Phytochemistry, Vol. 24, No. 11, pp. 2635–2639, 1985.
Printed in Great Britain.

0031–9422/85 $3.00 + 0.00

ELEMANOLIDES FROM *ZINNIA FLAVICOMA**

ALFREDO ORTEGA and EMMA MALDONADO

Instituto de Química de la Universidad Nacional Autónoma de México, Ciudad Universitaria, Circuito Exterior, Coyoacán, 04510, México, D.F.

(*Revised received* 19 *February* 1985)

Key Word Index—*Zinnia flavicoma*; Compositae; sesquiterpene lactones; zinnolides; zinaflavins.

Abstract—Zinaflavins A–F, six new $H_{5\beta}$, $C_{14\alpha}$ elemanolides were isolated from *Zinnia flavicoma*. Their structures and stereochemistry were determined by spectroscopic techniques and confirmed by X-ray analysis of zinaflavin F. Zinaflavins G and H, two new $H_{5\alpha}$, $C_{14\beta}$ elemanolides were also isolated from this species.

INTRODUCTION

The genus *Tragoceras* has been placed traditionally in the subtribe Zinninae along with *Aganippea*, *Sanvitalia*, *Heliopis*, *Philactis* and *Zinnia* [1]. As a result of artificial hybridization studies between *Zinnia* and *Tragoceras*, it has been proposed that *Tragoceras* should be considered as a new section of *Zinnia* [2]. In order to continue our studies of this genus and to establish if the chemical composition of *Tragoceras* is in agreement with its reclassification, we decided to undertake the chemical analysis of *Zinnia flavicoma* (DC.) Olorode & Torres, one of the five species of the new *Tragoceras* section.

RESULTS AND DISCUSSION

From aerial parts of *Zinnia flavicoma*, zinaflavins A–H were isolated. Zinaflavin A (**1**) exhibited IR absorptions at 1773 cm^{-1} (α,β-unsaturated-γ-lactone), 1754 cm^{-1} (saturated ester) 1655 and 1640 cm^{-1} (double bonds). Its ^1H NMR spectrum (Table 1) showed a vinylic ABX system and only one tertiary methyl group (δ1.09, *s*, 3H). These signals suggest an elemane skeleton for this compound. The signals at δ2.22 *br q*, 1.58 *br h*, 0.89 *t* (3H) and 1.1 *d* (3H) were attributed to a 2-methyl butyrate residue. The fragments at *m/z* 303 $[M-C_4H_9]^+$, 276 $[M-C_5H_8O]^+$, 258 $[M-C_5H_{10}O_2]^+$, 85 $[C_5H_9O]^+$ and 57 $[C_4H_9]^+$ in the mass spectrum, confirmed that assumption. The four low field doublets (one proton each) observed in the ^1H NMR spectrum might be due to the presence of two α,β-unsaturated-γ-lactones. Those at δ6.37 (J = 3 Hz) and 5.82 (J = 3 Hz) were attributed to the C-13 protons conjugated with an 8(12)-lactone and those at δ6.34 (J = 2 Hz) and 5.60 (J = 2 Hz) to the C-3 protons of a 6(15)-lactone. The signals for H-8 and H-6 were observed as two partially superimposed doublets of doublets at δ4.95 and 4.85, respectively. The proton under the ester function appeared as a doublet at δ5.40 indicating that this function is located at C-9. The broad doublet at δ3.34 was assigned to H-5 while the complex signal at 3.58 is believed to be due to H-7. These spectroscopic features are in concordance with structure **1** for zinaflavin A.

Zinaflavin B (**2**) has a tiglate at C-9 instead of the 2-methyl butyrate of zinaflavin A as it is evident from the ^1H NMR spectrum (Table 1) and the mass spectrum, the latter showing a molecular ion at *m/z* 358 and significant fragments at *m/z* 258 $[M-C_5H_8O_2]^+$, 83 $[C_5H_7O]^+$ and 55 $[C_4H_7]^+$.

Zinaflavins C–F have, instead of the Δ double bond, an epoxide function characterized by an ABX system ($\simeq \delta$2.85 *dd*, H-1 and $\simeq \delta$2.74 *m* H-2). The difference between these four compounds is the ester group attached to C-9. Zinaflavins C and D exist as a mixture which was very difficult to separate and they are esterified by 3-methyl butyrate and 2-methyl butyrate, respectively. Zinaflavin E possess a tiglate and finally, zinaflavin F contains an acetate residue. Taking into account the spectroscopic features observed for these compounds, structures **3–6** were assigned to them.

The stereochemistry of H-8 in zinaflavins A–F was deduced from the values of $J_{7,13}$, $J_{7,13'}$ and $J_{7,8}$ assuming an α-disposition of H-7. These J values indicate, according to the modified Samek's rule [3] a conformational type *S* for the 8(12)-lactone ring (Fig. 1), but not a *cis* or *trans* lactone closure. A comparison of these coupling constants with those observed in zinaflorin IV, a *cis*-8(12)-elemanolide (established by X-ray analysis) isolated from *Zinnia* [4] allowed us to assign the same stereochemistry of the 8(12)-lactone closure, therefore H-8 is α. H-9 has also an α-disposition as was indicated by the observed $J_{8,9}$. The stereochemistry of C-5 and C-6 was proposed based on the values of $J_{3,5}$, $J_{3',5}$ and $J_{5,6}$ exhibited by the 6(15)-lactone group, which are indicative of a conformational *cis* P(A) type of lactone ring (Fig. 1), in agreement with the above mentioned rule [3]. The observed values of $J_{6,7}$ = 3–5 Hz were inadequate to decide between the stereochemical possibilities I and II, in which $J_{6,7}$ is satisfied by both dihedral angles ($\sim$ 50° *cis* or $\sim$ 130° *trans*). Examination of Dreiding models of I and II revealed that only structure I can adopt a conformation with *S* type 8(12)- and P(A) type 6(15)-lactone rings simultaneously. In this way, zinaflavins A–F belong to the $H_{5\beta}$, $C_{14\alpha}$ elemanolide group (zinnolides), commonly present in *Zinnia* species.

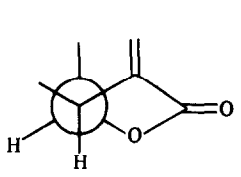
The above assumption was corroborated by an X-ray

*Contribution No. 735 of the Instituto de Química, UNAM.

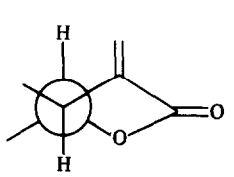
Table 1. ^{1}H NMR spectra of compounds 1–6 (80 MHz, $CDCl_3$, TMS as internal standard)

	1	2	3	4	5	6
H-1	5.67 *dd*	5.68 *dd*	2.84 *dd*	2.86 *dd*	2.85 *dd*	2.87 *dd*
	17, 11	17, 11	7, 3.5	7, 4	7, 4	8, 3
H-2	5.25 *d*	5.23 *d*				
	11	11				
			2.74 *c*	2.75 *c*	2.73 *c*	2.75 *c*
H-2′	5.08 *d*	5.06 *d*				
	17	17				
H-3	6.34 *d*	6.36*	6.44 *d*	6.43 *d*	6.47 *d*	6.44 *d*
	2		2	2.5	2.5	2
H-3′	5.60 *d*	5.58 *d*	5.72 *d*	5.83 *d*	5.81 *d*	5.8 *d*
	2	1.5	1.5	2	2	1.5
H-5	3.34 *dt*	3.3 *br d*	3.27 *ddd*	3.27 *ddd*	3.26 *ddd*	3.31 *ddd*
	8, 2	7	8, 2, 1.5	8, 2.5, 2	8, 2.5, 2	8, 2, 1.5
H-6	4.85 *dd*	4.88 *dd*	4.81 *dd*	4.81 *dd*	4.85 *dd*	4.84 *dd*
	8, 4	7, 3	8, 4.5	8, 5	8, 5	8, 3.5
H-7	3.58 *c*	3.67 *c*	3.60 *c*	3.51 *c*	3.60 *c*	3.59 *c*
H-8	4.95 *dd*	5.03 *dd*	4.92 *dd*	4.90 *dd*	4.97 *dd*	4.94 *dd*
	10, 4	9.5, 4	9.5, 4	9, 4	9, 4	9, 4
H-9	5.40 *d*	5.45 *d*	5.52 *d*	5.54 *d*	5.62 *d*	5.48 *d*
	4	4	4	4	4	4
H-13	6.37 *d*	6.36 *d*	6.36 *d*	6.39 *d*	6.36 *d*	6.37 *d*
	3	3.5	3.5	3.5	3.5	3.5
H-13′	5.82 *d*	5.79 *d*	5.82 *d*	5.88 *d*	5.84 *d*	5.82 *d*
	3	3	3	3	3	3
H-14	1.08 *s*	1.07 *s*	0.96 *s*	0.98 *s*	0.97 *s*	0.93 *s*
OCOR	2.22 *dq*		2.10*	2.25 *dq*	—	2.01 *s*
H-2″	7			7		
H-3″	1.48 *c*	6.66 *br q*	2.10*	1.50 *c*	6.67 *br q*	
		7.5			7.5	
H-4″	0.89 *t*	1.75 *s*		0.90 *t*	1.76 *s*	
	7		0.93 *d*	7		
H-5″	1.1 *d*	1.76 *d*	7 (6H)	1.1 *d*	1.78 *d*	
	7	7.5		7	7.5	

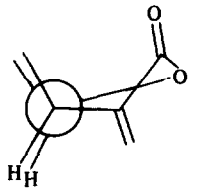
*Superimposed signal.



cis – lactone S – type

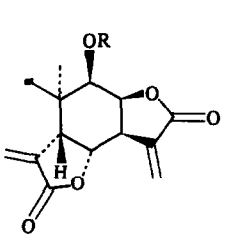


trans – lactone S – type

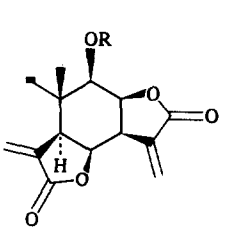


cis – lactone P (A) – type

Fig. 1.



I



II

analysis of zinaflavin F (**6**). The diagram shown in Fig. 2 represents the absolute configuration of **6**, if it is assumed that H-7 is α like in all the sesquiterpene lactones of authenticated stereochemistry. Crystal data are given in the experimental section. Lists of final atomic parameters and isotropic temperature factors, bond lengths, bond angles, anisotropic thermal parameters and hydrogen coordinates are available from the authors.

The more polar fractions of the chromatography yielded a gum, which seemed to be homogeneous on TLC,

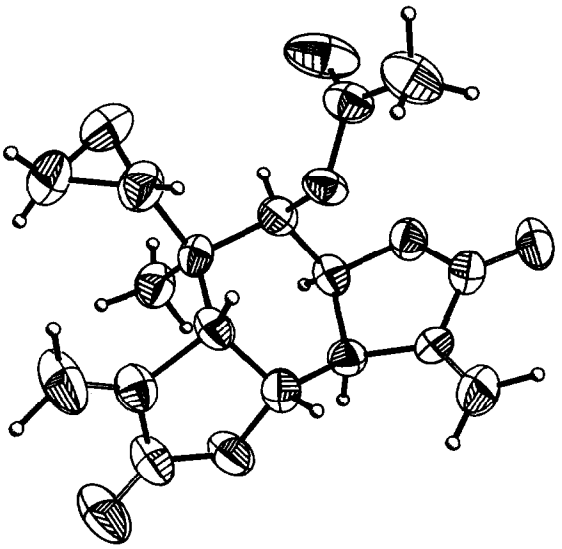


Fig. 2.

but whose ^{1}H NMR spectrum showed it to be a mixture of two closely related compounds, zinaflavins G and H (~ 2:1 ratio). These compounds were separated by HPLC. Careful examination of their ^{1}H NMR spectra and spin decoupling experiments allowed the assignments shown in Table 2, which are consistent with structures **7** and **8** for zinaflavins G and H, respectively.

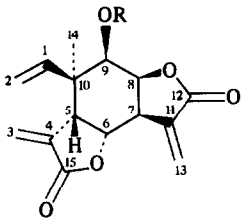
The values of $J_{7,8} = 7$ Hz, $J_{7,13} = 2$ Hz and $J_{7,13'} = 1.5$ Hz allowed us to propose, according to the modified Samek's rule [3], a *cis* closure for the lactone ring, which should be in a P(A) conformation. An α-disposition of H-9 was evident from the observed values of $J_{8,9}$). The coupling constant values showed by H-6 revealed a *trans* relationship with its neighbour protons H-5 and H-7. If it is assumed that H-7 is α, then H-6 is β and H-5 must have the opposite orientation (α), consequently the C-10 methyl group should be β-oriented as it is shown in **7** and **8**.

Formation of the diacetyl derivatives **9** and **10** proved the existence of two hydroxyl groups in zinaflavins G (**7**) and H (**8**). The more significant changes accompaning this transformation were the shift of the H-6 and H-15 signals to lower field and the disappearance of the hydroxyl band

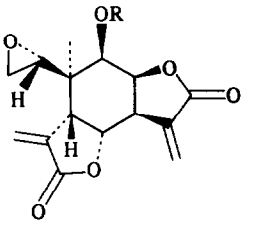
Table 2. ^{1}H NMR spectra of compounds **7–15** (80 MHz, $CDCl_3$, TMS as internal standard)

	7	**8**	**9**	**10**	**11**	**12**	**11+TAI**	**12+TAI**	**14**	**15**
H-1	5.62 *dd*		5.62 *dd*		5.56 *dd*		5.52 *dd*		5.96 *dd*	
	17, 11		17, 11		17, 11		17, 11		17, 11	
H-2	5.08 *d*		5.15 *d*		5.03 *d*		5.03 *d*		5.29 *d*	
	11		11		11		11		11	
H-2′	4.99 *d*		4.98 *d*		4.90 *d*		4.91 *d*		5.20 *d*	
	17		17		17		17		17	
H-3	5.44 *d*		5.26*		6.28*		6.46 *s*		6.34 *d*	
	1.5				(2H)				3.5	
H-3′	5.03*		5.08*				6.29*		5.58 *d*	
									3.5	
H-5	2.34 *d*		2.41 *d*		3.02 *d*		3.43 *d*		2.89 *tt*	
	12		12		12		12		11, 3.5	
H-6	3.89 *dd*		5.37 *dd*		4.05 *dd*		5.42 *dd*		4.41 *dd*	
	12, 9		12, 9.5		12, 9.5		12, 9.5		11, 9	
H-7	3.02 *br dd*		3.15 *br dd*		3.05*		3.32 *br dd*		3.53 *tt*	
	9, 7		9.5, 7						9, 2.5	
H-8	4.72 *dd*		4.71 *dd*		4.77 *dd*		4.78 *dd*		4.83 *dd*	
	7, 4		7, 4.5		6.5, 4		6.5, 4.5		9, 3.5	
H-9	5.07 *d*		5.17 *d*		5.12 *d*		5.16 *d*		5.27 *d*	
	4		4.5		4		4.5		3.5	
H-13	6.25 *d*		6.19 *d*		6.25*		6.29*		6.35 *d*	
	1.5		2						2.5	
H-13′	5.91 *d*		5.57 *d*		5.89 *br s*		5.67 *d*		6.00 *d*	
	1		1.5				1		2.5	
H-14	1.13 *s*		1.21 *s*		1.08 *s*		1.18 *s*		1.08 *s*	
H-15	4.03 AB		4.38 AB		9.45 *s*		9.38 *s*		—	
	(2H)		(2H)							
OCOR	2.48 *h*	2.25*	2.51 *h*	*	2.57 *h*	2.3*	2.58 *h*	*	2.52 *h*	2.27 *c*
H-2″	7		7		7		7		7	
H-3″		1.52 *br h*		1.53 *c*		1.49 *c*	1.17 *d*	1.50 *c*		1.55 *c*
	1.14 *d*	8	1.16 *d*		1.16 *d*		7		1.13 *d*	
H-4″	7 (6H)	0.88 *t*	7 (6H)	0.88 *t*	7 (6H)	0.89 *t*	1.16 *d*	0.89 *t*	7 (6H)	0.89 *t*
		8		7		7	7	7		7
H-5″		1.11 *d*		1.14 *d*		1.15 *d*		1.20 *d*		1.11 *d*
		7		7		7		7		7
OAc				2.09, 2.01						

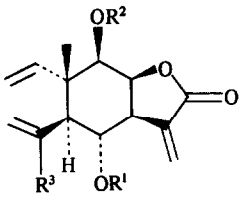
*Superimposed signal.



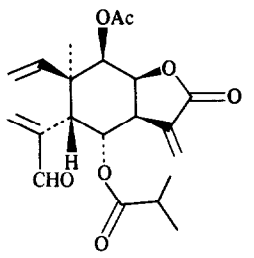
1 R = 2 – Mebu
2 R = Tigl



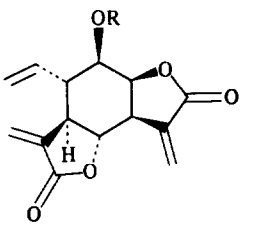
3 R = 3 – Mebu
4 R = 2 – Mebu
5 R = Tigl
6 R = Ac



7 R^1 = H, R^2 = ibu, R^3 = CH_2OH
8 R^1 = H, R^2 = 2 – Mebu; R^3 = CH_2OH
9 R^1 = Ac; R^2 = ibu; R^3 = CH_2OAc
10 R^1 = Ac; R^2 = 2 – Mebu; R^3 = CH_2OAc
11 R^1 = H; R^2 = ibu; R^3 = CHO
12 R^1 = H; R^2 = 2 – Mebu; R^3 = CHO



13



14 R = ibu
15 R = 2 – Mebu

in the IR spectrum. Partial oxidation of compounds **7** and **8** afforded the hydroxyaldehydes **11** and **12**. The difference of the chemical shift of the C-10 methyl group between these compounds or their urethanes (δ1.08 and 1.18, respectively) and the structurally similar $H_{5\beta}$, $C_{14\alpha}$-elemanolide, 9-acetyl-11(13)-dehydrozinarosin **13** (δ1.4) [5], gave additional support to the proposed stereochemistry at C-5 and C-10 for **7** and **8**.

The spectroscopic features of the dilactones obtained by oxidation of **7** and **8** are in agreement with structures **14** and **15**. The ^{1}H NMR spectra of these compounds were significantly different from those of zinaflavins A or B (**1** or **2**). The H-1 signals in the ^{1}H NMR spectra of **14** and **15** were shifted to lower field by approx 0.3 ppm while H-5 and H-6 were diamagnetically displaced by 0.45 ppm. Analysis of the allylic and vicinal coupling constants exhibited by the 6(15)- and the 8(12)-lactone rings present in these compounds showed that they should belong to the *trans*-fused *S* and *cis*-fused P(A) conformational types [3].

Chemical evidence obtained from *Zinnia flavicoma* favours the reclassification of the *Tragoceras* genus as a new section of *Zinnia*, but chemical investigations of other Zinninae genera are necessary in order to establish if elemanolides are characteristic of *Zinnia* or if they are distributed in all the subtribe.

EXPERIMENTAL

Above ground parts of *Zinnia flavicoma* (3.5 kg) collected in Salina Cruz, Oaxaca (voucher deposited in the Herbarium of the Instituto de Biología, UNAM, MEXU-359508) were extracted with CH_2Cl_2. The resulting extract (157 g) was percolated through bentonithic earth ['Tonsil'; chemical composition (%): SiO_2 (72.5), Al_2O_3 (13); Fe_2O_3 (5); MgO (1.5); CaO (0.8); humidity (8.5)] with hexane (3 l.), CH_2Cl_2 (5 l.) and Me_2CO (3 l.) yielding 44.5, 78.7 and 21.6 g of residue, respectively. The CH_2Cl_2 fraction was percolated on silica gel (Merck G) with hexane and EtOAc. The EtOAc fraction (50 g) was chromatographed over 1000 g of silica gel (70–230 Mesh) using as eluent hexane–EtOAc mixtures. Fractions eluted with hexane–EtOAc (7:3) afforded mixtures of zinaflavins A–F, which were separated by repeated

CC using silica gel (Merck G) in columns of 15 cm of height and variable diameter operated with vacuum and using as eluent hexane–EtOAc (7:3). In this way 0.023 g of **1**, 3.47 g of **2**, 5.03 g of **3** and **4**, 2.48 g of **5** and 1.68 g of **6**, were isolated. Fractions eluted with hexane–EtOAc (1:1) afforded [after CC silica gel (Merck G) as above], 8.36 g of the **7**, **8** mixture which was separated by HPLC (Si-10, 0.5 m × 8 mm; hexane–EtOAc, 3:5; 200 ml/hr; detection: refractive index).

Zinaflavin A (**1**). Mp 162–165° (EtOAc–hexane). UV λ_{max}^{EtOH} 212 nm (ε24 084); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1773, 1754, 1665, 1640; EIMS 70 eV, *m/z* (rel. int.): 360 $[M]^+$ ($C_{20}H_{24}O_6$), 332 $[M-CO]^+$, 316 $[M-CO_2]^+$, 303 $[M-C_4H_9]^+$, 276 $[M-C_5H_8O]^+$, 258 $[M-C_5H_{10}O_2]^+$, 230 $[332-C_5H_{10}O_2]^+$, 214 $[316-C_5H_{10}O_2]^+$, 85 $[C_5H_9O]^+$ (80.5), 57 $(C_4H_9)^+$ (100).

Zinaflavin B (**2**). Mp 196–198° (EtOAc–hexane). UV λ_{max}^{EtOH} 213 nm (ε29 248); $[\alpha]_D$ = +29.569 (*c* 0.183; $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1778, 1772, 1726, 1665, 1651; EIMS 70 eV, *m/z* (rel. int.): 358 $[M]^+$ ($C_{20}H_{22}O_6$), 330 $[M-CO]^+$, 314 $[M-CO_2]^+$, 258 $[M-C_5H_8O_2]^+$, 214 $[314-C_5H_8O_2]^+$, 83 $[C_5H_7O]^+$ (100), 55 $[C_4H_7]^+$ (25.3).

Zinaflavin C (**3**). Mp 145–147° (Me_2CO–hexane). UV λ_{max}^{EtOH} 213 nm (ε13 387); $[\alpha]_D$ +3.24 (*c* 0.154; $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1774, 1755, 1655; EIMS 70 eV, *m/z* (rel. int.): 376 $[M]^+$ ($C_{20}H_{24}O_7$), 348 $[M-CO]^+$, 332 $[M-CO_2]^+$, 292 $[M-C_5H_8O]^+$, 275 $[M-C_5H_9O_2]^+$, 261 $[348-C_5H_9O_2]^+$, 85 $[C_5H_9O]^+$ (72.3), 57 $[C_4H_9]^+$ (100).

Zinaflavin D (**4**). Mp 180–183° (EtOAc–hexane). UV λ_{max}^{EtOH} 214 nm (ε10 983); $[\alpha]_D$ +1.77 (*c* 0.226; $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1774, 1752, 1665; EIMS 70 eV, *m/z* (rel. int.): 376 $[M]^+$ ($C_{20}H_{24}O_7$), 348 $[M-CO]^+$, 332 $[M-CO_2]^+$, 292 $[M-C_5H_8O]^+$, 275 $[M-C_5H_9O_2]^+$, 261 $[348-C_5H_9O_2]^+$, 85 $[C_5H_9O]$ (74), 57 $[C_4H_9]^+$ 100.

Zinaflavin E (**5**). Mp 184–186° (Me_2CO–hexane). UV λ_{max}^{EtOH} 214 nm (ε30 855); $[\alpha]_D$ −14.2 (*c*, 0.169, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1776, 1774, 1730, 1665, 1652; EIMS, 70 eV, *m/z* (rel. int.): 374 $[M]^+$ ($C_{20}H_{22}O_7$), 346 $[M-CO]^+$, 344 $[M-CH_2O]^+$, 292 $[M-C_5H_6O]^+$, 275 $[M-C_5H_7O_2]^+$, 82 $[C_5H_6O]^+$ (100), 83 $[C_5H_7O]^+$ (94.7), 55 $[C_4H_7]^+$ (80.5).

Zinaflavin F (**6**). Mp 222–224° (Me_2CO–hexane). UV λ_{max}^{EtOH} 213 nm (ε17 674); $[\alpha]_D$ = −8.83 (*c* 0.181; $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1771, 1775, 1665; EIMS 70 eV, *m/z* (rel. int.): 334 $[M]^+$ ($C_{17}H_{18}O_7$), 292 $[M-C_2H_2O]^+$, 274 $[M-AcOH]^+$; 261 $[292-CH_2OH]^+$, 43 $[C_2H_3O]^+$ (100).

Zinaflavin G (**7**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3460, 1770, 1735, 1660, 1645; EIMS 70 eV, *m/z* (rel. int.): 333 $[M-OH]^+$, 262 $[M-C_4H_8O_2]^+$, 244 $[262-H_2O]^+$, 71 $[C_4H_7O]^+$ (100).

Zinaflavin H (**8**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3460, 1772, 1738, 1670, 1645; EIMS 70 eV, *m/z* (rel. int.): 364 $[M]^+$ ($C_{20}H_{28}O_6$); 347 $[M-OH]^+$, 262 $[M-C_5H_{10}O_2]^+$, 244 $[262-H_2O]^+$, 85 $[C_5H_9O]^+$.

Acetylation of zinaflavins G and H (**7** *and* **8**). A soln of **7** and **8** mixture (48 mg) in pyridine (1 ml) and Ac_2O (1 ml) was left 0.5 hr at room temp. and worked up as usual affording a mixture of the acetates **9** and **10**, which were not separated. Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1779, 1737, 1642; the CIMS exhibited the molecular ions of **9** and **10** at *m/z* 449 and 435 $[M+H]^+$, as well as significant peaks *m/z* 389 and 375 $[M+H-AcOH]^+$, 347 $[M+H-C_9$-ester side chain$]^+$ and 227 $[M+H-2AcOH-C_9$-ester side chain$]^+$ (100).

Oxidation of compounds **7** *and* **8**. Pyridinium dichromate (620 mg) [6] was added to a soln of **7** and **8** (310 mg) in CH_2Cl_2 (15 ml). The mixture was stirred for 4 hr. After addition of hexane (10 ml), the mixture was percolated through silica gel in order to remove the reagent. The residue exhibited three spots on TLC. The three compounds were separated by CC (silica gel G) eluted with Me_2CO–hexane (1:4). The less polar component was the mixture of dilactones **14** and **15** (48 mg) mp 149–153° (Me_2CO–hexane); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780, 1750, 1715, 1670, 1640; EIMS 70 eV, *m/z* (rel. int.): 360 and 346 $[M]^+$ for **14** and **15**, respectively. Other significant peaks were at *m/z* 250 $[M-$ester side chain$]^+$; 85 $[C_5H_9O]^+$ (87.8) and 71 $[C_4H_7O]^+$ (98.9). The mixture of **11** and **12** (137 mg) was obtained as a colourless gum. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 1770, 1738, 1700, 1670, 1645. EIMS 70 eV, *m/z* (rel. int.): 362 $[M]^+$ for **11** ($C_{20}H_{26}O_6$) and 348 $[M]^+$ for **12** ($C_{19}H_{24}O_6$); 242 $[M-H_2O-$ester side chain$]^+$, 231 $[M-CHO-$ester side chain$]^+$, 71 $[C_4H_7O]^+$ (39%), 85 $[C_5H_9O]^+$ (16%). The third component (77 mg) was the recovery material which was treated as above with 150 mg of pyridinium dichromate, until total transformation (16 hr) into dilactones **14** and **15** (57 mg).

X-ray analysis of compound **6**. Single crystals of **6** suitable for analysis were obtained by slow crystallization from EtOAc. They were orthorhombic, space group $P2_12_12_1$ with a = 9.7094 (4), b = 11.4289 (2), c = 14.7423 (4) Å, F (000) = 703.93, μ = 0.99 cm^{-1}, Z = 4. Intensity data were measured on a Nicolet R3m four circle diffractometer operated in the W scan mode using CuKα monochromatic radiation. 1249 reflections collected up to $2\theta < 45$, yielded 982 observed independent reflections with $I > 1.73\sigma(I)$. The structure was solved by direct methods [7] and refined by a matrix cascade procedure with anisotropic temperature factors for the non-H-atoms and a fixed isotropic temperature factor U = 0.040 Å^2 for H-atoms to converge until a final R of 0.051. The final difference map had no peaks greater than ±0.2 eA^{-3}.

Acknowledgement—We are indebted to M.Sc. Jose Luis Villaseñor for the classification of the plant material.

REFERENCES

1. Torres, A. M. (1963) *Brittonia* **15**, 290.
2. Olorode, O. and Torres, A. M. (1970) *Brittonia* **22**, 359.
3. Samek, Z. (1978) *Coll. Czech. Chem. Commun.* **43**, 3210.
4. Ortega, A., Romo de Vivar, A., Toscano, R. A. and Maldonado, E. (1983) *Chem. Letters* 1607.
5. Maldonado, E., Soriano-García, M., Guerrero, C., Romo de Vivar, A. and Ortega, A. (1985) *Phytochemistry* **24**, 991.
6. Corey, E. J. and Schmidt, G. (1979) *Tetrahedron Letters* 399.
7. Sheldrick, G. M. (1981) SHELXTL Revision 3. An integrated system for solving, refining and displaying crystal structures from diffractio data. Univ. of Göttingen, West Germany.