Antifeedant Activity of Sesquiterpenes from Celastraceae

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Abstract—Forty one sesquiterpenes with a dihydro- β -agarofuran skeleton, and 14 related synthetic compounds are assayed for antifeedant and insecticidal activities against the Egyptian cotton leafworm *Spodoptera littoralis* using the leaf disk method. The antifeedant activity is measured in terms of feeding ratio (FR₅₀) and the insecticidal activity as lethal dose LD₁₀₀. Thirty eight of the sesquiterpenes assayed show antifeedant activity, including 38 more active than triphenyl tin acetate used as a positive control in this assay. Three sesquiterpenes demonstrate insecticidal activity. Structure activity relations are examined.

Introduction

Clerodane diterpenes from various plant species (Kato *et al.*, 1972; Bellés *et al.*, 1985), drimane-type sesquiterpenes from *Warburgia* species (Kubo *et al.*, 1976), and limonoids such as azadirachtin from the Meliaceae (Ley, 1990) are some of the best studied natural products with insect antifeedant activity. For the clerodane diterpenes and azadirachtins, bioactivity has been related to specific structural features of the molecule. The presence of a furan or perhydrofuran moiety may be in part responsible for their antifeedant activity (Kojima and Kato, 1981), although when the furan system is replaced by a butenolide ring in some clerodanes, feeding is in fact further inhibited (Kubo *et al.*, 1976). Antifeedant activity has also been associated with the presence of a decalin ring system and with ester moieties (Geuskens *et al.*, 1983) but there is no clear indication of how structure is related with activity and mode of action.

Various species of Celastraceae have been used in Chinese traditional agriculture to protect crops from insect attack (Swingle *et al.*, 1941). The Chinese bittersweet *Celastrus angulatus* Max. has demonstrated activity against several insect species (Wakabayashi *et al.*, 1988) and there is a body of work on the antifeedant or insecticidal activity of extracts (Chiu, 1989), or of isolated products such as angulatin A (Maotian *et al.*, 1991), celangulins (Wakabayashi *et al.*, 1988; Wu *et al.*, 1992) and other sesquiterpenes (Kai *et al.*, 1991).

Sesquiterpenes with a dihydro- β -agarofuran skeleton (5.11-epoxv-5 β .10 α -eudesm-

(Brüning and Wagner, 1978). In a preliminary study we reported the antifeedant activity of 15 polyesterified sesquiterpenes from Celastraceae against the Egyptian cotton leafworm *Spodoptera littoralis* (González *et al.*, 1992a).

This paper reports the activity and structure–activity relations of 41 sesquiterpenes isolated from seven species of Celastraceae and 14 related synthetic compounds on the fifth-instar larvae of *S. littoralis*.

Materials and Methods

Insects. Newly ecdysed fifth-instar larvae of the Egyptian cotton leafworm *Spodoptera littoralis* Boisduval, taken from a laboratory culture were used for the antifeedant bioassays. The larvae were reared on a semi-artificial diet (Poitout and Bies, 1974) at $25 \pm 2^\circ\text{C}$, 60–70% relative humidity and 18 h photophase.

Compounds tested. Compounds **1–41** (Fig. 1), were isolated by repeated column chromatography on silica gel or Sephadex LH-20 from the EtOH extracts of seven Celastraceae species. All compounds were rigorously characterized by spectroscopic methods (UV, IR, ^1H NMR, ^{13}C NMR, HMBC, HMQC, MS) and chemical data. Compounds **1** (González *et al.*, 1992b), **11–13**, **31–33** (González *et al.*, 1994a) were isolated from *Maytenus boaria*; compounds **3**, **38–40** (González *et al.*, 1993b), **16**, **17**, **20** (González *et al.*, 1990), **19**, **35**, **36** (González *et al.*, 1989a), **21**, **22**, **34** (González *et al.*, 1994b), **18**, **23**, **25** (González *et al.*, 1993a), **24** (Jiménez, 1992) and **37** (celangulin) (Wakabayashi *et al.*, 1988; González *et al.*, 1993b) from *Maytenus canariensis*; compounds **7**, **8**, **14**, **15**, **26**, **27** (González *et al.*, 1994a) from *Maytenus chubutensis*; compounds **9**, **10** (González *et al.*, 1994a) from *Maytenus disticha*; compounds **28–30** (González *et al.*, 1994a) from *Maytenus magellanica*; compounds **4**, **5** (González *et al.*, 1988) and **41** from *Orthosphenia mexicana* (González *et al.*, 1989b) and compounds **2** (González *et al.*, 1987) and **6** (González *et al.*, 1988) from *Rzedowskia tolantongensis*.

Compounds **42–55** were racemic and/or optically active tetrahydrofuran synthetic compounds with different substituents on C-2 or C-3 and 2-methylbutanoic acid and derivatives (Fig. 2).

Triphenyl tin acetate (TTA) (Aldrich; 97%) was used as positive control, as it has antifeedant activity against *S. littoralis* (Bellés and Piulachs, 1983).

Antifeedant activity. The technique used was a choice test (Bellés and Piulachs, 1983; Bellés *et al.*, 1985) using lettuce disks of 1 cm^2 ($33.65 \pm 0.07\text{ mg fwt}$). The test compounds were uniformly distributed over the surface of the disk by application of $10\text{ }\mu\text{g}$ of compound in acetone ($10\text{ }\mu\text{l}$) that was allowed to evaporate to give the treated disks (TD). Control disks (CD) were prepared in the same manner but without test compounds. For each bioassay, four TD and four CD were placed alternately in a Petri dish with five larvae (weight 40–50 mg) and kept in a growth chamber in the dark at 30°C , 70% relative humidity. There were six replicates for each compound tested. The consumed area of the treated disks (CTD) and those of the controls (CCD) was visually estimated on millimetre paper simultaneously at regular 30 min intervals for 4–5 h to calculate the feeding ratio ($\text{FR} = \text{CTD}/\text{CCD}$). FR_{50} , the feeding ratio when the CD had been 50% consumed, was used as a measure of antifeedant activity.

Insecticidal activity. Compounds that showed insecticidal activity in the antifeedant assay were further assayed. For each bio-assay, four TD with different doses of the compound (10 , 1 , 0.1 , 0.01 , $0.005\text{ }\mu\text{g cm}^{-2}$) and four CD were placed in different Petri dishes with five larvae each. Experimental conditions were the same as those for the choice test and each test was repeated six times. Lethal dose of compounds for 100% mortality after 3 h exposure (LD_{100}) was based on direct observation.

Results and Discussion

Among the 55 compounds tested, only the sesquiterpenes (**1–41**) were active, **38** (**1–38**) of which showed antifeedant activity and **3** (**39–41**) insecticidal activity.

As shown in Table 1, sesquiterpenes **1–2**, **4**, **7**, **11–14**, **16**, **18**, **20**, **27–29**, **31–33**, **35** and **38** exhibited antifeedant activity at $10\text{ }\mu\text{g cm}^{-2}$ in the choice test; **5**, **8–10**, **15**, **19**, **21**, **25–26** and **30** at $1\text{ }\mu\text{g cm}^{-2}$; **3**, **6**, **22–24**, **34** and **36–37** at $0.1\text{ }\mu\text{g cm}^{-2}$ and a remarkable activity was observed for compound **17** (9α -benzoyloxy- $8\alpha,2$ -methylbutyryloxy- $1\alpha,6\beta,15$ -triacetox- 4β -hydroxydihydro- β -agarofuran) with a $\text{FR}_{50} = 0.69 \pm 0.08$ at the lowest concentration tested of $0.01\text{ }\mu\text{g cm}^{-2}$.

Regarding structure–activity relations, we observed that the most active compounds were those with isalatalol (**17**, **22–24**) or 4β -hydroxyalatalol skeletons (**34**, **36–37**) (Table 2). Comparing the activities of compounds with the same skeleton the activity increases with the number of acetate esters and decreases with the number of benzoate

Compound	OH	OBz	OAc	Others
1	3 β ,4 α			
2	4 β	1 α	9 β	6 β (ONic)
3	4 β	9 β	1 α ,6 β ,15	
4	4 β ,8 β	1 α	9 α	6 β (ONic)
5	4 β	1 α	6 β ,8 β ,9 α	
6	4 β	1 α	8 β ,9 α	6 β (ONic)
7		9 β	1 α ,2 α ,6 β ,15	
8	15	9 β	1 α ,2 α ,6 β	
9		9 β	1 α ,6 β ,8 α ,15	
10	8 α	9 β	1 α ,6 β ,15	
11	3 β ,4 β	1 α ,9 β	2 β	
12	3 β	1 α ,9 β	2 β ,6 β	
13	4 β	1 α ,9 β	2 β ,6 β	
14	15	9 α	1 α ,2 α ,6 β	8 (C=O)
15	4 β ,15	9 α	1 α ,2 α ,6 β ,8 α	
16	4 β	1 α ,9 α	6 β ,15	8 α (OMeBut)
17	4 β	9 α	1 α ,6 β ,15	8 α (OMeBut)
18	4 β	1 α ,8 α ,9 α	6 β ,15	
19	4 β	1 α ,9 α	6 β ,8 α ,15	
20	4 β	9 α	6 β ,8 α ,15	1 α (OCin)
21	4 β	1 α ,9 α	6 β ,15	8 α (OTig)
22	4 β	9 α	1 α ,6 β ,15	8 α (OTig)
23	4 β	9 α	1 α ,6 β ,8 α ,15	
24	1 α ,4 β	9 α	6 β ,15	8 α (OMeBut)
25	4 β	8 α ,9 α	1 α ,6 β ,15	
26		9 β	1 α ,2 α ,6 β ,8 α ,15	
27	15	9 β	1 α ,2 α ,6 β ,8 α	
28	4 β	1 α ,9 β	2 β ,3 β ,6 β	
29	2 β ,4 β	1 α ,9 β	3 β ,6 β	
30	3 β ,4 β	1 α ,9 β	2 β ,6 β	
31	3 β ,4 β	1 α	2 β ,6 β	9 β (OCin)
32	3 β ,4 β ,6 β	1 α ,9 β	2 β	
33	4 β	1 α ,9 β	2 β ,3 β ,8 β	
34	4 β	9 α	2 α ,6 β ,8 α ,15	1 α (OAng)
35	4 β	1 α ,9 α	2 α ,6 β ,8 α ,15	
36	4 β ,6 β	1 α ,9 α	2 α ,8 α ,15	
37	4 β	9 α	1 α ,2 α ,6 β ,8 α ,15	
38	4 β	1 α ,8 α ,9 α	2 α ,6 β ,15	
39	4 β	1 α ,9 α	2 α ,6 β ,15	8 (C=O)
40	4 β	9 α	1 α ,2 α ,6 β ,15	8 (C=O)
41	4 β		1 α ,2 α ,6 β ,9 α ,15	8 (C=O) 3 β ,13 (OCass)

FIG. 1. NATURAL COMPOUNDS ASSAYED.

Compound	R	Compound	R
42	(±) OH	48	(±) OH
43	(±) OAc	49	(±) OAc
44	(±) OBz	50	(±) OBz
45	(±) 3,5 (NO ₂) ₂ OBz	51	(±) 3,5 (NO ₂) ₂ OBz
46	(+) OH		
47	(+) OAc

Compound	R	Compound	R
52	(±) OH	54	(±)
53	(±) OAc	55	(+)

FIG. 2. SYNTHETIC COMPOUNDS ASSAYED.

esters, i.e. for compounds with the alatol skeleton the order of activity is **23** (4 OAc; 1 OBz) > **19** (3 OAc; 2 OBz) > **18** (2 OAc; 3 OBz) and **17** (3 OAc; 1 OBz) > **16** (2 OAc; 2 OBz); for compounds with the 4β-hydroxyalatol skeleton **37** (5 OAc; 1 OBz) > **35** (4 OAc; 2 OBz) > **38** (3 OAc; 3 OBz). In general, products with aromatic esters at C-1 and C-9, whatever their stereochemistry were only weakly active, i.e. **11–12**, **18** and **28**. The introduction of ester groups at C-2 had no effect on activity, i.e. in the pairs **18** vs. **38**, **19** vs. **35** and **23** vs. **37** (Fig. 1).

The three insecticidal sesquiterpenes, **39**, **40** and orthosphenine (**41**) showed an LD₁₀₀ of 0.1, 1 and 0.01 μg cm⁻², respectively. The only structural characteristic common to the compounds was a carbonyl group at C-8.

Comparing the antifeedant activity shown by the sesquiterpenes at the concentration of 10 μg cm⁻² with the well-known antifeedant agent triphenyl tin acetate (TTA, FR₅₀ = 0.37 ± 0.09), we found that 18 compounds (**3**, **5–6**, **8–10**, **15**, **17**, **21–27**, **34**, **36–37**) proved to be more active than TTA, ten compounds (**2**, **4**, **11–12**, **18**, **28–29**, **31–32**, **38**) were less active and no significant differences were found for ten compounds (**1**, **7**, **13–14**, **16**, **19–20**, **30**, **33**, **35**).

No antifeedant nor insecticidal activity was observed in the racemic and/or optically active tetrahydrofuran products with substituents in C-2 or C-3 and 2-methylbutanoid derivatives **42–55** (Fig. 2). All these compounds have a sesquiterpene skeleton and X-ray data (González *et al.*, 1992a) and conformational study by molecular mechanics (Jiménez, 1992) showed that in every instance with only slight variations, the *trans*-fused A and B rings formed a decalin system, chair–chair, slightly distorted by the presence of the 1,3-diaxial bond responsible for the tetrahydrofuran C ring, practically perpendicular to the plain formed by carbons C-5, C-7, C-8 and C-10.

These results allow us to conclude that the compact tricyclic system is a prerequisite for antifeedant or insecticidal activity in this type of sesquiterpene.

TABLE 1. ANTIFEEDANT ACTIVITY OF SESQUITERPENES AGAINST
Spodoptera littoralis

Compound	Dose ($\mu\text{g cm}^{-2}$)	FR ₅₀ $\pm$ SEM*
1	10	0.52 $\pm$ 0.10
2	10	0.68 $\pm$ 0.14
3	10	0.11 $\pm$ 0.04
	1	0.12 $\pm$ 0.01
	0.1	0.40 $\pm$ 0.07
4	10	0.74 $\pm$ 0.06
5	10	0.12 $\pm$ 0.07
	1	0.40 $\pm$ 0.02
6	10	0.04 $\pm$ 0.03
	1	0.15 $\pm$ 0.15
	0.1	0.45 $\pm$ 0.28
	10	0.36 $\pm$ 0.09
8	10	0.19 $\pm$ 0.06
	1	0.54 $\pm$ 0.09
9	10	0.04 $\pm$ 0.02
	1	0.44 $\pm$ 0.09
10	10	0.05 $\pm$ 0.01
	1	0.25 $\pm$ 0.06
11	10	0.61 $\pm$ 0.09
12	10	0.63 $\pm$ 0.11
13	10	0.35 $\pm$ 0.08
14	10	0.41 $\pm$ 0.11
15	10	0.16 $\pm$ 0.15
	1	0.65 $\pm$ 0.25
16	10	0.45 $\pm$ 0.12
17	10	0
	1	0
	0.1	0.23 $\pm$ 0.07
	0.01	0.69 $\pm$ 0.08
18	10	0.76 $\pm$ 0.08
19	10	0.24 $\pm$ 0.11
	1	0.58 $\pm$ 0.06
20	10	0.27 $\pm$ 0.16
21	10	0.12 $\pm$ 0.03
	1	0.29 $\pm$ 0.07
22	10	0.06 $\pm$ 0.03
	1	0.20 $\pm$ 0.06
	0.1	0.43 $\pm$ 0.06
23	10	0.03 $\pm$ 0.01
	1	0.20 $\pm$ 0.06
	0.1	0.64 $\pm$ 0.07
24	10	0.08 $\pm$ 0.03
	1	0.23 $\pm$ 0.02
	0.1	0.57 $\pm$ 0.09
25	10	0.15 $\pm$ 0.02
	1	0.40 $\pm$ 0.09
26	10	0.07 $\pm$ 0.06
	1	0.53 $\pm$ 0.32
27	10	0.13 $\pm$ 0.05
	1	0.71 $\pm$ 0.09
28	10	0.65 $\pm$ 0.15
29	10	0.56 $\pm$ 0.11
30	10	0.24 $\pm$ 0.19
	1	0.44 $\pm$ 0.12
31	10	0.76 $\pm$ 0.16
32	10	0.60 $\pm$ 0.07
33	10	0.38 $\pm$ 0.05

TABLE 1—*CONTINUED*

Compound	Dose ($\mu\text{g cm}^{-2}$)	FR ₅₀ $\pm$ SEM*
34	10	0.10 $\pm$ 0.03
	1	0.18 $\pm$ 0.02
	0.1	1.10 $\pm$ 0.02
35	10	0.35 $\pm$ 0.19
36	10	0.10 $\pm$ 0.06
	1	0.19 $\pm$ 0.08
	0.1	1.02 $\pm$ 0.07
37	10	0.05 $\pm$ 0.02
	1	0.24 $\pm$ 0.03
	0.1	0.40 $\pm$ 0.08
38	10	0.76 $\pm$ 0.16
TTA†	10	0.37 $\pm$ 0.09

*Standard Error Mean.

†Triphenyl tin acetate.

Sesquiterpenes with the basic dihydro- β -agarofuran skeleton represent a new family of active compounds with potential for use as crop protection agents in agriculture.

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TABLE 2. BASIC POLYHYDROXY SKELETONS OF THE SESQUITERPENES ASSAYED

Compound	Basic skeleton	No. oxygens
1	Boariol	3
2	4 β -Hydroxycelorbicol	5
3	2,3-Dideoxymaytol	6
4–6	2,3,13,15-Tetradexyisoeuonyminol	6
7–8	3,4-Dideoxymaytol	6
9–10	15-Hydroxycelapanol	6
11	6-Deoxymagellanol	6
12	4-Deoxymagellanol	6
13	3-Deoxymagellanol	6
14	3,4,13-Trideoxyevoninol	7
15	Alatol	7
16–25	Isoalatol	7
26–27	9-Epialatol	7
28–32	Magellanol	7
33	Isomagellanol	7
34–38	4 β -Hydroxyalatol	8
39–40	3,13-Dideoxyevoninol	8
41	Evoninol	10

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