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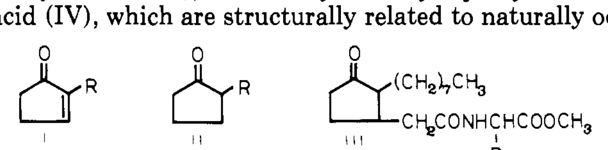
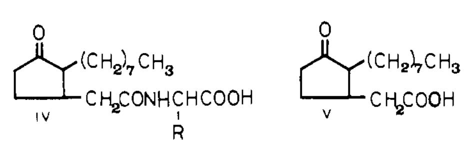
Effect of Substituted Cyclopentenones and Cyclopentanones on Lettuce Seed Germination and Radicle Growth

A series of 2-alkylcyclopent-2-ene-1-ones (I), 2-alkylcyclopentan-1-ones (II), and amides of 2-octyl-3-oxocyclopentyl-1-acetic acid (IV) were synthesized. The data suggest that 2-propylcyclopentan-1-one and *n*-[2′-octyl-3′-oxocyclopentyl-1′-acetyl)isoleucine are potent inhibitors of lettuce seedling growth as compared to other compounds described in Table I.

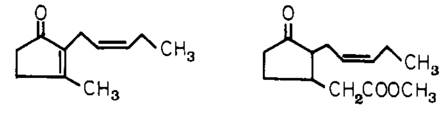
In a recent study (Ravid et al., 1975) we reported the effect of jasmonoids on the lettuce seedling growth.

In the following communication we wish to report the effect of alkylcyclopentenones (I), alkylcyclopentanones (II), as well as amides of methyl 2-octyl-3-oxocyclopentylacetate (III), and 2-acetyl-3-oxocyclopentyl-1-acetic acid (IV), which are structurally related to naturally oc-





curring jasmonoids such as jasmone and methyl jasmonate, on lettuce seedling growth.



EXPERIMENTAL SECTION

Synthesis. The structures of compounds studied in this work (Table I) are shown under the general formulae I to V. The general synthetic route for synthesizing these compounds was outlined by Katsin and Ikan (1977).

2-Propylcyclopent-2-ene-1-one (I, R = C_3H_7). IR (liquid) 1700, 1630, 1442, 1403, 1378, 1295, 1198, 1100, 1046, 1000, 785 cm^{-1}; NMR (CCl_4) 0.85 (3 H, t), 1.45 (2 H, m), 1.90–2.70 (6 H, m), 7.3 (1 H, m). Anal. Calcd for $C_8H_{12}O$: C, 77.42; H, 9.68. Found: C, 77.39; H, 9.73.

2-Octylcyclopent-2-ene-1-one (I, R = C_8H_{17}). IR (liquid) 1705, 1630, 1465, 1343, 1205, 998, 785 cm^{-1}; NMR ($CDCl_3$) 0.86 (3 H, t), 1.00–1.60 (12 H, m), 1.8–2.65 (6 H, m), 7.1 (1 H, m). Anal. Calcd for $C_{13}H_{22}O$: C, 80.41; H, 11.34. Found: C, 80.63; H, 11.45.

1-Propylcyclopentan-1-one (II, R = C_3H_7). IR (liquid) 1735, 1465, 1453, 1155 cm^{-1}. Anal. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.21. Found: C, 76.92; H, 11.73.

1-Octylcyclopentan-1-one (II, R = C_8H_{17}). IR (liquid) 1735, 1465, 1452, 1150 cm^{-1}; NMR ($CDCl_3$) 0.85 (3 H, t), 1.19 (12 H, m), 1.65–2.50 (7 H, m).

***N,N′*-(2′-Octyl-3′-oxocyclopentyl-1′-acetyl)glycine Methyl Ester (III, R = H).** A solution of glycine methyl ester hydrochloride (0.51 g, 2.04 mmol) in triethylamine (0.28 mL, 4.08 mmol) and *N,N*-dicyclohexylcarbodiimide (0.56 g, 2.72 mmol) in acetonitrile (4 mL) were added to a cooled (0 °C) solution of 2-octyl-3-oxocyclopentyl-1-acetic acid (0.69 g, 2.72 mmol) in acetonitrile (4 mL). The mixture was allowed to stay for 1 h at 0 °C and then stirred for 2 days at room temperature. A few drops of acetic acid are then added to the reaction mixture and the solvents removed under reduced pressure. Ethyl acetate was then added and the solid filtered off. The residue was washed with dilute hydrochloric acid, sodium bicarbonate solution, and water. Removal of ethyl acetate left an oily product: yield, 0.5 g (56.3%); IR (liquid) 3310, 1735, 1655, 1535, 1438, 1408, 1369, 1205 cm^{-1}; NMR ($CDCl_3$) δ 0.85 (3 H, t),

Table I. Structures and Growth Inhibition Data

Compd	R	% inhibition	% germination	Radicle length, mm ± SE
Control[a]			88	15.8 ± 1.1
I	C_3H_7	46.8	75	8.4 ± 0.9
II	C_3H_7	50.6	78	7.8 ± 0.8
I	C_8H_{17}	−6.3[b]	85	16.8 ± 1.2
II	C_9H_{19}	19.0	88	12.8 ± 1.0
III	H	15.8	88	13.3 ± 1.1
IV	H	−3.0	87	16.3 ± 1.2
III	$(CH_2)_2SCH_3$	36.7	93	10.0 ± 0.9
IV	$(CH_2)_2SCH_3$	−17.7	88	18.6 ± 1.2
IV	$CH(C_2H_5)CH_3$	50.0	83	7.9 ± 0.8
V		44.3	88	8.8 ± 0.9

[a] Control, acetone-water, 1:14. [b] Minus indicates growth promotion.

1.28 (14 H, m), 1.78–2.58 (8 H, m), 3.78 (3 H, s), 4.08 (2 H, d), 5.98 (1 H, m); MS *m/e* (%) 325 (M^+, 4), 195 (8), 131 (100), 83 (15), 69 (11), 67 (15), 55 (25), 41 (22). Anal. Calcd for $C_{18}H_{31}O_4N$: C, 66.46; H, 9.54. Found: C, 66.93; H, 9.52.

***N*-(2′-Octyl-3′-oxocyclopentyl-1′-acetyl)methionine Methyl Ester (II, R = $(CH_2)SCH_3$).** (Prepared as described for III, R = H.) Yield, 82%; IR (liquid) 3310, 1735, 1655, 1535, 1200 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (3 H, t), 1.1–1.63 (14 H, m), 1.78–2.68 (15 H, m), 3.78 (3 H, s), 4.73 (1 H, m), 6.28 (1 H, m); MS *m/e* (%) 399 (M^+, 5), 324 (9), 237 (8), 195 (34), 162 (18), 132 (100), 116 (10), 97 (26), 83 (12), 69 (14), 67 (12), 61 (25), 55 (28). Anal. Calcd for $C_{18}H_{31}NO_4$: C, 66.46; H, 9.54. Found: C, 66.93; H, 9.52.

***N*-(2′-Octyl-3′-oxocyclopentyl-1′-acetyl)glycine (IV, R = H).** A mixture of *N*-(2′-octyl-3′-oxocyclopentyl-1′-acetyl)glycine (0.10 g, 0.315 × 10^{-3} mol) and methanolic solution of potassium hydroxide (4 mL, 4%) was stirred for 1 h. Methanol was distilled and water added. The residue was extracted with ether and the aqueous layer acidified with hydrochloric acid (10%) and extracted with ether. The ethereal extract was washed with water and dried over anhydrous magnesium sulfate. Evaporation of ether left the products as an oil: yield, 51 mg (52%); IR (liquid) 3300, 3100, 1735, 1700, 1635, 1535, 1450 cm^{-1}; MS *m/e* (%) 311 (M^+, 2), 254 (2), 237 (2), 195 (30), 149 (10), 142 (40), 123 (14), 97 (18), 83 (100), 55 (28), 41 (22).

***N*-(2′-Octyl-3′-oxocyclopentyl-1′-acetyl)methionine (IV, R = $(CH_2)_2SCH_3$).** (Prepared as described for IV, R = H.) Yield, 67 mg (52%); IR (liquid) 3310, 3030, 1735, 1700, 1645, 1530 cm^{-1}; MS *m/e* (%) 385 (M^+, 16), 367 (15), 312 (13), 306 (55), 294 (14), 237 (19), 209 (12), 195 (97), 151 (45), 117 (100), 109 (14), 99 (30), 97 (28), 83 (62), 75 (31), 61 (40), 55 (52), 43 (40), 41 (58).

***N*-(2′-Octyl-3′-oxocyclopentyl-1-acetyl)isoleucine (IV, R = $CH(C_2H_5)CH_3$).** Yield, 103 mg (51%); IR (liquid) 3305, 3050, 1740, 1700, 1645, 1540 cm^{-1}; MS *m/e* (%) 367 (M^+, 9), 237 (7.5), 236 (6.5), 195 (38), 194 (14), 156 (12), 141 (18), 99 (21), 97 (34), 83 (100), 69 (43), 67 (3), 57 (32), 55 (68), 43 (46), 41 (74).

2-Octylcyclopentan-1-one-3-acetic Acid (V). [Prepared by Ravid (1975) according to the method described by Ravid and Ikan (1974).] Yield, 92%; bp 210 °C (4 mm); IR (liquid) 3050–3080, 1740, 1710, 1465, 1410, 1160 cm^{-1}; NMR ($CDCl_3$) δ 0.83 (3 H, t), 0.96–1.54 (14 H, m), 1.92–2.59 (8 H, m), 11.2 (1 H, s). Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.64; H, 10.11.

TEST PROCEDURE

Samples of substituted cyclopentenones and cyclopentanones described above and those reported by Katsin and Ikan (1977) were dissolved in acetone to give a 10^{-2} M concentration. A 1-mL aliquot of each sample was added to 14 mL of water to give the test concentration of 6.7 × 10^{-4} M. Whatman No. 1 filter paper disc was placed at the bottom of each petri dish, 5 mL of the test solution was then added, and 15 lettuce seeds (cv. "Grand Rapids") were placed on the paper. There were four replicate petri dishes per test. The control solution contained acetone–water in the ratio of 1:14. Germination and radicle length of the germinated seedlings were recorded after 69 h, in a 25 °C room temperature with 1500–2000 lux light intensity of cool-white fluorescent lamps. Percent inhibition of elongation was determined as follows: 100 × (radicle length, control; radicle length, test)/radicle length control.

RESULTS AND DISCUSSION

The data of Table I indicates that 2-propylcyclopentan-1-one (II, R = C_3H_7) and *N*-(2′-octyl-3′-oxocyclopentyl-1′-acetyl)isoleucine (IV, R = $CH(C_2H_5)CH_3$) are the most potent growth inhibitors. In the series of amides, it was found that most of the methyl esters (III) possess growth inhibitory effects, whereas the free acids (IV) have growth promoting effect. It is mainly the amide linkage and the type of amino acid that affect the germination and radicle length of lettuce seedling growth.

We have used radicle growth as an indication for the biological activity of the compounds. The effect of these compounds on stem growth and other biological parameters may be different as known from other growth substances.

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