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NEW TETRANORTRITERPENOIDS FROM *SWIETENIA HUMILIS*[1]

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ABSTRACT.—Four new tetranortriterpenoids, humilinolides A [**1**], B [**2**], C [**3**], and D [**4**], were isolated from the seeds of *Swietenia humilis* (Meliaceae). The structures of compounds **1–4** were established by spectroscopic methods. The structure of humilinolide A [**1**] was confirmed unequivocally by single crystal X-ray diffraction studies. The effect of the MeOH extract of the seeds and the isolated terpenoids **1–4** on the radicle growth of *Amaranthus hypochondriacus* and *Echinochloa crus-galli* was evaluated. The extract and compounds **1** and **3** caused significant inhibition on radicle elongation in both target species. In addition, the MeOH extract of seeds of *S. humilis* showed moderate inhibition to the growth and feeding of the third instar larvae of *Tenebrio molitor*.

Swietenia humilis Zuccarini (Meliaceae), locally known as "zopilote," "cobano," "caobilla," and "sopilocuahuilt," is a tree up to 20 m high. It grows commonly in the tropical areas of Mexico, in Guerrero, Michoacan, Colima, Sinaloa, and Chiapas, where the trees are most often seen as scattered and isolated individuals (1,2). The seeds of this plant are highly valued for their medicinal properties in some regions of Mexico (2–5). Decoctions or infusions of the ground seeds are used as anthelmintic agents and for the cure of amebiasis (4). They are also considered effective for treatment of chest pains, coughs, and cancer (5). *S. humilis* has recently been listed as an endangered species in need of conservation (1).

Previous phytochemical analysis conducted with the seeds led to the isolation and characterization of three tetranortriterpenoids of the mexicanolide group, namely, humilin B, 2-methyl-2-hydroxy-3-isobutyryloxymeliac-8(30)-enate, and 2-methyl-3-tygloyloxymeliac-8(30)-enate (5). Continuing our search for biologically active substances from Mexican medicinal plants (7,8), we have investigated the seeds of *S. humilis*. In this paper we describe the isolation and structure elucidation of four new tetranortriterpenoids, humilinolides A [**1**], B [**2**], C [**3**], and D [**4**], as well as their effect on the radicle growth of *Amaranthus hypochondriacus* L. and *Echinochloa crus-galli* (L.) Beauv. The feeding deterrence and growth inhibition of the MeOH extract of dry seeds of *S. humilis* on third instar larvae of *Tenebrio molitor* were also investigated.

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[1]Chemical Studies on Mexican Plants used in Traditional Medicine XXVIII. For part XXVII see M.R. Canacho *et al.*; *Fitoterapia* (in press).

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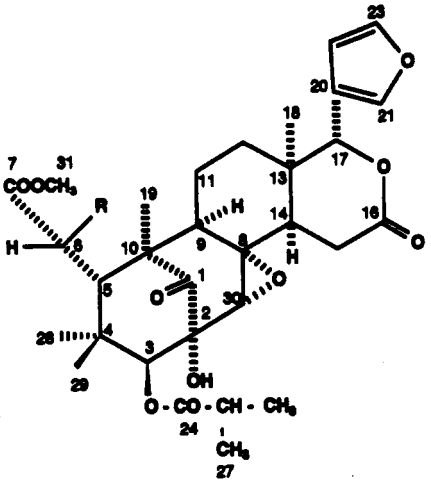
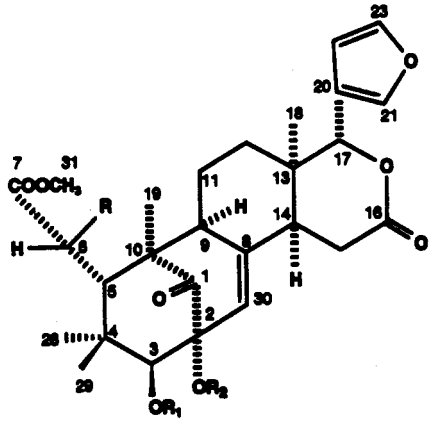


1 R=OH
2 R=OAc



3 R=H, R_1=CO-C(Me)=CH-Me, R_2=Ac

4 R=OAc, R_1=Ac, R_2=H

RESULTS AND DISCUSSION

Compound **1** analyzed for $C_{31}H_{40}O_{11}$. Its ir spectrum showed absorption maxima for hydroxyl (3477 cm^{-1}), carbonyl groups (1737, 1725, and 1710 cm^{-1}), and a furan moiety (1504 and 875 cm^{-1}). Both ^1H- and ^{13}C-nmr data (Tables 1 and 2) showed strong similarities with those of swietemahonin G (9). Comparative analysis indicated that the tigloyl group at C-3 in swietemahonin G was replaced by an isobutyryl moiety in **1** [δ_C 175.41, 34.20, 18.70, and 19.55; δ_H 2.82 (m), 1.25 (d), and 1.28 (d)]. As in the case of swietemahonin G, the signals attributable to H-3 (δ 4.93) and H-30 (δ 3.45) appeared as sharp singlets, consistent with the presence of one of the hydroxyl groups at C-2. From this comparative analysis, structure **1** was proposed for humilinolide A. The relative stereochemistry was ascertained on the basis of the coupling constants (Table 1) and by

TABLE 1. ^{1}H-nmr Data for Humilinolides A [**1**], B [**2**], C [**3**], and D [**4**].[a]

Proton	Compound			
	1	**2**	**3**	**4**
H-3	4.93 s	5.02 s	5.61 s	4.75 s
H-5	3.15 s	3.36 s	3.39 dd (8.8, 3)	3.50 s
H-6	4.45 s	5.48 s	2.37 dd (15.6, 2)	5.56 s
			2.40 dd (15.6, 9.6)	
H-9	1.94 m	1.94 m	2.30 m	2.28 m
H-11	1.71 m	1.71 m	1.83 m	1.81 m
	1.91 m	1.93 m	2.05 qd (13, 4)	2.01 m
H-14	1.61 dd (12, 7)	1.62 dd (12, 7)	2.29 ddd (5, 2, 1.5)	2.27 ddd (5, 2, 1.5)
H-15	2.79 dd (16, 5)	2.78 dd (16, 5)	2.88 dd (18, 1.5)	2.88 m
	3.31 dd (16, 14)	3.39 dd (16, 14)	2.90 dd (18, 5)	—[b]
H-17	5.16 s	5.18 s	5.68 s	5.64 s
H-21	7.49 dd (1.8, 1)	7.44 dd (1.8, 1)	7.83 dd, (1.8, 0.8)	7.72 dd (1.8, 0.8)
H-22	6.42 dd (1.8, 0.8)	6.44 dd (1.8, 0.8)	6.48 (dd, 1.8, 0.8)	6.45 dd (1.8, 0.8)
H-23	7.46 t (1.8)	7.44 t (1.8)	7.43 t (1.8)	7.45 t (1.8)
H-18	1.01 s	1.01 s	1.00 s	1.07 s
H-19	1.39 s	1.07 s	1.26 s	1.09 s
H-28	1.07 s	1.06 s	1.11 s	1.10 s
H-29	0.87 s	0.91 s	0.76 s	0.92 s
H-30	3.45 s	3.49 s	5.37 t (1.5)	5.37 t (1.5)
H-31	3.83 s	3.79 s	3.72 s	3.74 s
2-Ac	—	—	2.14 s	—
6-Ac	—	2.19 s	—	2.19 s
3-Ac	—	—	—	2.20 s
H-25	2.82 s (7)	2.77 m	—	—
H-26	1.28 d (7)	1.29 d (7)	6.93 qq (7, 1.5)	—
H-27	1.25 d (7)	1.26 d (7)	1.84 br s	—
H-32	—	—	1.75 br d (7)	—

[a]Chemical shifts (relative to TMS) are in ppm and coupling constants (in parentheses) in Hz. The assignments were made by a combination of COSY and HETCOR.

[b]Overlapped signal.

nOe experiments as previously described (9). Proof of the tetranortriterpenoid structure was made by single-crystal X-ray analysis. A computer-generated drawing of humilinolide A [**1**] is given in Figure 1. The molecule consists of four six-membered rings (A, B, C, and D). The A ring is fused at C-2–C-1–C-10 to the B ring. The B/C and C/D rings are trans- and cis-fused, respectively. The A, B, C, and D rings adopt an intermediate between a twist $^2T_4$ and boat $B_{4,1}$; a half chair $^1H_6$; an intermediate between boat $^{3,6}B$ and twist $^6T_2$; and an intermediate between a sofa $^6S_7$ and half-chair $^6H_1$ conformations, respectively (10). The furan ring is almost flat. The substituents at C-3 and C-5 occupy axial and equatorial positions, respectively. The crystal structure is stabilized by intra- and intermolecular hydrogen bonds with at least five C-H...O hydrogen bond interactions and van der Waals forces.

Humilinolide B [**2**] was obtained as a white crystalline solid, and the molecular formula $C_{33}H_{42}O_{12}$ was indicated by eims and ^{13}C nmr. The nmr spectra of **2** were nearly identical with those of **1**, except for the presence of signals for one acetyl group (δ_H 2.19 and δ_C 20.81 and 169.50) and the fact that the resonance due to H-6 was shifted downfield at δ 5.48. Acetylation of **1** with Ac_2O/pyridine gave an acetate which was identical with humilinolide B [**2**]. Thus humilinolide B [**2**] was proposed to be the 6-acetyl derivative of humilinolide A [**1**].

Humilinolide C [**3**], $C_{34}H_{42}O_{10}$, was obtained as a crystalline compound. The nmr

TABLE 2. ^{13}C nmr Data of Humilinolides A [**1**], B [**2**], C [**3**], and D [**4**].[a]

Carbon	Compound			
	1	**2**	**3**	**4**
C-1	212.41	211.82	208.02	213.80
C-2	80.71	79.27	85.09	77.42
C-3	85.74	85.22	79.22	85.52
C-4	40.42	40.37	40.48	39.39
C-5	46.06	45.18	41.37	44.81
C-6	72.03	71.80	32.62	72.37
C-7	175.15	170.73	173.82	170.89
C-8	62.73	62.62	137.52	136.25
C-9	54.55	55.19	56.41	56.91
C-10	49.25	49.19	50.21	49.55
C-11	20.45	19.73	20.42	20.34
C-12	32.54	33.02	34.27	34.18
C-13	35.70	36.01	35.85	36.50
C-14	43.53	44.74	45.09	44.81
C-15	32.21	33.02	29.66	29.87
C-16	170.56	170.73	168.77	170.47
C-17	78.03	78.06	76.82	76.58
C-18	26.90	26.37	21.72	20.71
C-19	17.11	15.98	15.62	15.53
C-20	120.64	120.01	120.57	120.63
C-21	140.55	140.81	141.86	141.24
C-22	109.55	109.94	109.58	109.43
C-23	143.47	143.13	142.94	142.98
C-28	22.40	22.44	21.49	22.04
C-29	21.00	21.74	22.10	21.78
C-30	67.20	67.34	125.52	129.24
C-31	53.50	53.32	52.17	53.27
2-COMe	—	—	169.05	—
2-CO*Me*	—	—	20.68	—
6-COMe	—	169.50	—	169.52
6-CO*Me*	—	20.81	—	20.93
3-COMe	—	—	—	169.00
3-CO*Me*	—	—	—	22.04
C-24	175.41	175.31	166.49	—
C-25	34.20	34.02	127.28	—
C-26	18.70	18.65	139.59	—
C-27	19.55	19.44	14.61	—
C-32	—	—	11.95	—

[a]Chemical shifts are in ppm. Assignments were supported by DEPT and by comparison of chemical shifts with those assigned to related compounds (9,10).

spectra of **3** were similar to those of compound **1**, except that the signals for the epoxide, the isobutyryl at C-3, the hydroxyl-bearing methine, and the quaternary carbinolic carbon (C-2) were missing. In their place were signals for a trisubstituted olefin (δ_C 137.52 and 125.52; δ_H 5.37), a tigloyl moiety (δ_C 166.49, 127.28 and 139.59; δ_H 6.93, 1.84 and 1.75), a methylene α to the carboxymethyl group [δ_C 32.62; δ_H 2.40 (dd), 2.37 (dd)], and for one quaternary carbon bearing an acetoxy group (δ_C 169.05, 85.05 and 21.49; δ_H 2.14), respectively. The signals due to H-3 (δ 5.61) and H-30 (δ 5.37) appeared as a sharp and broad singlet, respectively, and were consistent with the presence of a substituent at C-2. In this case H-30 exhibited long range coupling with H-9 and H-14. This long range coupling has been previously described for related compounds possessing a C-8/C-30 double bond (11). The placement of the tigloyloxy and acetoxy

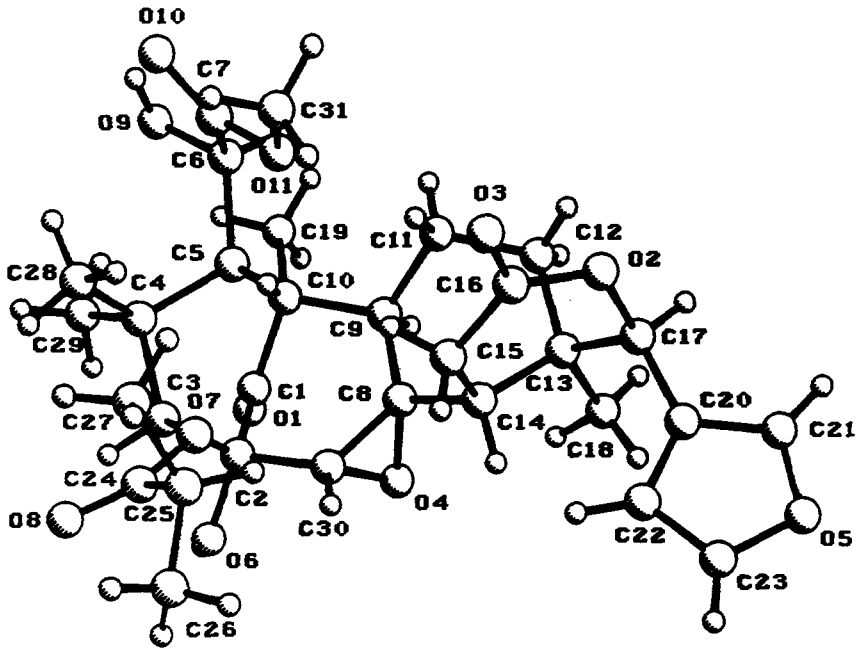


FIGURE 1. Molecular structure of compound **1**.

groups at C-3 and C-2, respectively, was confirmed by the ^{1}H and ^{13}C long range COSY spectrum. The carbonyl ^{13}C signal at 166.49 (C-24) showed long range correlation not only with the signal at δ 1.84 (H-27) but also with the resonance at δ 5.61 (H-3), in agreement with the tigloyloxy being at C-3. The carbonyl resonance at δ 169.05 correlated with H-3 and H-30, consistent with the presence of the acetoxy unit at C-2. The relative stereochemistry of **3** was determined from the coupling constants of each proton (Table 3) and by the NOESY spectrum; nOe's were observed between H-29 and H-3, H-5 and H-25; between H-19 and H-6, H-9 and H-28; between H-28 and H-3 and H-19; and between H-18 and H-21, H-22, H-15α, and H-14.

Humilinolide D [**4**] had the composition $C_{31}H_{38}O_{11}$. Its spectral properties suggested the same limonoid type of skeleton as compounds **1–3**. The nmr spectra (Tables 1 and 2) clearly indicated that in addition to the lactone, ketone, the carboxymethyl unit, and the β-substituted furanoid moiety, **4** contained a C-8/C-30 double bond (δ_C 136.25 and 129.24; δ_H 5.37), two acyloxy-bearing methines (δ_C 85.52 and 72.37; δ_H 4.75 and 5.56), and one quaternary oxygenated carbon (δ_C 77.42). Furthermore, the coupling pattern of the signals at δ 4.75 (H-3) and H-30 (δ 5.37) was similar to those observed for the respective resonances in **3**, consistent with the presence of a hydroxyl group at C-2. The second acyloxy-bearing methine was assignable to H-6 as in the case of compound **2**. The corresponding proton signal at δ 5.56 correlated with the band at δ 72.37 (C-6) in the HETCOR spectrum. The relative stereochemistry was determined in the same manner as for compound **1**; thus humilinolide D was determined to have structure **4**.

The MeOH extract of dry seeds of *S. humilis* produced significant inhibitions of radicle growth of *E. crus-galli* and *A. hypochondriacus*. The 50% phytogrowth inhibitory concentrations (IC_{50}) of the extract were 171.54 μg/ml and 275.95 μg/ml, respectively. Humilinolides A [**1**] and C [**3**] inhibited the radicle growth of *E. crus-galli* with IC_{50} values of 99.06 μg/ml and 163.0 μg/ml, respectively. *A. hypochondriacus* was less sensitive to compounds **1** and **3** with IC_{50} values of 199.0 μg/ml and 215.08 μg/ml,

TABLE 3. Effect of the MeOH Extract of Dry Seeds of *Swietenia humilis* on the Growth and Food Consumption on the Third Instar Larvae of *Tenebrio molitor*.[a]

Treatment	RGR (±SD)	Growth inhibition (%)	FCI (±SD)	Feeding inhibition (%)
Extract 0.5%	7.7±2.30	4.9	82.20±19.90[b]	22.0[b]
Extract 1%	6.4±0.81[b]	29.9[b]	74.20±18.20[b]	29.6[b]
Control	8.1±1.00	0.0	105.50±3.50	0.0

[a]Ten larvae were used for each treatment. RGR=relative growth rate. FCI=food consumption index.
[b]$P<0.05$.

respectively. Compounds **2** and **4** were not inhibitory at the tested concentrations.

In the artificial diet feeding assay, the MeOH extract of dry seeds of *S. humilis* showed moderate inhibition to the growth and feeding of third instar larvae of *T. molitor*. When the extract was administered to the larvae on a diet containing 1% of the extract, both feeding and growth were significantly reduced (Table 3). However, when the extract was incorporated in the artificial diet at a concentration of 0.5%, only a feeding deterrent action was obtained (Table 3). No mortality was observed at the concentrations tested.

Detailed investigations of the phytogrowth inhibitory action of *S. humilis* and compounds **1** and **3** as well as the potential antifeeding activity of compounds **1–4**, are now in progress. Limonoids possess a wide range of biological activities, including insect antifeedant and growth regulating properties, a variety of medicinal effects in animals and humans, and antifungal, bacteriocidal, and antiviral activity (12). As a result of the present study, it has been found that these compounds are also inhibitors of plant growth. In this sense it will be interesting to elucidate the ecological role of limonoids produced by species of the genus *Swietenia*.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Ir spectra were obtained in KBr on a Perkin Elmer 599 B spectrophotometer; optical rotations were measured with a JASCO DIP 360 digital polarimeter. ^{1}H-nmr and ^{13}C-nmr spectra were recorded at 300 MHz and 75 MHz, respectively, on a Varian VXR-300S apparatus; all nmr spectra were recorded in $CDCl_3$ with TMS as the internal standard. X-ray data were collected on a Nicolet R 3m diffractometer with Cu-Kα radiation (Ni-filtered). Si gel 60 (70–230 mesh) Merck was used for cc; tlc was done on Si gel 60 GF 254 plates (Merck).

PLANT MATERIAL.—The plant material was collected in Guerrero, Mexico in June 1990. Reference samples have been deposited at the ethnobotanical collection of the National Herbarium, Instituto de Biologia, UNAM. Voucher: R. Bye and E. Linares 17442.

ISOLATION PROCEDURES.—The air-dried and pulverized plant material (7.3 kg) was defatted with hexane and then repeatedly macerated with MeOH at room temperature. The combined MeOH extracts were concentrated under reduced pressure to yield 952 g of residue, which was subjected to cc on Si gel (2.5 kg); the column was eluted with mixtures of solvents of increasing polarity starting with hexane, followed by hexane/$CHCl_3$, $CHCl_3$, and $CHCl_3$/MeOH. A total of 178 fractions (1 liter each) were collected and pooled based on tlc profiles to yield 10 major fractions (F-1–F-10). Fraction F-6 [44 g, eluted with hexane-$CHCl_3$ (1:1)] was further chromatographed on a Si gel column (850 g) using C_6H_6 with increasing amounts of EtOAc, to yield **3** (200 mg). Further cc of fraction F-8 (56.7 g, eluted with $CHCl_3$) on Si gel (1200 g) using hexane-EtOAc (9:1, 8:2, and 7:3) as the eluent provided **2** (100 mg). Finally, fraction F-9 [92 g, eluted with $CHCl_3$-MeOH (95:5)] was subjected to cc on Si gel (1500 g); the column was eluted successively with hexane, hexane-$CHCl_3$ (9:1, 8:2, and 1:1), $CHCl_3$, and $CHCl_3$-MeOH (99:1) to afford **1** (1.2 g) and **4** (150 mg). In all cases final purification of the isolated compounds was achieved by preparative tlc, using C_6H_6-EtOAc (8:2) and repeated recrystallization from EtOAc/isopropyl ether.

Humilinolide A [**1**].—Crystalline solid (EtOAc/isopropyl ether): mp 256°; $[\alpha]_D$ −78.5 (2.7, $CHCl_3$); ir ν max (KBr) 3477, 1737, 1725, 1710, 1504, 1456, 1387, 1261, 875 cm^{-1}; eims *m/z* (rel. int.) $[M]^+$ 588 (12), 501 (10), 500 (20), 483 (5), 450 (4), 412 (7), 411 (13), 393 (4), 43 (100). *Anal.* calcd for $C_{31}H_{40}O_{11}$: C 63.26, H 6.80; found C 63.30, H 6.75.

Humilinolide B [**2**].—White crystals (EtOAc/isopropyl ether); mp 280–282°; [α]D −68.5 (2, $CHCl_3$); ir ν max (KBr) 3466, 1736, 1720–1710,, 1458, 1374, 1218, 875 cm^{-1}; eims *m/z* (rel. int.) $[M]^+$ 630 (55), 542 (20), 525 (5), 492 (30), 483 (10), 411 (15), 383 (15), 295 (5), 235 (5), 43 (100). *Anal.* calcd for $C_{33}H_{42}O_{12}$: C 62.85, H 6.66; found C 62.90, H 6.59.

Humilinolide C [**3**].—Crystalline solid (EtOAc/isopropyl ether): mp 211–212°; [α]D −55 (2, $CHCl_3$); ir ν max (KBr) 1730–1710, 1430, 1370,, 1220, 870 cm^{-1}; eims *m/z* (rel. int.) $[M]^+$ 610 (4), 568 (16), 551 (4), 550 (6), 511 (8), 453 (8), 451 (4), 379 (8), 83 (100). *Anal.* calcd for $C_{34}H_{42}O_{10}$: C 66.85, H 6.88; found C 66.79, H 6.75.

Humilinolide D [**4**].—Crystalline solid (EtOAc/isopropyl ether); mp 263–264°; [α]D −76.5 (2, $CHCl_3$); ir ν max (KBr) 3420, 1740, 1725–1710, 1430, 1375, 1280, 1220, 870 cm^{-1}; eims *m/z* (rel. int.) $[M]^+$ 586 (15), 568 (3), 527 (4), 526 (4), 509 (4), 484 (8), 469 (3), 467 (3), 456 (3), 448 (3), 425 (25), 410 (8), 379 (13), 43 (100). *Anal.* calcd for $C_{31}H_{38}O_{11}$: C 63.48, H 6.47; found C 63.02, H 6.55.

ACETYLATION OF HUMILINOLIDE A [**1**].—Compound **1** (50 mg) was treated with Ac_2O (1 ml) and pyridine (1 ml) at room temperature for 48 h. The reaction mixture was worked up as usual to yield 40 mg of **2**, mp 279–282°, which was identical to the natural product on tlc, ir and nmr comparisons.

SINGLE CRYSTAL X-RAY ANALYSIS OF HUMILINOLIDE A [**1**].[3]—Crystal data: $C_{31}H_{40}O_{11}\cdot 4H_2O$, mol wt=588.10, orthorhombic, space group $P2_12_12_1$, a=11.163 (4), b=14.887 (8), c=20.459 (9) Å, V=3399 (3) $Å^3$, Dc=1.29 g/cm^3, F(000)=1416. Lattice parameters were obtained from 24 centered reflections with $9.9<2\theta<41.8°$. For one octant 2460 reflections with $3°<2\theta<110°$ were measured with an index range *h*/0—11, *l*/0—15, *k*/0—21 using the 2θ:θ scanning mode with filtered CuKα radiation (1.54178 Å) on a Nicolet P3F four circle diffractometer, variable scan speed, scan width 1.0 (θ°), and two standard reflections (−21−5) and (−2−24), monitored every 50, measured 2077 observed with $I>3\sigma$ (I). The Lorentz and polarization effects were applied and no absorption correction was made. The structure was solved using direct methods with the program package Texsan (13). Full matrix least-squares refinement with anisotropic temperature factors was used for non-hydrogen atoms. Atoms O-12, O-13, O-14, and O-15 show some disorder. The position of hydrogen atoms was idealized, assigned isotropic thermal parameters of 1.2 times B (eq) of parent atoms. The function minimized was $w(Fo-Fc)^2$, $W=1/[\sigma^2(Fo)+(0.04\ Fo)^2]$, R=0.077, wR=0.098. Final ΔF map were 0.57 and 0.35 $eÅ^3$. Maximum Δ/σ 0.0077. Scattering factors for O, C, and H from International Tables for X-ray Crystallography (14).

EFFECT ON THE RADICLE GROWTH OF *AMARANTHUS HYPOCHONDRIACUS* AND *ECHINOCHLOA CRUS-GALLI*.—The effect of the MeOH extract of dry seeds of *S. humilis* and humilinolides A–D on the radicle growth of *A. hypocondriacus* and *E. crus-galli* was determined as previously described (6). The seeds of *E. crus-galli* were purchased from Valley Seed Service, Fresno, California, and those of *A. hypocondriacus* from Mercado de Tulyehualco, D.F., Mexico. Bioassays were performed in Petri dishes, and a completely randomized block design with four replicates per treatment was used. Ten seeds were sown in each Petri dish. The test materials were dissolved in MeOH-CH_2Cl_2 (1:1) to final concentrations of 50, 100, and 200 μg/ml and then poured on a filter paper disk into each Petri dish. After evaporation of the solvent, distilled H_2O was added (1.5 ml per plate), and the plates were kept at 27° in the dark. The radicle length was measured after 24 h for *Amaranthus* and 48 h for *Echinochloa*. The same procedure was used for negative controls containing only solvent. The data were analyzed by ANOVA ($P<0.05$), and IC_{50} values were calculated by Probit analysis based on percent inhibition obtained and are given in the text.

GROWTH INHIBITION TEST AND FEEDING INHIBITION ASSAY ON THIRD INSTAR LARVAE OF *TENEBRIO MOLITOR*.—The MeOH extract of *S. humilis* (5 and 10 mg) was dissolved in MeOH and mixed with wheat bran (995 and 990 mg, respectively) to yield 1 g of diet containing 0.5 and 1% of plant extract. The mixture was allowed to air dry. The control diet was prepared in the same way using only solvent and wheat bran (1 g).

Weighed third instar larvae of *T. molitor* (12–13 mg) were placed into glass cups containing treated diet or control diet in a complete block design with five treatments and four repetitions of 10 larvae each. After 8 days the larvae were weighed, and the relative growth rate (RGR) was obtained as previously described (15) from $(\ln W_2-\ln W_2)(t_2-t_1)$, where W_1 and W_2 are larval body wt at day 1 (t_1) and day 8 (t_2), respectively. The growth inhibitory rate (GIR) was expressed as follows:

$$\text{Growth inhibitory rate (\%)}=\frac{\text{RGR (control)}-\text{RGR (treated)}}{\text{RGR (control)}}\times 100$$

[3]Atomic coordinates for compound **1** have been deposited at the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK.

The effect of treatments on the larvae food consumption index (CI) was measured, and the CI was calculated as described by Waldbauer (16). Feeding inhibition was calculated the same way as the calculation for growth inhibitory rate. All data were analyzed by Duncan's Multiple Range test (17), and results are given in Table 3.

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