20$)	5.76 ($W_{1/2}=20$)	5.75 *m* ($W_{1/2}=20$)	4.45 *br s* ($W_{1/2}=10$)	5.48 *br s* ($W_{1/2}=10$)	5.47 *m* ($W_{1/2}=10$)
3	5.98 *br s*	6.18 *d* (1.6)	7.01 *br s*	5.94 *br s*	5.99 *br s*	5.99 *br s*	6.03 *br s*	6.01 *br s*	5.95 *br s*
6	5.25 *dd* (12.1, 4.2)	5.26 *dd* (11.6, 7.0)	3.95 *m* ($W_{1/2}=20$)	5.26 *dd* (12.1, 4.0)	4.04 *dd* (12.0, 4.0)	5.15 *dd* (12.0, 4.0)	5.05 *m*		5.03 *m*
7	1.89 *m*								
	1.72 *m*								
8	2.00 *m*			2.00 *m*	1.98 *m*				1.96 *m*
10	2.41 *dd* (13.9, 2.7)	2.61 *dd* (11.6, 7.0)	2.19 *m*	2.41 *dd* (14.1, 2.7)	2.43 *dd* (14.0, 2.7)	2.42 *dd* (14.0, 2.7)			2.33 *dd* (14.6, 3.8)
11	2.24 *dd* (16.7, 8.2)	2.28 *dd* (17.0, 7.8)	2.19 *m*						
	1.71 *m*								
12	5.38 *br d* (5.4)	5.40 *br d*	5.27 *br d*	5.38 *br d* (5.3)	5.39 *br d* (5.2)	5.38 *br d* (5.2)	5.47 *br d* (5.3)	5.46 *br d* (5.3)	
14	6.29 *dd* (17.3, 10.9)	6.31 *dd* (17.2, 10.1)	6.32 *dd* (17.3, 10.6)	6.30 *dd* (17.2, 10.8)	6.30 *dd* (17.0, 10.1)	6.31 *dd* (17.2, 10.0)	6.31 *dd* (17.4, 10.7)	6.32 *dd* (17.3, 10.5)	6.42 *dd* (17.2, 10.4)
15	5.09 *d* (17.3)	5.11 *d* (17.2)	5.09 *d* (17.3)	5.07 *d* (17.2)	5.09 *d* (17.0)	5.09 *d* (17.0)	5.09 *d* (17.4)	5.10 *d* (17.3)	5.23 *d* (17.2)
	4.94 *d* (10.9)	4.97 *d* (10.1)	4.95 *d* (10.6)	4.94 *d* (10.8)	4.95 *d* (10.1)	4.95 *d* (10.0)	4.94 *d* (10.7)	4.95 *d* (10.5)	5.04 *d* (10.4)
Me-16	1.66 *br s*	1.66 *br s*	1.70 *br s*	1.67 *br s*	1.66 *br s*	1.67 *br s*	1.67 *br s*	1.68 *br s*	5.06 *br s* (1H)
									4.95 *br s* (1H)
Me-17	0.92 *d* (6.8)	0.97 *d* (6.7)	0.95 *d* (6.4)	0.94 *d* (6.5)	0.93 *d* (6.6)	0.93 *d* (6.7)	0.94 *d* (6.6)	0.94 *d* (6.6)	0.94 *d* (6.6)
18	6.50 *dd* (1.7, 1.7)	6.70 *d* (1.6)	9.33 *s*	6.53 *dd* (1.7, 1.7)	6.72 *dd* (1.7, 1.7)	6.51 *dd* (1.7, 1.7)	6.55 *dd* (1.7, 1.7)	6.56 *dd* (1.7, 1.7)	6.47 *dd* (1.7, 1.7)
19	6.63 *s*	6.78 *s*	10.04 *s*	6.65 *s*	6.49 *s*	6.47 *s*	6.71 *s*	6.72 *s*	6.66 *s*
Me-20	0.87 *s*	0.86 *s*	0.85 *s*	0.88 *s*	0.86 *s*	0.89 *s*	0.88 *s*	0.86 *s*	0.97 *s*
Ac	1.96 *s*	1.99 *s*		1.96 *s*	1.96 *s*	1.97 *s*	1.97 *s*	2.00 *s*	1.94 *s*
	2.01 *s*	2.08 *s*		2.01 *s*	2.01 *s*	2.09 *s*	2.06 *s*	2.08 *s*	2.05 *s*
				2.09 *s*		2.10 *s*		2.09 *s*	2.13 *s*
2′	6.36 *d* (17.1)	6.40 *d* (16.1)		6.41 *d* (16.1)	6.35 *d* (16.1)	6.35 *d* (16.1)	6.37 *d* (16.0)	6.35 *d* (16.1)	6.38 *d* (16.0)
3′	7.77 *d* (17.1)	7.78 *d* (16.1)		7.78 *d* (16.1)	7.77 *d* (16.1)	7.76 *d* (16.1)	7.77 *d* (16.0)	7.77 *d* (16.1)	7.76 *d* (16.0)
6–8′	7.36 *m*	7.38 *m*		7.36 *m*	7.36 *m*	7.36 *m*	7.37 *m*	7.37 *m*	7.36 *m*
5′,9′	7.56 *m*	7.57 *m*		7.56 *m*	7.54 *m*	7.55 *m*	7.56 *m*	7.56 *m*	7.55 *m*

Table 2. ^{13}C NMR chemical shift values for isolated diterpenes, their derivatives and compound **1** [1]

C	1	3	9	10	11	4	5	6	14*
1	30.7 *t*	30.5	35.4	29.5	30.2	37.3	30.4	29.2	29.0
2	64.0 *d*	68.5	197.5 *s*	67.9	70.6	73.8	63.8	66.1	67.0
3	128.7 *d*	128.8	125.0	156.7	128.7	123.8	128.6	122.9	124.1
4	141.9 *s*	141.0	162.7	144.2	141.1	144.5	142.5	142.5	145.8
5	53.5 *s*	52.0	53.1	55.9	52.0	53.4	52.1	52.1	53.2
6	74.5 *d*	75.2	74.0	73.0	75.2	70.8	74.1	74.0	74.2
7	34.2 *t*	33.3	33.0	31.0	33.3	26.2	33.2	32.9	33.9
8	37.8 *d*	36.2	35.5	35.5	36.1	36.6	36.2	37.2	37.3
9	38.4 *s*	38.2	38.0	39.2	38.3	38.2	37.7	37.4	38.2
10	37.5 *d*	42.5	42.1	44.8	42.1	41.4	43.8	36.6	35.2
11	29.3 *t*	29.9	29.7	29.3	29.7	29.9	29.6	26.9	27.5
12	25.1 *t*	129.0 *d*	128.0 *d*	126.5 *d*	128.9 *d*	128.7 *d*	129.0 *d*	23.9	24.8
13	146.9 *s*	135.7 *s*	136.1 *s*	136.7 *s*	135.9 *s*	135.6 *s*	135.6 *s*	144.3	146.8
14	141.4 *d*	141.0	140.8	141.3	141.1	141.0	141.2	140.3	141.6
15	113.1 *t*	110.9	111.3	110.9	111.1	110.8	110.9	112.4	113.3
16	115.7 *t*	11.8 *q*	11.8 *q*	12.1 *q*	11.7 *q*	11.9 *q*	11.9 *q*	115.4	116.0
17	16.1 *q*	15.4	15.2	15.3	15.5	15.4	15.5	15.5	16.0
18	96.2 *d*	94.8	94.6	195.5 *s*	94.9	96.7	95.5	95.3	96.1
19	99.2 *d*	97.0	97.3	202.8 *s*	97.1	95.1	97.6	98.3	99.1
20	25.9 *q*	25.0	24.0	25.6	25.1	24.7	25.0	25.3	25.6
AcC=O	170.6 *s*	169.8	169.3		169.8	169.9	170.0	170.3	170.9
	169.9 *s*	169.4	169.0		169.8	169.3	169.9	169.8	170.8
					169.5 *s*			169.8	170.0
Ac-Me	21.9 *q*	21.6	21.5		21.7	21.4	21.6	21.6	21.8
	21.3 *q*	21.0	21.0		21.1	20.9	21.2	21.3	21.3
					21.1 *s*			21.1	21.2
1′		166.0 *s*	165.5		165.9	166.4	166.0	165.9	
2′		117.7 *d*	11.7.7		117.7	117.7	117.7	117.6	
3′		146.0 *d*	146.4		146.1	145.2	146.1	146.1	
4′		134.3 *s*	134.0		134.3	134.3	134.3	134.3	
5′		128.7 *d*	128.8		128.8	128.7	128.8	128.8	
6′		128.3 *d*	128.3		128.4	127.9	128.4	128.7	
7′		130.3 *d*	130.5		130.3	130.2	130.4	130.3	
8′		128.3 *d*	128.3		128.4	127.9	128.4	128.7	
9′		128.7 *d*	128.8		128.8	128.7	128.8	128.8	

*Run in acetone-d_6.

H-10 while H-6 showed a small interaction with H-1_{ax}. These observations support the relative stereochemistry shown in Fig. 1 in which the B-ring forms a chair. (ii) The C-9 side chain showed several revealing NOE interactions with the ring system. In particular one C-11 proton was enhanced by irradiation of Me-17, so confirming the equatorial position of the latter. Most significantly H-12 was found to have a strong interaction with H-10 while Me-16 caused strong enhancement of H-19. This clearly allows for some rotation around C-11/C-12 and requires H-19 to be on the same face as H-10. This differs from **1** in which H-19 is β [3] and exhibited NOE interactions with H-11 and H-7β: no such interactions were observed here. (iii) The final problem of relative stereochemistry, the configuration of H-18, was solved by an NOE experiment that involved irradiation of the H-3′ proton of the cinnamoyl substituent (δ7.77). This caused an 8% enhancement of H-18 which could only occur if H-18 were on the opposite face of the acetal to H-19.

Following these arguments compound **3** can be depicted as shown in Fig. 1 or as the enantiomer. The strongly positive optical rotation of **3** (+79°) is opposite to that observed for **1** (−72°); **2** is positive, but less so (+40°) than **3**. While the variation in relative stereochemistry at C-2 and C-19 make direct analogy impossible this suggests that **1** and **3** should be based on enantiomeric diterpene skeleta.

The structures of the remaining three compounds can be rationalized by comparison with **3**. Isolate B showed similar optical rotation, UV and IR spectra with the EIMS failing to show a molecular ion, the highest fragment once more being for $[M-H_2O]^+$. The ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) revealed the same substitution patterns and substituents. However, changes in chemical shift values relating to H-2 and H-6 required placement of the cinnamoyl ester at C-2, leading to structure **4**. A notable feature in **4** was the deshielding effect that the 2-cinnamoyl group had on the resonances for H-18 and C-18. The 6β-acetoxy derivative (**12**) was prepared and the ^{1}H NMR spectrum (Table 1) showed the anticipated changes and, in addition, reversed this deshielding of H-18.

Analysis of compound D again revealed the same substituents, with a free hydroxyl at C-2 and a cinnamoyl ester at C-6. The major change in the ^{1}H NMR spectrum

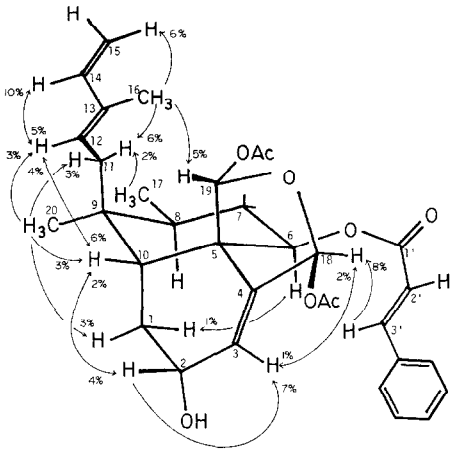

Fig. 1.

was the appearance of H-2 as a sharper resonance suggesting a pseudoequatorial disposition. This was confirmed by the ^{13}C NMR spectrum where C-2 was found to resonate at δ63.8, which is comparable to **1** (Table 2) in which the 2-hydroxyl is pseudoaxial (β) [3]. The other interesting feature observed for D was a molecular ion ($C_{33}H_{44}O_8$) in the EIMS. In the ^{1}H NMR spectrum H-6 was masked by the H-15 olefinic protons and so its stereochemistry could not be determined from coupling constants. However, the ^{13}C NMR resonance for C-6 (δ74.1) is comparable to those found in **1** and **3** so it can be presumed that the cinnamoyl ester remains equatorial (β) so leading to the formulation of D as (*rel*)-2β-hydroxyzuelanin-6β-cinnamate (**5**).

The remaining compound (A) was found to possess (NMR analysis) three acetoxy and one cinnamoyl substituents. The stereochemistry at C-2 and C-6 appeared to be the same as in **5** because A had comparable optical rotation and NMR chemical shift values. The relatively deshielded ^{1}H resonance for H-19 was typical of those compounds with a 6-cinnamoyl substituent so that the additional acetoxyl must be placed at C-2. The major variation in A compared to the other compounds was in the C-9 side-chain where the 12,14-diene was replaced by a 13(16),14-diene. We have given compounds with this side-chain the trivial name isozuelanin so that A must be (*rel*)-2β-acetoxyisozuelanin-6β-cinnamate (**6**). This compound has an identical diterpene skeleton to pitumbin acetate (**14**) [2] with the exception of C-19 stereochemistry and this is reflected in the close similarity of their ^{13}C NMR spectra (Table 2).

The four compounds reported here are the major diterpenes to be isolated from *Zuelania guidonia* in this study. Further work is underway on minor compounds which possess the zuelanin nucleus but are substituted with other esterifying groups, notably benzoyl and octanoyl moieties.

EXPERIMENTAL

UV: MeOH. IR: KBr discs or liquid film; ^{1}H NMR spectra were recorded at 250 MHz or 360 MHz and were referenced to $CHCl_3$ at 7.25 ppm. For homonuclear ^{1}H NOE difference spectroscopy secondary irradiation at 41 dB below 0.2 W was applied during a 8 sec delay followed by spin excitation with a 90° pulse. Blocks of 16 scans preceeded by two dummy scans were accumulated for each irradiation site to give a total of 352 scans per site. Multiplets were irradiated by cycling the irradiation frequency through each of the multiplet line positions in turn. A control spectrum was obtained with irradiation at 0.1 ppm. Subtraction of the control spectrum from the selectively irradiated spectra gave the enhancements shown in Fig. 1. ^{13}C NMR spectra were obtained at 90.56 MHz and referenced to $CDCl_3$ at 76.9 ppm. 2D 1-bond ^{1}H–^{13}C correlation spectra were obtained using the sequence proposed in ref. [5] in which proton coupling is removed in both dimensions. A relaxation delay of 3 sec was used between scans, other parameters being SW (C) = 10 000 Hz, 4000 data points; SW (H) = 1450 Hz, 256 FIDs each of 200 scans. EIMS were run at 70 eV with probe temp of 100–120°. Optical rotation measurements were made with a Perkin–Elmer 240 polarimeter. Petrol refers to petrol (bp 60–80°).

Plant material. Stem bark of *Z. guidonia* was collected in the Santa Rosa National Park, Costa Rica. A voucher specimen is deposited, as part of a general collection from SRNP, at the Missouri Botanic Gardens, St. Louis.

Extraction and isolation of diterpenes. The ground stem bark (500 g) was extracted with petrol, then $CHCl_3$ and finally MeOH. TLC analysis on silica gel revealed petrol and $CHCl_3$ extracts to be comparable, they were bulked and subjected to CC over silica gel eluting with petrol containing increasing amounts of EtOAc. Numerous fractions were obtained of which the four most abundant and pure were: with 8% EtOAc **6** (20 mg); with 20% EtOAc **4** (50 mg); with 30% EtOAc **3** (70 mg); with 33% EtOAc **5** (40 mg).

(rel)-2α-*Hydroxyzuelanin-6β-cinnamate* (**3**). Amorphous, $[\alpha]_D$ +79° ($CHCl_3$; *c* 0.48), R_f 0.44 (silica gel, petrol–EtOAc, 1:1); UV λ_{max} nm: 275; IR ν_{max} cm^{-1}: 3450, 3080, 2960, 2930, 1750, 1710, 1660, 1640, 1450, 1370, 1220; ^{1}H NMR see Table 1; ^{13}C NMR see Table 2; EIMS *m/z* (rel. int.): 546 $[M-H_2O]^+$ (1); 504 (9), 444 (3), 313 (11), 296 (11), 204 (3), 131 (100), 103 (23), 81 (13), 67 (2), 43 (32).

(rel)-2-*Oxozuelanin-6β-cinnamate* (**9**). Compound **3** (20 mg) in Me_2CO was treated with chromic acid–H_2SO_4 (1:1) (1 ml) at room temp for 2 hr. The reaction mixture was diluted with H_2O and extracted with Et_2O. On conc the Et_2O extract gave **7** (10 mg) as an oil; UV λ_{max} nm: 280; IR ν_{max} cm^{-1}: 3080, 2960, 2930, 1755, 1710, 1680, 1640, 1450, 1370, 1220; ^{1}H NMR see Table 1; ^{13}C NMR see Table 2.

(rel)-2α,6β-*Dihydroxy-10β,17β,19β,20α-clerod*-3,12,14-*trien*-18,19-*dial* (**10**). Compound **3** (30 mg) was dissolved in 15% ethanolic KOH (20 ml) and kept at room temp for 2 hr. The reaction mixture was acidified with 2 M HCl and extracted into Et_2O. The ethereal extract was purified by circular prep. TLC (silica gel, petrol–EtOAc, 7:3) to give **8** (15 mg) as an oil; UV λ_{max} nm: 232; IR ν_{max} cm^{-1}: 3080, 2960, 2930, 1750, 1710, 1670, 1650, 1450, 1370, 1220; ^{1}H NMR see Table 1; ^{13}C NMR see Table 2.

(rel)-2α-*Acetoxyzuelanin-6β-cinnamate* (**11**). Compound **3** (10 mg) in pyridine (5 ml) was treated with Ac_2O at room. temp for 24 hr. Normal work-up gave **6** (8 mg) as an oil; UV λ_{max} nm: 275; IR ν_{max} cm^{-1}: 3080, 2960, 2930, 1750, 1710, 1650, 1560; ^{1}H NMR see Table 1.

(rel)-6β-*Hydroxyzuelanin-2α-cinnamate* (**4**). Amorphous, $[\alpha]_D$ +83.0° ($CHCl_3$; *c* 0.12), R_f 0.68 (silica gel, petrol–EtOAc, 1:1). UV λ_{max} nm: 275. IR ν_{max} cm^{-1}: 3500, 3080, 2915, 1750, 1710, 1640, 1450, 1370, 1230, 1170, 1010. ^{1}H NMR see Table 1; ^{13}C NMR see Table 2; EIMS *m/z* (rel. int.): 546 $[M-H_2O]^+$ (1), 504 (2), 444 (7), 356 (3), 315 (3), 295 (2), 187 (36), 171 (16), 131 (100), 81 (36), 67 (8), 43 (51).

(rel)-6β-*Acetoxyzeulanin-2α-cinnamate* (**12**). Compound **4** (10 mg) in pyridine (5 ml) was treated with Ac_2O at room temp

for 24 hr. Normal work-up gave **12** (8 mg) as an oil. UV λ_{max} nm: 275. IR ν_{max} cm^{-1}: 3080, 2960, 2910, 1750, 1710, 1640, 1450, 1230, 1170, 1100. ^{1}H NMR see Table 1.

(rel)-2*β*-*Hydroxyzuelanin*-6*β*-*cinnamate* (**5**). Oil, $[\alpha]_D$ +59° ($CHCl_3$; *c* 0.11); R_f 0.41 (silica gel, petrol–EtOAc, 1:1). UV λ_{max} nm: 275. IR ν_{max} cm^{-1}: 3450, 3080, 2970, 2940, 1750, 1710, 1630, 1450, 1370, 1270, 1220, 1160, 1110. ^{1}H NMR see Table 1; ^{13}C NMR see Table 2; EIMS *m/z* (rel. int.): 564 $[M]^+$ (1), 546 (2), 504 (28), 444 (14), 419 (4), 314 (22); 159 (4), 131 (100), 105 (38), 81 (8), 43 (34); calcd for $C_{33}H_{40}O_8$ 564.2723; found (EIMS) 564.2719.

(rel)-2*β*-*Acetoxyzeulanin*-6*β*-*cinnamate* (**13**). Compound **5** (20 mg) in pyridine (5 ml) was treated with Ac_2O at room temp for 24 hr. Normal work-up gave **13** (10 mg) as an oil; UV λ_{max} nm: 275; IR ν_{max} cm^{-1}: 3080, 2960, 2930, 1750, 1730, 1710, 1640, 1450, 1370, 1230, 1160, 1100; ^{1}H NMR see Table 1.

(rel)-2*β*-*Acetoxyisozuelanin*-6*β*-*cinnamate* (**6**). Oil, $[\alpha]_D$ +50° ($CHCl_3$; *c* 0.04); R_f 0.52 petrol–EtOAc, 7:3); UV λ_{max} nm: 225, 275; IR ν_{max} cm^{-1}: 3080, 2930, 1740, 1715, 1660, 1450, 1370, 1270, 1220, 1170, 1105; ^{1}H NMR see Table 1; ^{13}C NMR see Table 2; EIMS *m/z* (rel. int.): 458 (1), 370 (2), 310 (11), 292 (2), 237 (3), 177 (12), 131 (100), 81 (2), 43 (61).

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