The *n*-propyl esters of the nine mono- and dichlorobenzoic acids have been tested for their effectiveness in inhibiting or destroying selectively the apical meristems of *Nicotiana* cv. Xanthi-nc plants. The esters were formulated in 2.5% methyl iso-butyl ketone and 1% Tween-20 and applied as spray emulsions. The effectiveness of the *n*-propyl chlorobenzoate isomers in reducing terminal bud growth was in the order: 3,4 > 2,6 > 2,3 > 2,5 > 3,5 >

sters of fatty acids and the corresponding higher alcohols  $(C_9 - C_{11})$  selectively inhibit or kill terminal and axillary buds of tobacco, while the fatty acids exhibit poor selectivity and caused excessive plant injury (Steffens et al., 1967; Tso, 1964). The use of these esters and alcohols has been expanded to "chemically prune" a wide range of plants (Cathey et al., 1966; Cathey and Steffens, 1968). The agents act upon contact with the meristematic tissues and affect only the growing tip of the plant. Similar inhibitory activity has now been obtained with some of the mono- and disubstituted chlorobenzoic acids, salts, and esters.

## EXPERIMENTAL

The three mono- and six disubstituted acids were obtained commercially or prepared from the corresponding chloroanilines by diazotization (Hodgson and Walker, 1933), treatment with cuprous cyanide, and basic hydrolysis of the resulting nitrile. The acids were converted to their potassium salts or *n*-propyl esters for further study. Compounds to be tested were dissolved in methyl iso-butyl ketone, combined with a surfactant, polyoxyethylene(20) sorbitan monolaurate (Tween-20), and mixed with water to give an emulsion. Five ml of the stable emulsion which contained 1% Tween-20 and 2.5% methyl iso-butyl ketone were sprayed on each Nicotiana cv. Xanthi-nc plant (Marth and Mitchell, 1964; Steffens et al., 1967), so that upper leaves and terminal buds were well wetted. Duplicate greenhouse tests were conducted and a minimum of three plants were used per treatment. The plants were harvested 14 days after treatment.

2,4 > 3 > 2 > 4; the optimum concentration of active chemical used was  $2.5 \times 10^{-2} M$ . The activities of the n-propyl benzoates were generally enhanced when compared with the underivatized Esters of several hydroxy, methoxy, acids or salts. methyl, and nitro-substituted benzoic acids were found to be less active than the corresponding chlorobenzoates as plant growth inhibitors.

## RESULTS AND DISCUSSION

The growth regulating activities found with the mono- and dichlorobenzoic acids are in general agreement with the findings of previous workers (James and Wain, 1969; Pybus et al., 1959). The 2,3 and 2,5-dichlorobenzoic acids caused slight retardation of bud growth and morphogenetic effects on the plants. The 2,6 isomer caused marked growth inhibition, extensive damage to the bud, and severe epinasty of the upper leaves. The remainder of chlorinated benzoic acids had little effect upon the treated plants. The activities obtained with the potassium chlorobenzoates agreed closely with those of the acids.

The *n*-propyl esters of these chlorinated benzoic acids inhibited or destroyed selectively the apical meristem of the test plants (Table I). The most effective isomer in terms of reducing terminal bud growth was n-propyl 3,4-dichlorobenzoate. At 2.5  $\times$  10<sup>-2</sup>M, it completely controlled terminal bud growth by killing the meristematic tissue with no accompanying formative effects or noticeable leaf injury. This concentration is considerably lower than that required for the chemical pruning of plants with the fatty acid esters and similar alcohols. It also effectively controlled the growth of axillary buds of decapitated field-grown Maryland tobacco when applied at 5 to 7  $\times$  10<sup>-2</sup>M. The *n*-propyl ester of the 2,6 isomer inhibited growth, caused terminal bud damage, and induced formative effects comparable to those of the 2,6 acid. The *n*-propyl ester of the 2,3 isomer was somewhat less active at this concentration and caused inhibition of growth of expanding leaves and the terminal bud. The 3,5 *n*-propyl

Benzoic Acid n-Propylester Applied <sup>b</sup>	% Reduction in Fresh Weight of Terminal Growth			Type Growth Regulation <sup>c</sup>			Relative Leaf Injury Rating <sup>d</sup> Concentration (Molar)		
	$\frac{\text{Concentration (Molar)}}{1.25 \times 2.5 \times 5.0 \times$								
	10-2	2.5 × 10 <sup>-2</sup>	$10^{-2}$	$\overline{1.25  imes 10^{-2}}$	$2.5  imes 10^{-2}$	$5.0  imes 10^{-2}$	10-2	$10^{-2}$	$10^{-2}$
2-Chloro	6	11	85	N	N	D	0	0	0
3-Chloro	20	23	84	Ν	Ν	D	0	0	1
4-Chloro	0	7	91	N	N	D	0	0	0
2.3-Dichloro	41	69	98	R	R. F	K. F	0	1	2
2.4-Dichloro	0	35	95	Ν	D	ĸ	Ō	1	2
2.5-Dichloro	22	49	97	N	D	К	Ō	1	2
2.6-Dichloro	67	87	96	R.F	D. R. F	D. R. F	2	3	7
3.4-Dichloro	43	100	100	D	K	K .	ō	1	4
3 5-Dichloro	35	48	96	N	R	R	1	2	2

Table I. Effect of *n*-Propyl Esters of Mono- and Dichlorobenzoic Acids on Terminal Growth of Xanthi-nc Tobacco Plants<sup>a</sup>

<sup>a</sup> Data obtained 14 days after treatment.
 <sup>b</sup> Applied as sprays containing 1% Tween-20 and 2.5% methyl iso-butyl ketone (no ketone added to K salt); 5 ml spray per plant.
 <sup>c</sup> N = no marked visual affects on terminal buds; D = terminal buds damaged but not completely killed; K = terminal buds killed; R = terminal bud growth retarded; and F = formative effects usually including epinasty, leaf curl, and strap leaf.
 <sup>d</sup> 0 = no injury and 10 = severe leaf injury.

ester caused little damage to the bud but at the highest concentration used retarded its growth. The remainder of the *n*-propyl esters of the di- and monochlorobenzoic acids were less active at  $2.5 \times 10^{-2}$  M, but application of increased concentrations of the compounds resulted in almost complete destruction of the terminal bud accompanied by somewhat more leaf damage.

Other substituted *n*-propyl benzoates were tested for bud growth inhibiting activity. The *n*-propyl esters of all of the mono- and disubstituted methyl- and hydroxybenzoic acids were screened and were found to be much less effective than the corresponding chlorosubstituted compounds. The hydroxybenzoates were less active than the corresponding methyl compounds. Several other 3,4 disubstituted *n*-propyl benzoates were examined and the following order of effectiveness as bud growth inhibitors was found: 3,4-di Cl  $\gg$  3,4-di NO<sub>2</sub>; 3,4-di MeO; 3,4-di Me > 3,4-di OH.

The chlorinated compounds are the most effective in inhibiting terminal bud growth among the *n*-propyl benzoates tested and the 3,4-chloro substituted ester gave the maximum selective contact activity. The activities of the *n*-propyl benzoates are generally enhanced when compared with the underivatized acids or salts. The best example of this effect is the highly active *n*-propyl 3,4-dichlorobenzoate contrasted to the relatively inactive acid and salt. A reasonable explanation for the inhibitory activities of the esters compared to the acids should include the increased ability of the esters to penetrate lipoidal barriers of the plant surfaces (Foy, 1964).

The esters would be more lipid soluble because of their decreased polarity; and the most effective *n*-propyl chlorobenzoates are probably more lipid soluble than the corresponding hydroxy or methyl benzoate esters.

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