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TETRANORTRITERPENOID INSECT ANTIFEEDANTS FROM *SEVERINIA BUXIFOLIA*

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Key Word Index—*Severinia buxifolia*; Rutaceae; root bark; antifeeding effect; limonoids; severinolide; cycloseverinolide.

Abstract—Two new tetranortriterpenoids, severinolide and cycloseverinolide, together with four known compounds, were isolated and characterized from the root bark of *Severinia buxifolia*. Severinolide, atalantin and cycloepiatalantin showed significant antifeeding effects against *Plutella xylostalla*.

INTRODUCTION

Severinia buxifolia (*Atalantia buxifolia*) is a Chinese folk medicine and has been used for treatment of chronic rheumatism, paralysis, snake-bite and malaria [1]. Essential oils, coumarins, acridone alkaloids, sesquiterpenoids and triterpenoids have been isolated from this plant [2–9]. The leaves of this plant show resistance to phytophagous insects and the ethanol extract of the root bark of *S. buxifolia* was found to show significant antifeedant activity. This led us to reinvestigate its constituents. Bioassay-directed fractionation of the plant extract led to isolation and characterization of severinolide (**1a**), atalantin (**3**) and cycloepiatalantin (**6**) as the antifeedant principles of the chloroform soluble fraction. We now describe the structural elucidation of two new limonoids, severinolide (**1a**) and cycloseverinolide (**2a**) together with four known compounds (**3–6**) which were isolated from the root bark of *S. buxifolia* and their antifeeding activity.

RESULTS AND DISCUSSION

All of the limonoids except atalantolide (**5**) isolated in this study showed four C-Me resonances in their ^{1}H NMR spectra instead of five C-Me expected for an obacunone system. This fact suggested that these natural products belong to the limonin series and that C-19 has been oxidized.

Severinolide (**1a**) was isolated as optically active colourless plates and its elemental analysis indicated a molecular formula $C_{31}H_{38}O_{11}$. The signals of **1a** at δ 165.4 (*s*), 167.3 (*s*), 170.3 (*s*) and 170.8 (*s*) in the ^{13}C NMR spectrum, together with the IR bands at 1750, 1735 and 1710 cm^{-1}, revealed the presence of an α,β-unsaturated ester, δ-lactone and ester groups in the molecule. The ^{1}H NMR spectrum of **1a** showed typical signals [10, 11] for a β-substituted furan ring: H-17, H-15 an α,β-unsaturated ester system and an AB quartet for H-19 of a limonoid system as well as four C-Me resonances (Table 1). Two singlet acetyl signals appeared at δ 2.27 and 1.98 (each 3H). Severinolide (**1a**) was hydrolysed with sodium hydroxide and then acidified by hydrochloric acid to give **1b**. Methylation of **1b** with diazomethane afforded the diol derivative (**1c**). Oxidation of **1c** with Jones' reagent resulted in the formation of yellow crystals, which were identified as dehydroatalantin (**4**) by comparison of their spectral data and mixed melting points with an authentic specimen [12]. This result suggested that the two acetyl groups were located at C-6 and C-7. This arrangement was also supported by the fact that hydrolysis of **1a** to give diol (**1c**) results in a downfield shift of the H-15 resonance and an upfield shift of the H-5, H-6, H-7 and H-9 signals (Table 1). An AMX system [δ 2.90 (1H, *d*, J = 11 Hz), 5.11 (1H, *dd*, J = 3, 11 Hz) and 4.89 (1H, *d*, J = 3 Hz)] was attributed to H-5α (axial), H-6β (axial) and H-7β (equatorial). Acetylation of **1c** gave **1a** (21%) and **1d** (72%), consistent with the α (axial)-configuration of the 7-hydroxyl group. The complete structure and relative stereochemistry of **1a** was determined by single crystal X-ray analysis (Fig. 1). Thus severinolide has structure **1a**.

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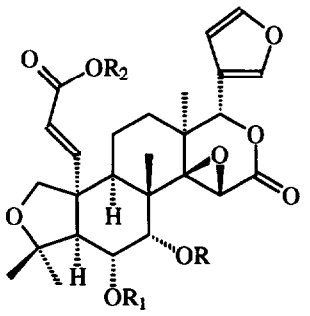
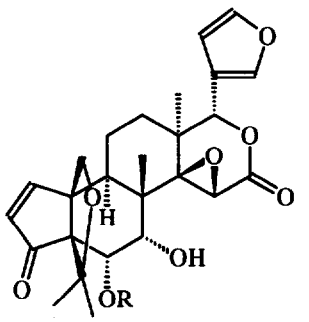
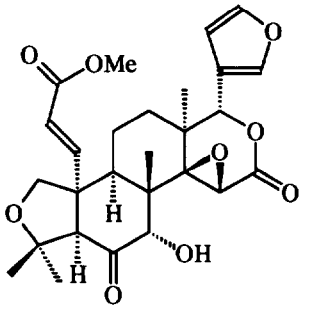


1a R=R1=Ac, R2=Me
1b R=R1=R2=H
1c R=R1=H, R2=Me
1d R=H, R1=Ac, R2=Me



2a R=H
2b R=Ac



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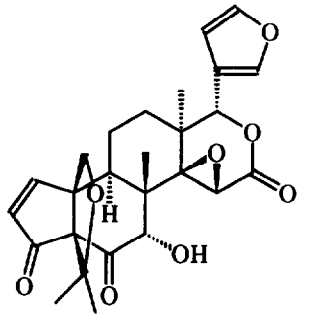

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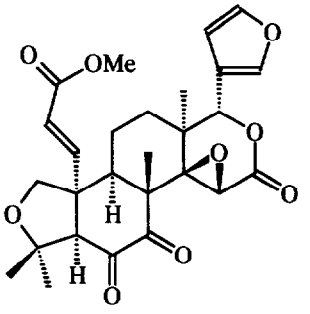

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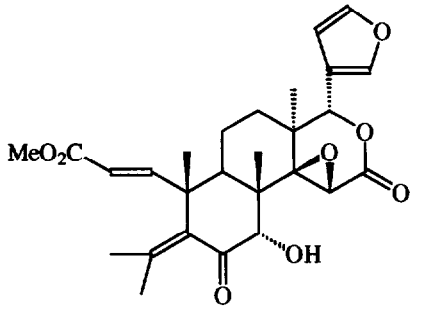

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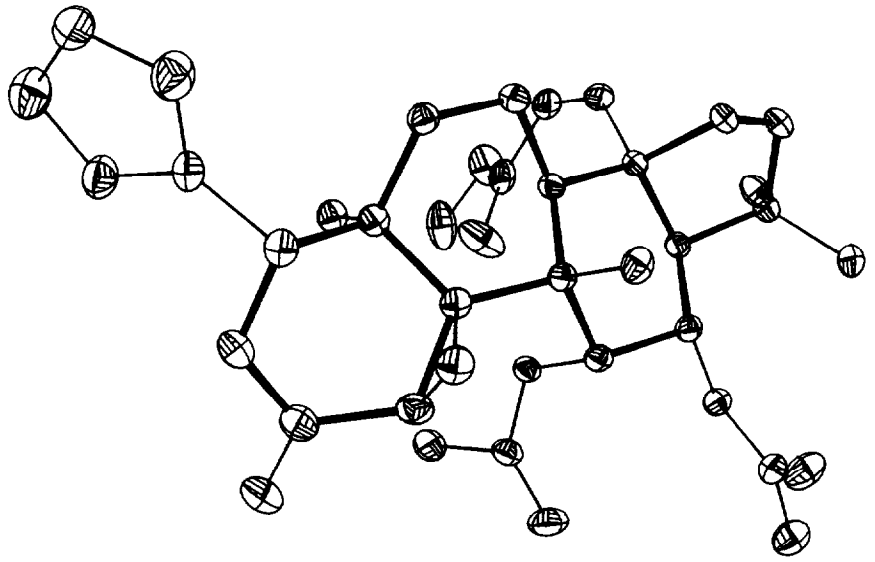
Cycloseverinolide (**2a**) was obtained as optically active colourless plates with the molecular formula $C_{26}H_{30}O_8$. Its UV spectrum exhibited maxima at 217 and 319 nm characteristic of the presence of a cyclopentenone system [13]. The IR spectrum of **2a** showed absorption bands at 3530, 3300, 1725, 1662, 1030 and 895 cm^{-1} indicating the presence of two hydroxyl groups, a δ-lactone, an α,β-unsaturated carbonyl system and a β-substituted furan ring in the molecule. The ^1H NMR spectrum (Table 1) revealed typical H-15 and H-17 signals in a β-substituted furan ring, ring D epoxylactone, an α,β-unsaturated ketone and two hydroxyl protons (exchanged with D_2O). The appearance of four tertiary methyl signals and an AB quartet at δ 3.79 and 3.96 (each 1H, *d*, J = 9.5 Hz) suggested a carbon skeleton related to that of limonin with an ether bridge from C-19 to C-4. The above data suggested that cycloseverinolide (**2a**) was similar to

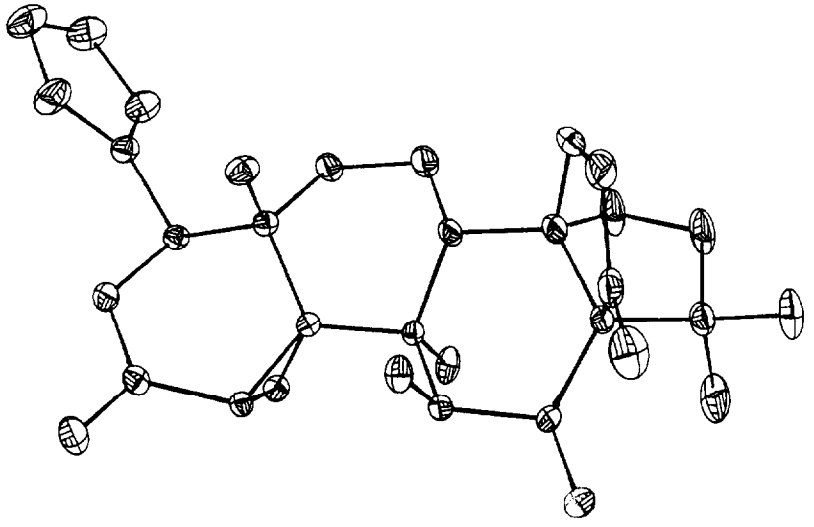
Table 1. ^{1}H NMR spectra of *Severinia* tetranortriterpenoids

	1a	1b*	1c	1d	2a	2a†	2b
H-1	6.15(1H, *d*, 13)	6.53(1H, *d*, 13)	6.52(1H, *d*, 13)	6.47(1H, *d*, 13)	7.69 (1H, *d*, 5.6)	7.76(1H, *d*, 6)	7.58(1H, *d*, 6)
H-2	5.85(1H, *d*, 13)	5.91(1H, *d*, 13)	5.88(1H, *d*, 13)	5.87(1H, *d*, 13)	6.14(1H, *d*, 5.6)	6.06(1H, *d*, 6)	6.07(1H, *d*, 6)
H-5	2.90(1H, *d*, 11)	2.35(1H, *d*, 10)	2.24(1H, *d*, 10)	2.74(1H, *d*, 11)			
H-6	5.11(1H, *dd*, 3, 11)	3.82(1H, *m*)	3.84(1H, *m*)	5.08(1H, *dd*, 3, 11)	4.29(1H, *dd*, 3, 8)	4.16(1H, *dd*, 3, 10)	5.51(1H, *d*, 3)
6-OH			2.55(1H, *d*, 11)		6.29(1H, *d*, 8)	5.69(1H, *d*, 10)	
6-OAc	1.98(3H, *s*)			2.09(3H, *s*)			2.18(3H, *s*)
H-7	4.98(1H, *d*, 3)	3.22(1H, *m*)	3.30(1H, *dd*, 3, 13)	3.52(1H, *dd*, 3, 12)	3.42 (1H, *t*, 3)	3.28(1H, *dd*, 3, 4)	3.46(1H, *dd*, 2, 3)
7-OH			4.84(1H, *d*, 13)	4.74(1H, *d*, 12)	2.50(1H, *d*, 3)	5.45(1H, *d*, 4)	2.31(1H, *d*, 2)
7-OAc	2.27(3H, *s*)						
H-9	3.21(1H, *dd*, 7, 13)	3.00(1H, *m*)	3.06(1H, *dd*, 6, 12)	3.05 (1H, *dd*, 5, 12)	2.64(1H, *dd*, 7, 12)	2.56(1H, *m*)	2.78(1H, *m*)
H-15	3.62(1H, *s*)	3.95(1H, *s*)	4.09(1H, *s*)	3.98(1H, *s*)	3.83(1H, *s*)	3.86(1H, *s*)	3.78(1H, *s*)
H-17	5.57(1H, *s*)	5.60(1H, *s*)	5.62(1H, *s*)	5.57(1H, *s*)	5.58(1H, *s*)	5.55(1H, *s*)	5.58(1H, *s*)
H-19	3.90(1H, *d*, 10)	3.76(1H, *d*, 10)	3.71(1H, *d*, 9)	3.72(1H, *d*, 10)	3.79(1H, *d*, 9.5)	3.76(1H, *d*, 10)	3.75(1H, *d*, 10)
	4.02(1H, *d*, 10)	3.96(1H, *d*, 10)	3.98(1H, *d*, 9)	4.06(1H, *d*, 10)	3.96(1H, *d*, 9.5)	3.91(1H, *d*, 10)	4.03(1H, *d*, 10)
H-21,23	7.40(2H, *d*, 1)	7.52(2H, *d*, 2)	7.40(2H, *d*, 2)	7.35(2H, *d*, 2)	7.38(2H, *d*, 1.5)	7.45(2H, *d*, 1)	7.41(2H, *d*, 1)
H-22	6.30(1H, *d*, 1)	6.43(1H, *d*, 2)	6.32(1H, *d*, 2)	6.27(1H, *d*, 2)	6.31(1H, *d*, 1.5)	6.36(1H, *d*, 1)	6.33(1H, *d*, 1)
18-Me	1.12(3H, *s*)	1.13(6H, *s*)	1.08(3H, *s*)	1.08(3H, *s*)	1.11(3H, *s*)	1.10(3H, *s*)	1.12(6H, *s*)
28-Me	1.14(3H, *s*)	1.21(3H, *s*)	1.13(3H, *s*)	1.21(6H, *s*)	1.13(3H, *s*)	1.12(3H, *s*)	1.20(3H, *s*)
29-Me	1.25(3H, *s*)	1.38(3H, *s*)	1.25(3H, *s*)	1.24(3H, *s*)	1.19(3H, *s*)	1.15(3H, *s*)	1.27(3H, *s*)
30-Me	1.24(3H, *s*)		1.44(3H, *s*)		1.51(3H, *s*)	1.47(3H, *s*)	
CO_2Me	3.67(3H, *s*)		3.77(3H, *s*)	3.75(3H, *s*)			

* Run in $(CD_3)_2CO$.
† Run in $CDCl_3$ + 10% DMSO-d_6.
Figures in parentheses are coupling constants in Hz.



1a



2a

Fig. 1. Structure and solid-state conformation of compound **1a** and **2a**.

cycloepiatalantin (**6**) [14]. Oxidation of **2a** with Jones' reagent afforded colourless needles which had identical spectral data and TLC behaviour with an authentic sample of **6**. This indicated that the two hydroxyl groups were located at C-6α and C-7α [$J_{6,7}$ = 3 Hz]. The complete structure and relative stereochemistry of **2a** was determined by a single crystal X-ray analysis (Fig. 1). Thus cycloseverinolide has structure **2a**.

The known compounds, atalantin (**3**) [15], dehydroatalantin (**4**) [12], atalantolide (**5**) [16] and cycloepiatalantin (**6**) [14] were also isolated and characterized by comparison of their spectroscopic data (UV, IR, NMR and mass spectrometry) with literature values.

The isolated compounds were subjected to antifeedant activity evaluation [17, 18]. Severinolide (**1a**), atalantin (**3**) and cycloepiatalantin (**6**) showed strong antifeedant activity against third instar larvae of the Diamondback moth (*Plutella xylostella*) with ED_{50} at concentrations of 0.0625, 0.0625 and 0.25%, respectively (Table 2).

EXPERIMENTAL

Mps: uncorr. ^{1}HNMR (100, 200, 400 MHz) were recorded in $CDCl_3$ except where noted. Chemical shift values are showed in ppm (δ) with TMS as an int. standard. MS were recorded using a direct inlet

Table 2. Antifeeding activity of tetranortriterpenoids from *Severinia buxifolia*

Compd	Method concn. (%)	I Time (day) 1	2	5	II Time (day) 1 C	T	2 C	T	5 C	T
1a	0.5	±	±	±	++++	±	++++	±	++++	+
	0.25	±	±	±	++	±	++++	±	++++	+
	0.125	±	±	±	+	±	++++	±	++++	±
	0.0625	+	+	++	+++	±	++++	++	++++	+++
	0.03125	+	+++	+++	+++	+	++++	+++	++++	++++
2a	0.5	++	+++	++++	+	++	++++	++++	++++	++++
	0.25	+	+++	+++	+	++	++++	++++	++++	++++
3	0.5	±	±	±	+++	±	++++	+	++++	++
	0.25	±	±	±	++	±	++++	+	++++	++
	0.125	±	±	+	++	±	++++	++	++++	+++
	0.0625	±	++	+++	+++	±	++++	++	++++	++++
	0.03125	+	+++	++++	+++	±	++++	+++	++++	++++
4	0.5	±	±	+	+++	±	++++	++	++++	+++
5	0.5	++	++++	++++	+++	+	++++	++++	++++	++++
	0.25	++	++++	++++	++++	+	++++	++++	++++	++++
6	0.5	±	±	±	+++	+	++++	+++	++++	+++
	0.25	±	±	±	++++	±	++++	++	++++	++
Galecron	0.5	±	+	+	+++	±	++++	±	++++	±
	0.25	±	+	++	++	±	++++	+++	++++	++
	0.125	±	++	+++	++	±	++++	++	++++	++
	0.0625	±	++	++++	++	+	++++	+++	++++	++++
	0.03125	+	+++	++++	+	±	++++	++	++++	++++
Control	—	++	++++	++++	++	/	++++	/	++++	/

C: no treatment with compound; T: treatment with compound.

Observation: Consumptions of the cabbage leaf disks were evaluated by the index of 6 grades as shown below at 1, 2 and 5 days after treatment.

Grades of leaf disk consumption: −: 0%; ±: 1–20%; +: 21–40%; ++: 41–60%; +++: 61–80%; ++++: 81–100%.

system. UV were determined in MeOH and IR were recorded in KBr disc.

Plant material. Severinia buxifolia (Pior.) Tenore was collected from Tainan, Taiwan and identified by Prof. C. S. Kuoh. A voucher specimen is deposited in the Herbarium of the National Cheng Kung University, Tainan, Taiwan, R.O.C.

Extraction and separation. The procedure of extraction and sepn was as related reference [6]. The benzene eluted fr. was rechromatographed on silica gel and eluted with *i*-Pr_2O and Et_2O to afford **1a** (5.1 g), **3** (0.61 g), **5** (0.37 g), **4** (0.03 g) and a mixt. This mixt. was chromatographed on silica gel using EtOAc–benzene (1:4) as eluent and 20 ml frs were collected and monitored by TLC. The frs giving an identical spot were combined together. Compound **6** (0.62 g) and **2a** (0.57 g) were obtained, respectively.

Severinolide (**1a**). Colourless plated (Me_2CO), mp 219–221°. $[\alpha]_D$ +53.08° (*c* 1.3, $CHCl_3$). Anal. calcd for $C_{31}H_{38}O_{11}$: found: C, 63.42; H, 6.55%, required: C, 63.48; H, 6.48%. UV λ_{max} nm: 214. IR ν_{max} cm^{-1}: 1750, 1735, 1710, 1640. EIMS *m/z* (rel. int.): 586[M]$^+$, 511, 463, 451, 432, 403, 393, 361, 343, 311, 303, 285, 253, 225, 95(100), 43. ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8(*s*), 170.3(*s*), 167.3(*s*), 165.4(*s*), 157.3(*d*), 143.0(*d*), 141.2(*d*), 120.4(*s*), 120.2(*d*), 109.8(*d*), 82.9(*s*), 78.0(*d*), 73.2(*t*), 70.6(*d*), 69.8(*s*), 69.2(*d*), 56.7(*d*), 54.6(*s*), 51.3(*q*), 51.1(*d*), 42.3(*s*), 38.8(*s*), 35.4(*d*), 30.3(*q*), 25.5(*t*), 23.9(*q*), 21.0(*q*), 20.7(*q*), 18.0(*t*), 18.0(*q*), 17.1(*q*).

Hydrolysis of **1a**. Compound **1a** (0.5 g) was dissolved in MeOH (50 ml) containing NaOH (2.5 g) and stirred at room temp. for 7 hr. The reaction product was treated in the usual way to yield colourless needles of **1b** (310 mg) (Me_2CO), $C_{26}H_{32}O_9$, mp 245–247°. IR ν_{max} cm^{-1}: 3340, 1732, 1705, 1625. EIMS *m/z*: 448[M]$^+$, 452, 444, 426, 422(100%), 408, 394, 380, 366, 210, 95.

Methylation of **1b**. Treatment of **1b** (300 mg) with excess CH_2N_2 in the usual way afforded **1c** (290 mg) as colourless syrup, $C_{27}H_{34}O_9$. IR ν_{max} cm^{-1}: 3430, 1740, 1700, 1625. EIMS *m/z*: 469([M]$^+$-43), 368, 361(100), 256, 249, 236, 223, 213, 185, 171, 129, 121, 111, 97, 95.

Oxidation of **1c**. Jones' reagent was added dropwise to stirring soln of **1c** (0.07 g) in Me_2CO. After standing for 20 min at room temp., excess of reagent was destroyed by using two drops of MeOH. Standard workup afforded yellowish crystals (0.053 g) (Me_2CO), mp 204°, which were identified as dehydroatalantin (**4**) by comparison of their spectral data, TLC and mixed mp with authentic sample [12].

Acetylation of **1c**. Compound **1c** (0. 15 g) was dissolved in C_5H_5N (2 ml) and Ac_2O (3 ml) and the mixt.

allowed to stand overnight at room temp. Standard workup gave a residue which showed two spots on TLC (benzene–Me_2CO, 4:1). The mixt. was sepd by prep. TLC using the same solvent system as TLC. The front spot (32 mg) was identified with **1a** by direct comparison. The second spot, compound **1d** (107 mg), was recrystallized from Me_2CO as colourless needles, $C_{29}H_{36}O_{10}$, mp 238–240°. UV λ_{max} nm: 215. IR ν_{max} cm^{-1}: 3450, 1740, 1720, 1695, 1620. EIMS *m/z*: 544[M]$^+$, 513, 511, 469, 451, 421, 403(100%), 361, 345, 343, 303, 285, 253, 225, 95.

Crystal data of **1a**. M = 586, triclinic, space group P2 $a = 18.6659(73)$, $b = 13.1231(35)$, $c = 11.9066(28)$ Å, $\alpha = \beta = \gamma = 92.909(3)°$, $U = 2912.84$ Å^3, $Z = 4$, $D_c = 1.336$ mg m^{-3}, μ (MoKα radiation, $\lambda = 0.70923$ Å) crystal dimensions: $0.1 \times 0.2 \times 0.3$ mm. Intensity data ($\pm h$, $\pm k$, $\pm l$, $\theta_{max} = 67°$) were recorded on a Siemens R3m/V diffractometer. The crystal structure was solved by a direct method. Full-matrix least-squares refinement of atomic parameters (anisotropic C, O; isotropic H) converged at $R = 5.10$ ($R_w = 6.33$) over 5753 reflections with $1 > 3.0\sigma(1)$.

Cycloseverinolide (**2a**). Colourless plates (Me_2CO), mp > 360°. $[\alpha]_D + 50.75°$ (*c* 0.4, $CHCl_3$). Anal. calcd for $C_{26}H_{30}O_8$: found: C, 66.29; H, 6.55%, required: C, 66.37; H, 6.43%. UV λ_{max} nm: 217, 319. IR ν_{max} cm^{-1}: 3530, 3300, 1725, 1662, 1590. EIMS *m/z*: 470[M]$^+$, 455, 329(100%), 271, 123, 121, 107, 105, 95.

Oxidation of **2a**. Compound **2a** (0.1 g) was oxidized as above to give a colourless needle (0.075 g)(Me_2CO), mp 325–328°(dec.). Anal. calcd for $C_{26}H_{28}O_8$: found: C, 66.29; H, 6.11%, required: C, 66.65, H; 6.02%. UV λ_{max} nm: 215, 327. IR ν_{max} cm^{-1}: 3480, 1725, 1715, 1690, 1590. $[\alpha]_D - 77.02°$ (*c* 0.47, $CHCl_3$). EIMS *m/z*: 468[M]$^+$, 456, 422, 345, 327(100%), 287, 269, 121, 95, 91, identical with cycloepiatalantin (**6**) [13].

Acetylation of **2a**. Compound **2a** (50 mg) was heated in Ac_2O (10 ml) and pyridine (2 ml) at 105° for 7 hr. The usual workup gave rectangular prisms of **2b** (45 mg)(Me_2CO), $C_{28}H_{32}O_9$, mp 298–300°. UV λ_{max} nm: 219, 326. IR ν_{max} cm^{-1}: 3340, 1730, 1720, 1690, 1605. EIMS *m/z*: 512[M]$^+$, 497, 389, 371, 329, 313, 271(100%), 95.

Crystal data of **2a**. M = 470, triclinic space group P2, $a = 11.3099(17)$, $b = 11.7209(17)$, $c = 16.9764(28)$ Å, $\alpha = \beta = \gamma = 90(3)°$, $U = 2250.43$ Å^3, $Z = 4$, $D_c = 1.39$ mg m^{-3}, μ (MoKα radiation, $\lambda = 0.70923$ Å) crystal dimensions: $0.1 \times 0.2 \times 0.3$ mm. Intensity data ($\pm h$, $\pm k$, $\pm l$, $\theta_{max} = 70°$) were recorded on a Siemens R3m/V diffractometer. The crystal structure was solved by a direct method. Full-matrix least-squares refinement of atomic parameters (anisotropic C, O; isotropic H) converged at $R = 5.53$ ($R_w = 4.07$) over 3490 reflections with $1 > 3.0\sigma(1)$.

Antifeeding activity test. The test insect was third instar larvae of Diamondback moth (*Plutella xylostella*). (*a*) A filter paper moistened with 1 ml of H_2O was placed in each Petri dish (2 cm(H) × 9 cm(D)). (*b*). Both sides of cabbage leaf disks (2 cm diameter) were treated with 20 μl MeOH of chemicals and air dried, then these were placed on the filter paper. Method I: 4 treated disks were placed in a dish. Method II: 3 treated disks and 3 untreated disks were placed alternately. (*c*) In method I and II, two larvae per disk were released in a dish.

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