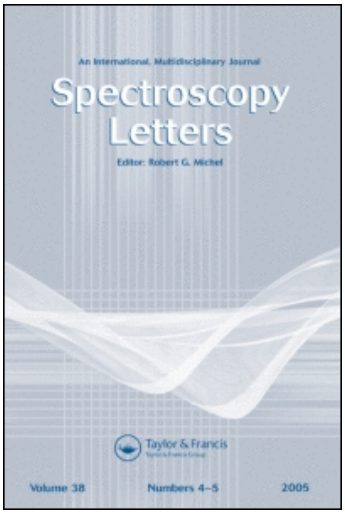

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Sesquiterpenes from *Chrysoma Pauciflosculosa*

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SESQUITERPENES FROM *CHRYSOMA PAUCIFLOSCULOSA*

Key Words: *Chrysoma pauciflosculosa*; Asteraceae; Heliantheae; sesquiterpenes; bisabolanes; allelopathy.

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Abstract - The aerial parts of *Chrysoma pauciflosculosa* (syn. *Solidago pauciflosculosa*) gave two new sesquiterpenes, (+)-β-turmerone and a bisabolane endoperoxide, together with the known (-)-α-*trans*-bergamotene and (+)-β-sesquiphellandrene. When exposed to air and light, (+)-β-turmerone and (+)-β-sesquiphellandrene gave oxidative degradation products, involving hydroperoxide intermediates. Photosensitized singlet oxygen reactions of (+)-β-turmerone provided a series of bisabolane-type endoperoxides. The structures of the natural compounds as well as those of the degradation products and derivatives were elucidated by chemical and spectroscopic methods, mainly NMR and MS. Aqueous solutions of (+)-β-turmerone,(+)-β- sesquiphellandrene and (-)-α-*trans*-bergamotene were tested for their effects on the germination and radicle growth of three Florida sandhill species, *Rudbeckia hirta, Schizachyrium scoparium, Leptochloa dubia,* as well as *Lactuca sativa.* (+)-β-Turmerone significantly inhibited germination of *L. sativa*, stimulated radicle growth of *L. sativa* and *S. scoparium* at the 10^{-4} M level, and mildly inhibited radicle growth of *R. hirta,* as did (+)-β-sesquiphellandrene. (-)-α-*trans*-Bergamotene stimulated germination of *S. scoparium* and *L. sativa* and significantly enhanced radicle growth of *S. scoparium.*

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INTRODUCTION

We have been investigating the hypothesis that members of the fire-sensitive Florida scrub community release allelopathic agents that inhibit the growth of sandhill grasses and herbs which provide the fuel for frequent surface fires in the sandhill community [1]. In continuation of our directed search for phytotoxic constituents from scrub species, which affect the germination and growth of native grasses and herbs of the Florida sandhill community [2], we have chemically analyzed the woody goldenrod (*Chrysoma pauciflosculosa*) of the family Asteraceae, a dominant shrub on open, immature scrub sites in the dunes of the Florida panhandle. In preliminary tests, water, hexane and dichloromethane extracts of fresh aerial parts of *C. pauciflosculosa* showed inhibitory effects on both the germination and radicle growth of lettuce (*Lactuca sativa*) and little bluestem (*Schizachyrium scoparium*), a native grass of the sandhill. The water and hexane extracts completely inhibited germination of lettuce. Germination of little bluestem was unaffected by the water extract, but radicle growth was reduced.

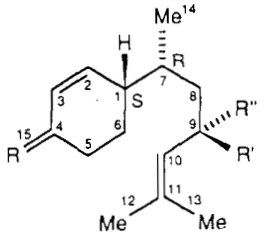
Root extracts of *C. pauciflosculosa* provided a mixture of matricaria ester and closely related compounds, which were highly active against native sandhill grasses and herbs [3]. Investigations of the polar chromatographic fractions of extracts from aerial parts of *C. pauciflosculosa* contained diterpenes related to grindelic acid, which exhibited considerable allelopathic activity against two sandhill grasses as well as *L. sativa* and *Rudbeckia hirta* [2,4].

Chemical investigations of the nonpolar chromatographic fractions of aerial part extracts of *C. pauciflosculosa* gave a mixture of sesquiterpenes. The major sesquiterpenes were the known (+)-β-sesquiphellandrene (**2**), (-)-α-*trans*-bergamotene (**3**) as well as the new (+)-β-turmerone (**1**) and sesquiphellandrene endoperoxide **4**. When exposed to air, (+)-β-sesquiphellandrene and (+)-β-turmerone decomposed oxidatively. Since photochemical activation is involved in the allelopathic action of *C. pauciflosculosa* diterpenes [2,4], the structures of the oxidative decomposition products of (+)-β-turmerone (**1**) as well as its singlet oxygen reaction products were also studied.

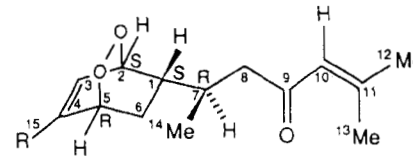
RESULTS AND DISCUSSION

Chemical Data

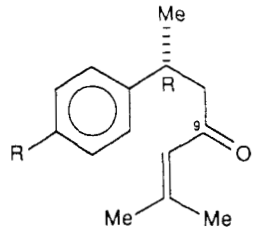
The sesquiterpene hydrocarbon **2**, $C_{15}H_{24}$, showed IR bands at 876 and 831 cm^{-1}, suggesting the presence of a vinylidene and isopropylidene group, respectively. The ^1H NMR



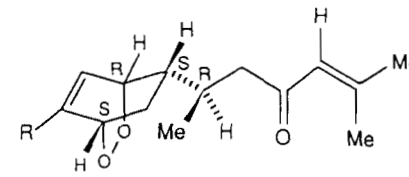
	R	R'	R''
1	CH_2	=O	
2	CH_2	H	H
9	O	=O	
10	O	H	H



	R
4	Me, 9 - desoxy
12	Me
14	CHO
16	CH_2OH
18	CH_2OOH



	R
6	Me, 9 - desoxy
7	CHO
8	CH_2OOH



	R
5	Me, 9 - desoxy
11	Me
13	CHO
15	CH_2OH
17	CH_2OOH

spectral data indicated that **2** must be a 4(15), 10-bisaboladiene and the chemical shifts of all proton absorptions were in full agreement with the structure of β-sesquiphellandrene [5,6]. This was confirmed by high-field ^1H and ^{13}C NMR DEPT experiments (Tables 1 and 2). The optical rotation value reported for (+)-β-sesquiphellandrene was $[\alpha]_D^{29} = +4.0°$ [6], and compound **2** exhibited a rotation of $[\alpha]_D^{25} = +5.7°$. The similar rotation values together with essentially identical ^1H and ^{13}C NMR parameters were used as evidence that the two sesquiterpenes are identical. Since the absolute configuration of (-)-β-sesquiphellandrene from *Zingiber officinale* was previously established as 1*R*,7*S* [5], the absolute configuration of the enantiomeric (+)-β-sesquiphellandrene (**2**) must be 1*S*,7*R*.

Compound **3**, $C_{15}H_{24}$, exhibited ^1H NMR signals typical for the bergamotene skeleton [7,8]. ^1H and ^{13}C NMR as well as optical rotation data were essentially identical with (-)-α-*trans*-bergamotene [7].

(+)-β-Turmerone (**1**), $C_{15}H_{22}O$, showed IR bands at 1686 and 878 cm^{-1} suggesting the presence of a conjugated ketone and a vinylidene moiety, respectively. Detailed assignments of the ^{13}C and ^{1}H NMR signals in **1** were achieved by COSY and ^{13}C-^{1}H NMR correlation experiments. The ^{1}H NMR spectrum indicated that **1** must represent a bisabolane-type sesquiterpene and its ^{1}H and ^{13}C NMR spectral data (Tables 1 and 2) were essentially identical with values previously reported for the sesquiterpene (-)-β-turmerone [9] which before its structural revision [9] was reported under the name (-)-curlone [10]. (-)-β-Turmerone had been isolated from the rhizomes of the Japanese drug plant *Curcuma longa* [9,10]. Since compound **1** exhibited NMR data essentially identical with those reported for (-)-β-turmerone [9] and (-)-curlone [10] but gave a positive optical rotation ($[\alpha]_D$ = +2.0°, MeOH), the two compounds must be enantiomeric .

Since the absolute configuration of (-)-β-turmerone had been determined as 1*R*, 7*S* [9], the absolute configuration of (+)-β-turmerone (**1**) has to be 1*S*, 7*R* as in the cooccuring (+)-β-sesquiphellandrene (**2**). To our best knowledge, compound **1** represents a new natural product.

Compound **4**, $C_{15}H_{24}O_2$, exhibited IR bands at 810 and 866 cm^{-1}, indicating the presence of an isopropylidene and endoperoxide, respectively. The ^{1}H NMR spectrum exhibited signals at δ 4.63 (ddd, *J* = 6.1, 3.7, 1.7 Hz) and 4.33 (ddd, *J* = 6.2, 1.8, 1.8 Hz) which were assigned to protons of endoperoxide-bearing carbons. This was corroborated by the ^{13}C NMR spectral data for the oxygen-bearing carbons C-2 and C-5 which were in good agreement with data reported for ascaridol [11]. Signals for a secondary methyl group at δ 0.81 (d, *J* = 6.5 Hz) and three olefinic methyls at δ 1.60, 1.68 and 1.94 (d, *J* = 1.7 Hz) were apparent from the ^{1}H NMR spectrum. The band at δ 1.94 was assigned to the C-4 methyl group (H-15), its downfield chemical shift being caused by the endoperoxide moiety at C-5. Also, the signal for the olefinic C-3 proton at δ 6.26 (dq, *J* = 6.2, 1.8, 1.8 Hz) is strongly deshielded by the C-2 endoperoxide moiety [12]. The stereochemistry of the endoperoxide group in **4** was deduced from chemical shift comparisons of the C-7 methyl protons (H-14) with equivalent signals of the synthetic endoperoxide isomers **11** and **12** (Table 3), which will be discussed below. The chemical shift of the methyl absorption (H-14) was near δ 0.8 in **4** and **12**. In **11** a downfield shift of the methyl signal to *ca* δ 1.0 indicated that the methyl group at C-7 is oriented towards the face of the deshielding endoperoxide function. Therefore, in **4** and **12** the C-7 methyl group must be oriented away from the endoperoxide moiety, which requires a 2*S*, 5*R*-configuration in both endoperoxides **2** and **12**.

Table 1. ^{1}H NMR spectral data of compounds **1, 2, 4** and **7** to **10** (200 or 400 MHz,* $CDCl_3$, $CDCl_3$ as internal standard).

H	1*	2*	4*	7	8	9	10
1	2.25 m	2.24 m	2.09	----	----	----	----
2	6.12 dd	6.10 dd	4.63 ddd	7.39 d	7.24 d	6.84 dt	6.84 dt
3	5.67 d	7.70 d	6.26 dq	7.80 dd	7.32 d	6.03 dd	6.03 dd
4	----	----	----	----	----	----	----
5	2.43 ddd	2.45 ddd	4.33 ddd	7.80 dd	7.32 d	----	----
5'	2.29 m	2.29	----	----	----	----	----
6	1.73 dddd	1.70	2.34 ddd	7.39 d	7.24 d	----	----
6'	1.39 dddd	1.41	1.11 ddd	----	----	----	----
7	2.17 m	1.57	1.01	3.43 m	3.35 m	----	----
7'	----	----	----	----	----	----	----
8	2.48	1.38	1.39 dddd	2.78 dd	2.68 dd	----	----
8'	2.20	1.20	1.11	2.67 dd	2.68 dd	----	----
9	----	2.02	2.01	----	----	----	----
9'	----	1.97	1.87	----	----	----	----
10	6.07 m	5.10 m	5.10 m	6.01 m	6.02 m	6.07 m	5.10 m
12	1.89 d	1.61	1.60	1.86 s	1.86 s	1.90 d	1.61 s
13	2.14 d	1.71	1.68	2.10 d	2.10 s	2.16 d	1.70 s
14	0.88 d	0.86 d	0.81 d	1.29 d	1.23 d	0.93 d	0.90 d
15	4.77 s	4.76 s	1.94 d	9.96 s	4.97 s	----	----
15'	4.85 s	4.74 s	----	----	----	----	----
OOH	----	----	----	----	7.98 s	----	----

J (Hz): **1**: 2 = 10.0, 2.0, 3 = 10.0, 5 = 12.0, 3.7, 6 = 13.1, 8.3, 4.2, 3.9, 6' = 13.1, 12.7, 10.0, 3.8, 12 = 1.0, 13 = 1.0, 14 = 6.3; **2**: 2 = 10.0, 2.4, 3 = 9.9, 5 = 14.8, 3.9, 3.9, 14 = 6.7; **4**: 2 = 6.7, 3.7, 1.7, 3 = 6.2, 1.8, 1.8, 5 = 6.2, 1.8, 1.8, 6' = 13.1, 8.8, 4.3, 8 = 13.1, 8.4, 6.3, 3.6, 10 = 7.0, 7.0, 1.2, 1.2, 14 = 6.5, 15 = 1.7; **7**: 2,6 = 8.1, 3,5 = 8.2, 1.6, 7 = 7.1, 8 = 16.3, 7.1, 8' = 16.2, 7.6, 13 = 0.9, 14 = 7.2; **8**: 2,6 = 8.6, 3,5 = 8.1, 7 = 7.1, 8,8' = 15.9, 7.3, 14 = 6.8. **9**: 2 = 10.3, 1.9, 3 = 10.7, 3.2, 12 = 1.0, 13 = 1.0, 14 = 6.6; **10**: 2 = 10.2, 1.9, 3 = 10.2, 2.8, 14 = 6.8.

When exposed to air and light, (+)-β-turmerone (**1**) and (+)-β-sesquiphellandrene (**2**) were oxidized to yield compound **9** from **1**, and **6** plus **10** from **2**. Based on our observation, that photochemical activations of diterpenes contributes to the allelopathic action of *Chrysoma* [2,4], oxidation reactions of **1** and **2** were also studied. The presence of photosensitizers in *Chrysoma* could possibly cause singlet oxygen-type reactions of **1** and **2** under formation of hydroperoxide derivatives and endoperoxides [13]. Subsequent hydroperoxide rearrangements [14] could result in the formation of formaldehyde plus conjugated ketones such as compounds **9** and **10**, respectively. Due to their newly introduced alkylating property, **9** and **10** could be phytotoxic and therefore contribute to the allelopathic activity of Chrysoma. The two oxidative cleavage products **9** and **10** could also be formed via a free radical route [15]. This was supported by the fact that

Table 2. ^{13}C NMR spectral data of compounds **1**, **2**, **4**, **8**, **9**, **14** and **18** (100 MHz or 50 MHz*, $CDCl_3$, $CDCl_3$ as internal standard).

C†	1	2	4	8*	9*	14*	18*
1	40.3 d	40.6 d	40.1 d	133.5 s	40.6 d	40.4 d	40.1 d
2	129.9 d	129.5 d	73.9 d[a]	127.1 d	154.2 d	67.3 d	73.6 d[a]
3	133.5 d	135.2 d	122.9 d	129.2 d	130.0 d	145.1 d	128.2 d
4	143.0 s	143.7 s	142.0 s	147.3 s	199.6 s[a]	143.5 s	140.9 s
5	29.9 t	30.4 t	75.7 d[b]	129.2 d	37.3 t	73.4 d	72.6 d[b]
6	24.7 t	24.5 t	24.8 t	127.1 d	24.2 t	28.2 t	28.4 t
7	33.1 d	36.6 d	36.7 d	35.4 d	32.7 d	32.2 d	33.0 d
8	48.4 t	34.3 t	34.0 t	52.4 t	48.2 t	49.6 t	49.2 t
9	200.3 s	26.1 t	28.3 t	199.5 s	199.7 s[b]	199.2 s	199.8 s
10	123.8 d	124.8 d	124.3 d	124.0 d	123.8 d	123.7 d	123.9 d
11	154.6 s	131.2 s	131.6 s	155.5 s	156.2 s	156.8 s	156.3 s
12	27.4 q	17.6 q	17.7 q	27.6 q	20.8 q	20.9 q	20.8 q
13	20.4 q	25.7 q	25.7 q	21.9 q	27.7 q	27.7 q	27.7 q
14	16.3 q	15.8 q	16.0 q	20.7 q	16.5 q	17.8 q	17.6 q
15	110.1 t	109.9 t	18.5 q	79.1 t	----	187.2 d	75.8 t

† Peak multiplicities were determined by DEPT experiments.
[a,b]Signals may be interchangeable within a column.

(+)-β-turmerone (**1**) did not decompose in the presence of a free radical quencher, 2,6-(1,1-dimethylethyl)-4-methylphenol (BHT).

The ^1H NMR spectrum of **9** indicated no significant shift in the methyl absorption (H-14), when compared to compound **1**. However, the olefinic protons H-2 and H-3 had shifted downfield to δ 6.84 (dt, J = 10.3, 1.9 Hz) and 6.03 (dd, J = 10.7, 3.2 Hz), respectively, strongly suggesting the presence of a carbonyl group at C-4 in **9**. This was confirmed by the ^{13}C NMR spectrum which showed the presence of 14 carbon signals including an additional carbonyl absorption near δ 200 besides that of C-9. Similar changes were also observed in the ^1H NMR spectrum of compound **10**.

In order to establish the stereochemistry at C-2 and C-5 of the new endoperoxide (**4**), isomeric endoperoxide model compounds were required for ^1H NMR spectral differentiation between stereostructures **4** and **5**. Using methylene blue as a photosensitizer, singlet oxygen reaction [16] of (+)-β-turmerone (**1**) yielded a mixture of compounds **7** - **9** and **11** - **18**. The ^1H NMR spectra of compounds **11** to **18** (Table 3) indicated the presence of an endoperoxide moiety bridging C-2 and C-5 of the cyclohexyl ring. In the ^1H NMR spectra of **11** and **12** the exocyclic

Table 3. ^{1}H NMR spectral data of compounds **11** to **18** (200 MHz, $CDCl_3$, $CDCl_3$ as internal standard).

H	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
2	4.54 d	4.50 m	4.88 d	4.71 ddd	4.64 dd	4.69 dd	----	4.77 dd
3	6.33 dt	6.17 m	7.53 dd	7.43 dd	6.56 dd	6.40 dd	6.7 brd	6.52 brd
4	----	----	----	----	----	----	----	----
5	4.40 m	4.44 m	5.22 m	5.24 dd	4.64 dd	4.58 m	----	4.58 m
10	6.11m	6.03 m	6.11brs	6.06 m	6.11 m	6.04 m	6.1m	6.04 m
12	1.86 s	1.89 s	1.90 s	1.91 d	1.89 s	1.90 s	----	1.90 s
13	2.13 s	2.15 d	2.15 s	2.17 d	2.14 s	2.15 s	----	2.15 s
14	1.02 d	0.84 d	1.08 d	0.85 d	1.04 d	0.86 d	1.05 d	0.86 d
15	1.94 d	1.95 d	9.64 s	9.64 s	4.33 brs	4.33 brs	----	4.65 s
15'	----	----	----	----	4.33 brs	4.33 brs	----	4.63 s
OOH	----	----	----	----	----	----	8.4 brs	8.64 brs

J (Hz): **11**: 2 = 6.4, 3 = 6.5, 1.8, 14 = 6.5, 15 = 1.5; **12**: 13 = 0.9, 14 = 6.7, 15 = 1.7; **13**: 2 = 6.2, 3 = 6.4, 1.8, 14 = 1.1; **14**: 2 = 6.0, 3.7, 1.7, 3 = 6.1, 1.8, 5 = 4.4, 1.7, 12 = 0.8, 13 = 0.8, 14 = 6.7; **15**: 2 = 6.0, 0.9, 3 = 6.8, 1.3, 5 = 6.0, 0.9, 14 = 6.3; **16**: 2 = 6.1, 1.7, 3 = 4.0, 1.6, 14 = 6.7; **17**: 3 = 6.0, 14 = 6.8; **18**: 2 = 3.9, 1.7, 3 = 6.0, 14 = 6.7; **7**: 2,6 = 8.1, 3,5 = 8.2, 1.6, 7 = 7.1, 8 = 16.3, 7.1, 8' = 16.2, 7.6, 13 = 0.9, 14 = 7.2; **8**: 2,6 = 8.6, 3,5 = 8.1, 7 = 7.1, 8,8' = 15.9, 7.3, 14 = 6.8.

methylene and the two olefinic protons H-2 and H-3, characteristic for **1**, were absent. Instead, vinyl methyls at δ 1.94 (d, J = 1.5 Hz) and 1.95 (d, J = 1.7 Hz) and the respective olefinic proton signals (H-3) appeared at δ 6.33 and 6.17. The relative stereochemistry of the endoperoxide was based on the chemical shift of the C-7-methyl (H-14). In **11**, H-14 absorbed at δ 1.02, and in comparison to the value of 0.84 in **12**, the downfield chemical shift of the methyl protons (H-14) in **11** must be due to the deshielding effect of the endoperoxide moiety. This indicated that in **11** the endoperoxide oxygens are oriented towards the C-7-methyl, but reside on the opposite side of the rigid bicyclic ring in **12**.

The ^{1}H NMR spectra of **13** and **14** suggested the presence of a conjugated aldehyde indicated by a singlet at δ 9.64 and an olefinic signal appearing as a doublet of a doublet at δ 7.53 in **13** and 7.43 in **14**. The ^{13}C NMR spectrum of **14** confirmed the presence of a conjugated aldehyde moiety by the appearance of a carbonyl signal at δ 187.0. The ^{1}H NMR spectrum of compounds **15** and **16** showed a broad two-proton singlet at δ 4.33, indicating the presence of a primary alcohol at C-15. This was confirmed by the IR spectra which showed hydroxyl bands at 3445 and 3426 cm^{-1}, respectively. In compounds **17** and **18** the presence of a hydroperoxide function at C-15 was evident from the characteristic broad one-proton singlets at δ 8.4 and 8.64, respectively. In **18**, the two methylene protons at C-15 bearing the hydroperoxide group appeared at δ 4.65 and 4.63. The stereochemistry of the endoperoxides functions in **13-18** was determined using the same chemical shift arguments that were applied to the stereochemical assignments of endoperoxides **11** and **12**.

The ^{1}H NMR spectra of compounds **7** and **8** indicated aromatic protons. In compound **7**, the presence of an aldehyde (H-15, δ 9.96) was evident while in **8** a hydroperoxide was suggested by a one-proton singlet at δ 7.98. In **7** protons at C-2 and C-6 absorbed at δ 7.39 and in **8** at 7.24 while protons 3 and 5 in **7** and **8** absorbed at 7.80 and 7.32, respectively. When compared with **1**, the methyl doublet (H-14) was shifted downfield to δ 1.29 in **7** and 1.23 in **8** due to the attachments to benzylic positions. In **8**, a methylene carbon signal at δ 79.1 supported the presence of a benzylic hydroperoxide. The mass spectral molecular ion (m/z = 248) was also in agreement with the proposed structure.

Bioassay Data

At the concentrations tested, three *C. pauciflosculosa* sesquiterpenes (**1-3**) had only minor effects on the germination and radicle growth of test species. *Schizachyrium* radicle growth was significantly stimulated by 10^{-4} M solutions of (+)-β-turmerone and (-)-α-*trans*-bergamotene but *Leptochloa* was not affected by all three sesquiterpenes (**1-3**). *Rudbeckia* radicle growth was slightly reduced by 10^{-4} M solutions of (+)-β-turmerone and (-)-α-*trans*-bergamotene. Lettuce germination was inhibited by saturated aqueous as well as 10^{-4} and 10^{-5} M solutions of (+)-β-turmerone, and was stimulated significantly by a 10^{-4} M solution of (-)-α-*trans*-bergamotene.

Bioassays of aqueous solutions of compound **9** as well as a mixture of oxidative decomposition products of (+)-β-turmerone (**1**), which had been obtained by photochemical air oxidation, showed no significant effects on the germination or radicle growth of test species. The above findings suggest that it is not likely that the sesquiterpenes **1-3** as well as the decomposition mixture of (+)-β-turmerone or its major decomposition product **9** are significantly involved in the allelophatic action of *C. pauciflosculosa*. Synergistic effects with *Chrysoma* diterpenes were also excluded [2, 4].

EXPERIMENTAL

Plant material. Aerial parts of *Chrysoma pauciflosculosa* (Michx.) Greene were collected in June 1987, 2 km West of the entrance of Hwy 292 into Perdido Key, Florida by Dr. G. Bruce Williamson; voucher deposited at the Louisiana State University Herbarium, Voucher No. 70385.

Extraction and isolation. Fresh leaves (1.5 kg) were separated from the stems and soaked twice with 4.5 l of H_2O for 24 hr at 25°. The combined H_2O extracts were re-extracted (X5) with 0.5 l each of CH_2Cl_2 per 1.0 l of H_2O and the combined CH_2Cl_2 extracts were evapd *in vacuo* to yield 7.5 g of crude extract termed H_2O-CH_2Cl_2 extract. The extrd leaves were air-dried for 12 hr and soaked with hexane (3.5 l; X3), twice with CH_2Cl_2 (4.0 l each) and once with MeOH (4.0 l), yielding 37 g, 102 g, and 27 g of crude extracts, respectively. Part of the hexane extract (6 g) was treated with cold Me_2CO and the fatty acids ppt. removed by suction filtration. The Me_2CO solubles (4.0 g) were subjected to CC over silica gel (60-200 mesh) eluting with hexane and hexane:CH_2Cl_2 mixtures of gradually increasing polarity which provided 500 mg of (+)-β-turmerone (**1**).

Part of the CH_2Cl_2 extract (20.5 g) was treated with charcoal to remove chlorophyll, yielding 19.8 g of chlorophyll-free extract which was chromatographed on silica gel (SILICAR TLC-7GF) using VLC [17], eluting with hexane : CH_2Cl_2 mixts of gradually increasing polarity yielding 260 fractions of 22 ml each. Frs 8 and 9 were combined and chromatographed by prep. TLC on silica gel with hexane yielding compounds **2** (70 mg), **3** (41 mg) and traces of **6** (by ^1H NMR only). Fr. 2 (1.3 g) from the VLC run was chromatographed by CC on silica gel, with hexane:EtOAc (20:1), giving 104 frs of 22 ml each. Frs 25 - 29 were combined and chromatographed on prep. TLC with hexane: CH_2Cl_2 (2:1, X3) giving 5 frs., fr. 2 of which was re-chromatographed by prep. TLC with hexane: CH_2Cl_2 (2:1, X3) yielding compound **4** (1.7 mg).

Oxidative degradation of (+)-β-turmerone (**1**) and (+)-β-sesquiphellandrene (**2**). (+)-β-Turmerone (90 mg) was left at room temp. exposed to air and artificial light for 45 days. Column chromatography and prep. TLC separation afforded compounds **9** (7 mg) and **7** (1 mg). A fraction from the VLC run of the CH_2Cl_2 extract, which mainly contained **2**, decomposed under conditions described above to yield, after prep. TLC, 2 mg of **10.**

Singlet oxygen reaction of (+)-β-turmerone (**1**). (+)-β-Turmerone (603 mg) and methylene blue (11 mg) were dissolved in 50 ml of CH_2Cl_2. A constant stream of oxygen was bubbled through the solution for 24 hr while exposed to light from a 150 W, 120 V reflector spot lamp, the solution being maintained at room temp. More CH_2Cl_2 had to be added due to solvent evaporation. The reaction was monitored by TLC and after most of the starting material had disappeared the reaction was stopped. The solution was then passed through silica gel and washed with EtOAc *in vacuo* to remove the methylene blue. The filtrate was chromatographed by CC on silica gel using CH_2Cl_2:EtOAc mixts of gradually increasing polarity collecting 80 fractions (22 ml each). Frs 17 - 25, after prep. TLC, yielded pure **11** (1.4 mg), **12** (1.1 mg), **13** (0.3 mg) and **14** (7.9 mg). Prep. TLC of frs. 31 - 40 gave 2.7 mg of **8.** Frs 51 - 57 provided, after prep. TLC, compounds **18** (4.2 mg) and a mixture containing **17** and **18.** Fractions 70 - 79 afforded, after prep. TLC , compounds **15** (0.7 mg) and **16** (1.8 mg) and less than 0.5 mg of compounds **7** and **9.**

(+)-β-Turmerone (**1**). $C_{15}H_{22}O$, oil; $[\alpha]_D^{25}$ = + 2.0° (MeOH; c 0.014); IR ν_{max}^{KBr} cm^{-1}: 1686 (conj. ketone), 787 (vinylidene); UV ν_{max}^{MeOH} cm^{-1}: 236 (conj. ketone and conj. diene); EIMS *m/z* (rel. intl): 218 $[M]^+$ (2), 120 (100), 83 (34), 55 (15).

(+)-β-Sesquiphellandrene (**2**). $C_{15}H_{24}$, oil; $[\alpha]_D^{25}$ = + 5.7° ($CHCl_3$; c 0.008).

In all compounds listed below, names recommended by the IUPAC convention were used. This numbering system is different from the conventional numbers of terpenes , which are used on the structural drawings of this paper.

(6R)-2-Methyl-6-[(1S)-(2S,5R)-endoperoxy-4-methyl-3-cyclohexen-1-yl]-2-heptene (**4**). $C_{15}H_{24}O_2$, oil; IR ν_{max}^{KBr} cm^{-1}: 810 (isopropylidene), 866 (endoperoxide); EIMS *m/z* (rel. int.): 236 $[M]^+$ (6), 218 (4), 204 (1), 200 (1), 152 (6), 83 (35), 69 (86), 55 (69), 41 (100).

(6R)-2-Methyl-6-[4-formylphenyl]-2-hepten-4-one (**7**). $C_{15}H_{18}O_2$, oil; IR ν_{max}^{NaCl} cm^{-1}: 1686 (conj. ketone); EIMS *m/z* (rel. int.): 230 $[M]^+$ (14), 215 $[M-CH_3]^+$ (5), 91 $[C_7H_7]^+$ (7), 83 (100), 77 (8), 55 (19).

(6R)-2-Methyl-6-[4-methylenehydroperoxyphenyl]-2-hepten-4-one (**8**). $C_{15}H_{20}O_3$, oil; IR ν_{max}^{NaCl} cm^{-1}: 3378 (OOH), 1684 (conj. ketone); EIMS *m/z* (rel. int.): 248 $[M]^+$ (4), 233 $[M-CH_3]^+$ (3), 230 (12), 151 (9), 105 (10), 91 $[C_7H_7]^+$ (11), 83 (100), 77 (14), 55 (18).

(6R)-2-Methyl-6-[(1S)-2-cyclohexen-4-one]-2-hepten-4-one (**9**). $C_{14}H_{20}O_2$, oil; $[\alpha]_D^{25}$ = -17.2° ($CHCl_3$; c 0.003); IR ν_{max}^{NaCl} cm^{-1}: 1684 (conj. ketone); EIMS *m/z* (rel. int.): 220 $[M]^+$ (3), 205 $[M-CH_3]^+$ (1), 123 (3), 95 (7), 83 (44), 55 (100).

(6R)-2-Methyl-6-[(1S)-2-cyclohexen-4-one]-2-heptene (**10**). $C_{14}H_{22}O$, oil; $[\alpha]_D^{25}$ = -19.5° ($CHCl_3$; c 0.002); IR ν_{max}^{NaCl} cm^{-1}: 1686 (conj. ketone); EIMS *m/z* (rel. int.): 206 $[M]^+$ (4), 191 $[M-CH_3]^+$ (0.2), 123 (9), 95 (16), 77 (21), 69 (37), 55 (28), 41 (100).

(6R)-2-Methyl-6-[(1S)-(2R,5S)-endoperoxy-4-methyl-3-cyclohexen-1-yl]-2-hepten-4-one (**11**). $C_{15}H_{22}O_3$, oil; IR ν_{max}^{NaCl} cm^{-1}: 1686 (conj. ketone); EIMS *m/z* (rel. int.): 250 $[M]^+$ (0.1), 218 $[M-O_2]^+$ (5.9), 203 $[218-CH_3]^+$ (1.6), 120 (19), 105 (20.6), 91 $[C_7H_7]^+$ (14), 83 (100), 77 (13), 55 (22), 39 (27).

(6R)-2-Methyl-6-[(1S)-(2S,5R)-endoperoxy-4-methyl-3-cyclohexen-1-yl]-2-hepten-4-one (**12**). $C_{15}H_{22}O_3$, oil; IR ν_{max}^{NaCl} cm^{-1}: 1686 (conj. ketone); EIMS *m/z* (rel. int.): 250 $[M]^+$ (0.1), 218 $[M-O_2]^+$ (7), 203 $[218-CH_3]^+$ (0.8), 120 (15), 111 (10), 105 (15), 83 (100), 77 (11), 55 (28), 39 (22).

(6R)-2-Methyl-6-[(1S)-(2R,5S)-endoperoxy-4-formyl-3-cyclohexen-1-yll-2-hepten-4-one (**13**). $C_{15}H_{20}O_4$, oil; IR ν_{max}^{NaCl} cm^{-1}: 1690 (conj. ketone), 1728 (conj. aldehyde); EIMS *m/z* (rel. int.): 264 $[M]^+$ (0.4), 232 $[M-O_2]^+$ (2), 217 $[232-CH_3]^+$ (2), 162 [217-55]$^+$ (0.7), 134 [217-83]$^+$ (17), 83 (100), 77 (9), 55 (52).

(6R)-2-Methyl-6-[(1S)-(2S,5R)-endoperoxy-4-formyl-3-cyclohexen-1-yl] 2-hepten-4-one (**14**). $C_{15}H_{20}O_4$, oil; IR ν_{max}^{NaCl} cm^{-1}: 1684 (conj. ketone); EIMS *m/z* (rel. int.): 264 $[M]^+$ (0.1), 232 $[M-O_2]^+$ (2), 217 $[232-CH_3]^+$ (0.7), 134 $[217-83]^+$ (49), 105 (10), 91 $[C_7H_7]^+$ (6), 83 (100), 77 (7), 55 (35).

(6R)-2-Methyl-6-[(1S)-(2R,5S)-endoperoxy-4-methylene-oxy-3-cyclohexen-1-yl]-2-hepten-4-one (**15**). $C_{15}H_{22}O_4$,oil; IR ν_{max}^{NaCl} cm^{-1}: 3445 (OH) 1684 (conj. ketone); EIMS *m/z* (rel. int.): 266 $[M]^+$ (0.6), 251 $[M-CH_3]^+$ (0.1), 238 (4), 177 (36), 159 (25), 149 (100), 93 (16), 81 (29), 51 (9), 41 (58).

(6R)-2-Methyl-6-[(1S)-(2S,5R)-endoperoxy-4-methyleneoxy-3-cyclohexen-1-yl]-2-hepten-4-one (**16**). $C_{15}H_{22}O_4$, oil; IR ν_{max}^{NaCl} cm^{-1}: 3426 (OH), 1684 (conj. ketone); EIMS *m/z* (rel. int.): 266 $[M]^+$ (0.1), 216 $[M-O_2-H_2O]^+$ (4), 201 $[216-CH_3]^+$ (1), 105 (10.9), 83 (100), 77 (7), 55 (36), 39 (15).

(6R)-2-Methyl-6-[(1S)-(2S,5R)-endoperoxy-4-methyleneperoxy-3-cyclohexen-1-yl]-2-hepten-4-one (**18**). $C_{15}H_{22}O_5$, oil; IR ν_{max}^{NaCl} cm^{-1}: 1687 (conj. ketone); EIMS *m/z* (rel. int.): 250 $[M-O_2]^+$ (0.02), 235 $[250-CH_3]^+$ (0.03), 216 $[250-H_2O_2]^+$ (2), 134 (12), 105 (20), 91 $[C_7H_7]^+$ (5), 77 (6), 55 (28), 39 (14).

Bioassays. Bioassays were carried out in large glass jars (480 ml, 8 cm diameter) with foil-lined lids to provide a firm seal. Each dish was lined with one layer of Whatman No.1 filter paper and contained twenty-five seeds of one of four species [Lettuce (*Lactuca sativa* L.); Blackeyed-susan (*Rudbeckia hirta* L.); little bluestem (*Schizachyrium scoparium* (Michx.) Nash) and green sprangletop (*Leptochloa dubia* (H.B.K.) Nees]. Each treatment was replicated three times, and in the case of little bluestem, six times.

Compounds were added to the center of the filter paper in 50µl Me_2CO and the solvent allowed to evaporate (>3 min). Five µl of DMSO was added to the center of the filter paper as a solubilization agent, followed by 5ml H_2O. Test solutions were 10^{-4}, 10^{-5} and 10^{-6} M of (+)-β-turmerone (**1**), (+)-β-sesquiphellandrene (**2**), and (-)-α-*trans*-bergamotene (**3**), satd. aq. soln of each (no DMSO), and H_2O and H_2O+DMSO controls. Satd sols were prepared by sonication followed by filtration. The assay was performed in the dark at room temp. for 3 days (lettuce) or 5 days (all others). Dishes were frozen to terminate growth prior to measurement of radicle length and germination. Seeds were considered germinated if the radicle protruded at least 1mm through

the seed coat. Data were analyzed by comparing the treatment mean to the corresponding control using Student's t-test.

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