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## Thermal Acid-Catalyzed Rearrangement of *trans*-Methyl Chrysanthemate to Lavandulyl Derivatives and Their Effect on Lettuce Seedling Growth

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Acid-catalyzed rearrangement of *trans*-methyl chrysanthemate in aqueous sulfuric acid gave only lavandulyl methyl esters at room temperature and a mixture of unsaturated  $\gamma$ - and  $\delta$ -lactones at 130 °C. Acid-catalyzed methanolysis afforded the methoxylavandulyl methyl ester and its isomer methyl 2,2-dimethyl-3-(2-methoxy-2-methylpropyl)cyclopropanecarboxylate. The starting material was obtained from a mixture of *cis/trans*-chrysanthemate acid by lactonizing the *cis* isomer to *cis*-dihydrochrysanthemate- $\delta$ -lactone which was separated and then esterifying the *trans* chrysanthemate acid. It was found that the  $\delta$ -lactone, certain lavandulyl methyl esters, and certain unsaturated  $\gamma$ - and  $\delta$ -lactones displayed potent inhibitory effect on root elongation and lettuce seed germination at  $10^{-4}$  and  $10^{-5}$  M concentrations. The relation of structure and lettuce seedling growth inhibitory activity is discussed. Structural determination of the saturated  $\delta$ -lactone was carried out by single-crystal X-ray diffraction analysis.

The cyclopropane monoterpene *trans*-chrysanthemate acid [3] is found in three of the six natural insecticidal esters (Pyrethrin I, Cinerin I, Jasmolin I) of the pyrethrum flower *Chrysanthemum cinerariaefolium*. During our investigation of the acid-catalyzed reactions of *trans*-methyl chrysanthemate [5] (Goldschmidt et al., 1984b) obtained by known procedures from readily available *cis/trans*-ethyl chrysanthemate [1], it was found that three principal methyl lavandulyl esters were obtained when 5 was stirred with 50% aqueous sulfuric acid and pentane at room temperature. Spectral and microanalytical data confirmed that these esters were methyl *trans*-5-methyl-2-(2-propenyl)-3-hexenoate [7], methyl *trans*-5-methyl-2-(2-hydroxy-2-propyl)-3-hexenoate [8], and methyl *trans*-5-methyl-2-(2-propylidene)-3-hexenoate [10]. The methoxy lavandulyl ester methyl *trans*-5-methyl-2-(2-methoxy-2-

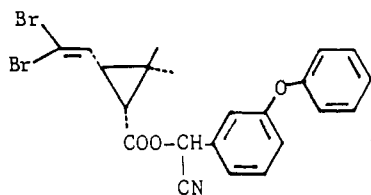
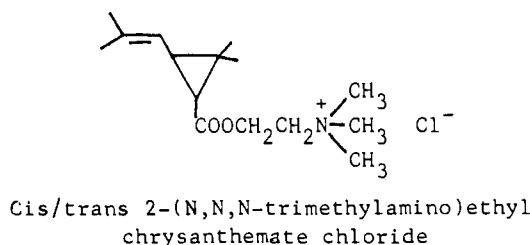
propyl)-3-hexenoate [9] was detected in low yield but was obtained in good yield from 5 and 50% methanolic sulfuric acid in pentane at room temperature. The isomer of 9, 2,2-dimethyl-3-(2-methoxy-2-methylpropyl)cyclopropanecarboxylate [6], was also isolated from the reaction. When *trans*-methyl chrysanthemate [5] was stirred with a mixture of 50% aqueous sulfuric acid in hexane at 130 °C for 44 h there was obtained the principal  $\gamma$ -lactone, dihydro-5-(2-propyl)-3-(2-propylidene)-2(3*H*)-furanone [12], and the  $\delta$ -lactone, 5,6-dihydro-6,6-dimethyl-3-(2-propyl)-2*H*-pyran-2-one [11] (Figure 1).

During the last decade certain chrysanthemate acid esters were found to possess plant growth regulatory activity. It was reported that *cis/trans*-2-(*N,N,N*-trimethylamino)-ethyl chrysanthemate chloride caused stunting in corn, milo, and cotton plants (Faucher, 1974). The synthetically insecticidally active pyrethroid decamethrin was found to inhibit the gibberellin-stimulated growth of rice (Herve and Motillon, 1981).

### MATERIALS AND METHODS

**Spectroscopy.** Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker WX 300 spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer

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157G spectrophotometer. Electron-impact (EI) and chemical-ionization (CI) mass spectra were recorded on a Finnigan 4021 gas chromatograph mass spectrometer with data system using methane as the reagent gas. The conditions used for the GC/MS were an XE-60 column, programmed 50–180 °C at 5 °C/min.

**Chromatographic Separations and Analyses.** Preparative gas-liquid chromatography (GLC) separations were carried out on a F & M Model 720 dual-column programmed-temperature gas chromatograph on a two-meter 10% OV 17 on Chromosorb W. The conditions were as follows: detector temperature, 300 °C; inlet temperature, 245 °C; rate, 4 °C/min, programmed from 50 to 210 °C. Elemental analyses were carried out at the Analytical Laboratories of the Hebrew University of Jerusalem.

**Experimental Procedures.** *trans*-Methyl chrysanthemate [5] was obtained from commercially available racemic *cis/trans*-ethyl chrysanthemate [1] by alkaline hydrolysis to *cis/trans*-chrysanthemic acid [2] followed by lactonizing the *cis*-chrysanthemic acid in the presence of anhydrous zinc chloride in ethylene dichloride according to the procedure described by Goldschmidt et al. The methyl ester of the *trans* isomer 5 was derived from 2 according to the general procedure of Clinton and Laszkowski (1948).

**Acid-Catalyzed Rearrangement of *trans*-Methyl Chrysanthemate [5].** (a) A mixture of 5 (3 mL) and 50% aqueous sulfuric acid (3 mL) in pentane (10 mL) was stirred for 53 h to afford a mixture of methyl esters that was separated on a preparative GLC column. The order of elution and composition of each component were as follows: 7, 27%; 5, 31%; 10, 10%; 8, 32%. Microanalyses together with the spectral data confirmed the assigned structures.

(b) A mixture of 5 (1 mL) and 50% methanolic sulfuric acid (1 mL) in pentane (4 mL) was stirred for 93 h at room temperature. Workup gave an oil of composition eluted in the following order from the column: 7, 16%; 5, 8%; 10, 33%; 8, 16%; 9, 19%; methyl *trans*-5-methyl-3-hexenoate, 3%.

(c) A mixture of 5 (6 mL) was refluxed with 5% methanolic sulfuric acid (20 mL) for 24 h to afford, after workup, an oil of composition eluted in the following order from the column: 7, 7%; 5, 37%; 6, 44%.

(d) Formation of lactones 11 and 12 from 5 was accomplished when a mixture of 5 (2 mL) was stirred with a mixture of 50% aqueous sulfuric acid (3 mL) in heptane (12 mL) at 130 °C for 48 h. Workup gave an oil of composition eluted in the following order from the column: 11, 14%; 12, 55%; 3,5-diisopropyl-2(5*H*)-furanone, 12%; di-

Table I. Structural and Growth Inhibition Data

compd	% inhibn	% germin	radicle length, <sup>a</sup> mm
control <sup>b</sup>		95	37
Pyrethrin extract	69	45	12
Allethrin	99	2	0.4
3	0	47	37
4	100	0	0
5	70	37	11
1	40	88	22
7	85	25	6
8	96	3	1.5
9	28		27
10	36	25	24
11	89	5	4
12	100	0	0

<sup>a</sup>LSD: 0.01, 4 mm; 0.05, 3 mm. <sup>b</sup>Control: acetone-water (1:14).

hydro-5-(2-ethyl-2-methyl)-3-(2-propylidene)-2(3*H*)-furanone, 10%; unassigned lactones, 9%.

Initial X-ray diffraction experiments with single crystals of 4 indicated that the cell constants were orthorhombic with  $a = 11.165$  (2) Å,  $b = 10.065$  (2) Å, and  $c = 8.709$  (1) Å with  $Z = 4$  for a calculated density of 1.14 g/cm<sup>3</sup>. Of the 1014 unique reflections measured with  $2\theta < 50^\circ$ , 854 (84%) were considered observed ( $I > 2\sigma(I)$ ). The lactone structure was solved with routine application of direct methods (Main et al., 1978) and Fourier techniques (Sheldrick, 1976). Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were located by using the results of the Multan direct analysis. After several cycles of refinements, the positions of the hydrogen atoms were found in the Fourier difference map and added with a constant isotropic temperature factor of 0.5 Å. The function  $\sum w(|F_o| - |F_c|)^2$  with  $w = 1/\sigma(|F_o|)^2$  was minimized to give a final weighted residual index of 0.065. Figure 2 is a computer drawing of one of the molecules of the  $\delta$ -lactone 4 in the unit cell.

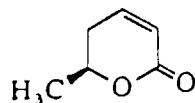
There are few reports relating to the conformation of simple  $\delta$ -lactones. (Cheung et al., 1965; Philip et al., 1981.) X-ray crystallographic structures are known for a variety of condensed systems containing a  $\delta$ -lactone ring (Mathieson, 1963; Johnson and Riggs, 1967; Beecham et al., 1979; Sinica, 1980). The X-ray analysis of the relatively simple  $\delta$ -lactone 4 shows a near planar conformation due to the cyclopropane ring except for the *gem*-dimethyl carbon that is flipped anti to the cyclopropane ring.

## EXPERIMENTAL SECTION

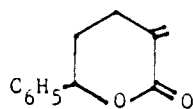
**Test Procedure.** The samples were dissolved in acetone to give a 10<sup>-2</sup> M concentration. A 10- $\mu$ L aliquot of each sample was added to 140  $\mu$ L of water in a 10-mL beaker to give the test concentration of  $6.7 \times 10^{-4}$  M. A filter paper disk was placed at the bottom of each beaker, and 10 lettuce seeds (*cv.* Grand Rapids) were placed on the paper. There were two replicate beakers per test. Germination and radicle length of the germinated seedlings were recorded after 72–90 h in a  $22 \pm 2$  °C room with low-intensity fluorescent light (50 ft-c Cool White (General Electric Co.) at seed level). Radicle length was measured by scale, visually, to the nearest millimeter. Percent inhibition of elongation was determined as follows:  $100 \times (\text{radicle length, control} - \text{radicle length, test}) / \text{radicle length, control}$ . Percent germination figures are the averages of the two beakers. The above test procedure was repeated at a test concentration of  $6.7 \times 10^{-5}$  M.

## RESULTS AND DISCUSSION

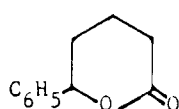
Inspection of Table I shows that the products derived from *cis/trans*-chrysanthemic acid [2] have a broad



Parasorbic acid

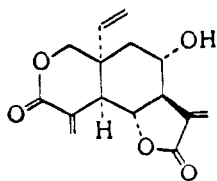


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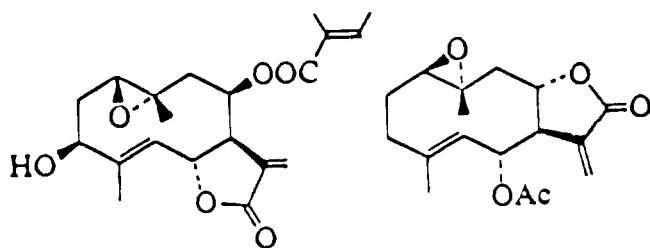
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spectrum on lettuce radicle growth and germination, ranging from no inhibitory activity as in *trans*-chrysanthemic acid [3] to potent inhibitory activity in *cis*-dihydrochrysanthemo- $\delta$ -lactone [4]. An a priori requirement for a lactone to have good plant growth inhibitory activity is that there should be present a source of unsaturation in the molecule. The natural  $\delta$ -lactone, parasorbic acid which is structurally similar to the  $\alpha,\beta$ -unsaturated  $\delta$ -lactone 11, was shown to be an effective inhibitor on tomato roots (Buston et al., 1949). Tanaka supported the contention that a double bond is necessary in  $\delta$ -lactones for good inhibitory activity (Tanaka et al., 1973). For example they showed that  $\alpha$ -methylene- $\delta$ -phenyl- $\delta$ -valerolactone [13] completely inhibited the growth of rice seedlings at  $10^{-4}$  M whereas the saturated  $\delta$ -phenyl- $\delta$ -valerolactone [14] was less than 10% active at the same concentration. Surprisingly there are very few known  $\delta$ -lactones that are plant growth inhibitors. Kupchan had reported that vernolepin, an  $\alpha$ -methylene  $\delta$ -lactone fused to a bicyclic ring system, was an effective inhibitor in wheat coleoptiles (Kupchan et al., 1968).



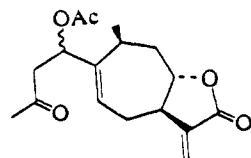
Vernolepin

A number of norditerpenoid dilactones known as podolactones contain an  $\alpha,\beta$ -unsaturated  $\delta$ -lactone moiety



Heliangine

Pyrethrosin



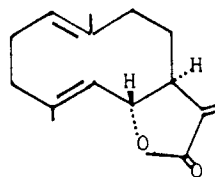
Xanthinin

Table II. Effect of Methyl Lavandulyl Esters and Lactones on Lettuce Seedling Growth

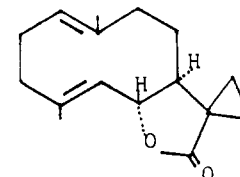
	% inhibn		% germin		radicle length, <sup>a</sup> mm	
	$6.7 \times 10^{-4}$ M	$6.7 \times 10^{-5}$ M	$6.7 \times 10^{-4}$ M	$6.7 \times 10^{-5}$ M	$6.7 \times 10^{-4}$ M	$6.7 \times 10^{-5}$ M
control <sup>b</sup>	0	0	72	72	21	21
( $\pm$ )-4	100	96	0	5	0	1
(-)-4	100	81	0	7	0	4
7	85	44	25	68	3	12
8	96	44	3	67	1	12

<sup>a</sup>LSD: 0.01, 4 mm; 0.05, 3 mm. <sup>b</sup>Control: acetone-water (1:14).

that, according to Galbraith, is most essential for effective plant growth inhibitors (Galbraith et al., 1972). From the hundreds of now known  $\alpha$ -methylene  $\gamma$ -lactones that form part of a condensed system of sesquiterpene lactones, some have been discovered to be plant growth inhibitors such as for example Heliangine, Pyrethrosin, and Xanthinin. These sesquiterpenes all contain an *exo*-methylene group conjugated to the carbonyl moiety of the lactone ring. Gross suggested that the  $\alpha$ -methylene moiety is responsible for plant growth inhibitory activity in lactone systems (Gross, 1975). Iino had synthesized a number of noncondensed  $\alpha$ -methylene- $\gamma$ -valerolactones that, as expected, were as active as Heliangine and Pyrethrosin, thus showing that an  $\alpha$ -methylene group was responsible for good inhibitory activity (Iino et al., 1972). Iino had found that the partially substituted  $\alpha$ -methylene group in  $\alpha$ -benzylidene- $\gamma$ -butyrolactone was only 14% active at a concentration of  $5 \times 10^{-4}$  M on rice seedlings whereas the dimethyl-substituted *exo*-methylene  $\gamma$ -lactone 12 was 100% effective on lettuce seedlings at essentially the same concentration (Table I). Recent studies have established that the plant growth activity associated with the  $\alpha$ -methylene  $\gamma$ -lactone moiety in terpenoid lactones such as germacranolide [17] is further enhanced when the methylene group is replaced by a cyclopropane ring [18] (Kalsi et al., 1983).

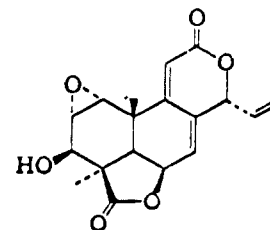


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Perhaps the most surprising result was the high inhibitory activity of the  $\delta$ -lactone 4 (Crammer et al., 1983), which was found to be as active as the naturally occurring norditerpenoid dilactone, Podolactone E (Galbraith et al.,



Podolactone E

1972). It was found that this highly unsaturated dilactone was 18% active in the expansion of hook segments from etiolated dwarf peas, at concentrations as low as  $10^{-7}$  M. This is comparable to the same order of activity of the stable  $\delta$ -lactone 4 on lettuce seedling roots (Figure 3). Saturated  $\gamma$ - and  $\delta$ -lactones have been reported to be in-

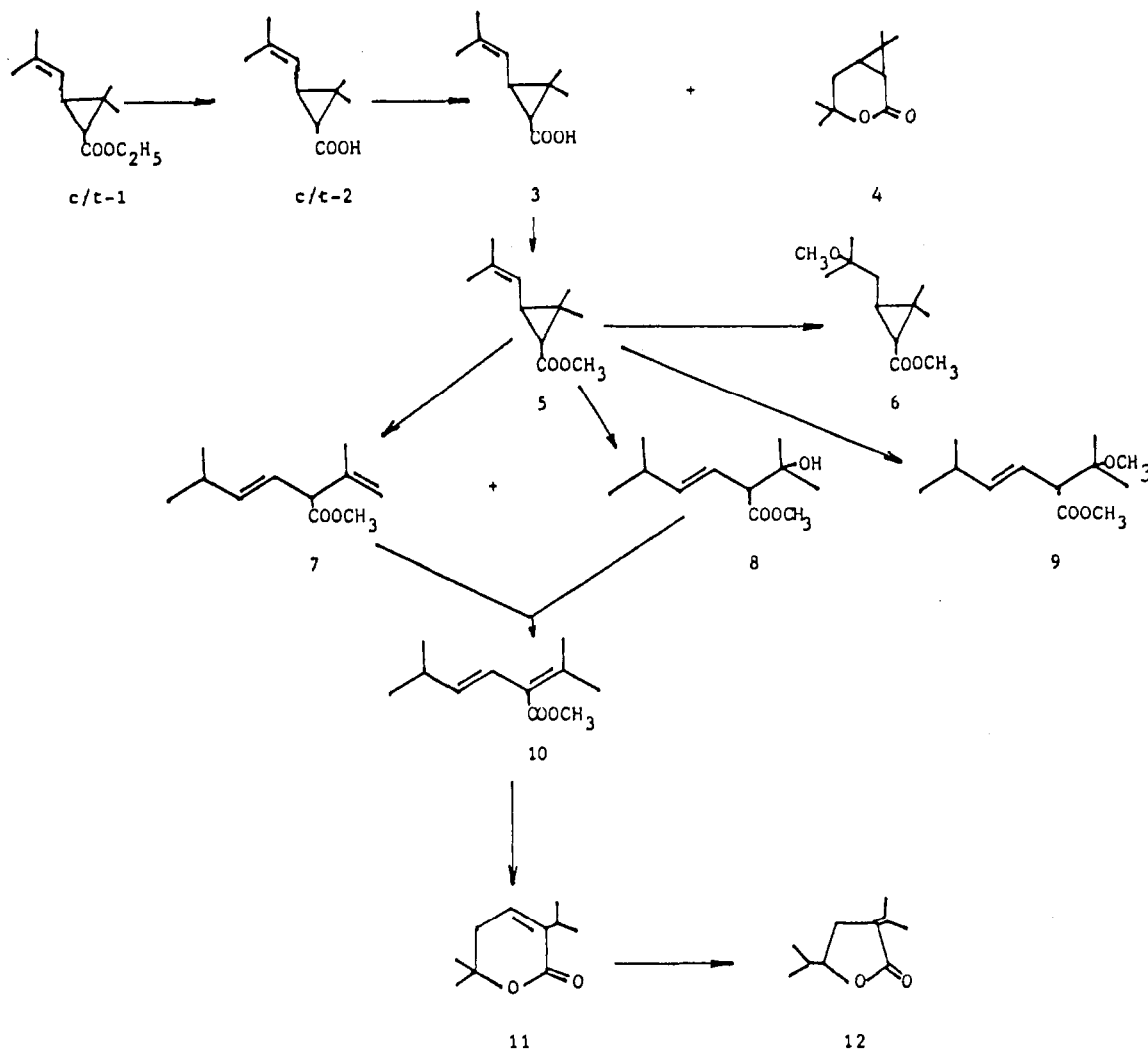
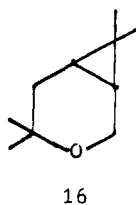


Figure 1. Schematic route of products obtained from the acid-catalyzed rearrangement of *trans*-methyl chrysanthemate [5].

effective as plant growth inhibitors (Iino et al., 1972; Tanaka et al., 1973; Galbraith et al., 1972). We found that a number of saturated lactones such as, for example,  $\alpha$ -butyrolactone and  $\beta$ -propiolactone were also inactive inhibitors to lettuce seedling growth. The racemic  $\delta$ -lactone derived from *dl*-*cis*-chrysanthemic acid was a more effective inhibitor than the optically active  $\delta$ -lactone [ $\alpha$ ]<sup>20</sup>  $-77.24^\circ$  (Table II), implying the possibility that the optically active (+)- $\delta$ -lactone may even be more potent than the racemic counterpart.

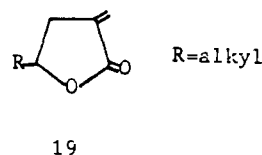
Thus it appears that the exchange of the double bond in the  $\delta$ -lactone 11 by a cyclopropane ring in 4 enhances the inhibitory activity in lettuce seedlings. This observation is analogous to the enhancement of activity caused by a similar exchange in germacranolides as reported by Kalsi. Furthermore, it was observed that the reduced lactone 4, 4,4,7,7-tetramethyl-3-oxabicyclo[4.1.0]heptane [16] (Crammer et al., 1984), still had significant activity of 43% at a concentration of  $10^{-4}$  M on lettuce seedlings.



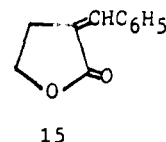
Notably, cyclic ethers have not been reported to be plant growth inhibitors. It is not surprising that the simple

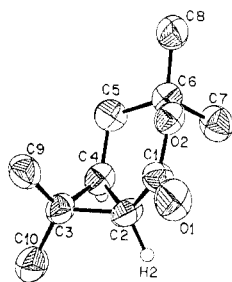
pyrethroid *trans*-methyl chrysanthemate [5] is also effective as an inhibitor to lettuce seedling growth (Table I) due to the presence of three active functional groups: a cyclopropane ring, a double bond, and an ester group in the same molecule. Herve and Motillon have previously shown an analogous inhibitory effect of the pyrethroid decamethrin to rice seedlings. Removing one of these functional groups in the molecule 5 reduced the activity quite markedly as can be seen in the dihydromethoxy-pyrethroid [6] where methanol has been added to the double bond.

It has been stated that an *exo*-methylene group conjugated to the  $\gamma$ -lactonic carbonyl is desirable for good plant growth inhibition. If the methylene group is alkylated such as in 12 the inhibitory activity increases compared to the unsubstituted methylene lactone 19 (Weinstein, 1983).

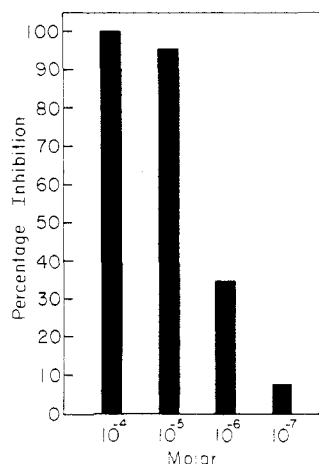


However, the phenyl-substituted methylene lactone 15 was





**Figure 2.** Computer-generated drawing of *cis*-dihydrochrysanthemo- $\delta$ -lactone. The hydrogens except the *cis* hydrogens of the cyclopropane ring are omitted for clarity.



**Figure 3.** Inhibitory activity of *cis*-dihydrochrysanthemo- $\delta$ -lactone [4] on lettuce seedlings at different molar concentrations.

shown to have no inhibitory activity in rice seedlings (Iino et al., 1972). It has been reported that certain methyl esters (Ando and Tsukamoto, 1974) including 1-acetoxy-2,4-dihydroxy-*n*-heptadeca-16-ene (Bittner et al., 1971) are plant growth inhibitors. The two lavandulyl methyl esters 7 and 8 were as effective as the two unsaturated  $\delta$ - and  $\gamma$ -lactones 11 and 12 (Table I). It seems essential, even in lavandulyl esters, that there should be present a methylene group as in 7 or alternatively the hydroxy lavandulyl ester 8, which has been shown to dehydrate to 7 (Goldschmidt et al., 1984) as a characteristic requirement for inhibitory activity in lettuce seedlings. Blocking the active site with a methoxy group as in 9 or extending conjugation as in the lavandulyl ester 10 reduces the inhibitory activity.

In conclusion it can be seen that substituting the double bond adjacent to the carbonyl moiety of the unsaturated  $\delta$ -lactone 11 by a cyclopropane ring as in the saturated  $\delta$ -lactone 4 enhances quite effectively the inhibitory activity of lettuce seedling growth. It was also found that the cyclopropane methyl ester 5 was as active as the lavandulyl methyl esters 7 and 8. In a previous study, Kalsi had shown that the plant growth activity of unsaturated lactones is enhanced when a cyclopropane ring replaces a methylene group. It would be of interest to see whether this enhancement in plant growth activity in different plants occurs in unsaturated esters and lactones where the double bond is interchanged by a cyclopropane ring.

#### ACKNOWLEDGMENT

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**Registry No.** 1, 97-41-6; 2, 10453-89-1; *trans*-3, 827-90-7; ( $\pm$ )-4, 18689-27-5; (-)-4, 14087-71-9; *trans*-5, 24141-52-4; 6, 97466-22-3; 7, 98875-56-0; 8, 98875-57-1; 9, 98875-58-2; 10, 61263-92-1; 11, 97411-31-9; 12, 62687-41-6; allethrin, 584-79-2.

**Supplementary Material Available:** Listings of positional parameters, anisotropic thermal parameters, bond lengths, bond angles, and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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