2. Studies on the Phytohormones. (I)

On the Growth Promoting Activity for Plants of Aryl Thioglycolic Acid Derivatives

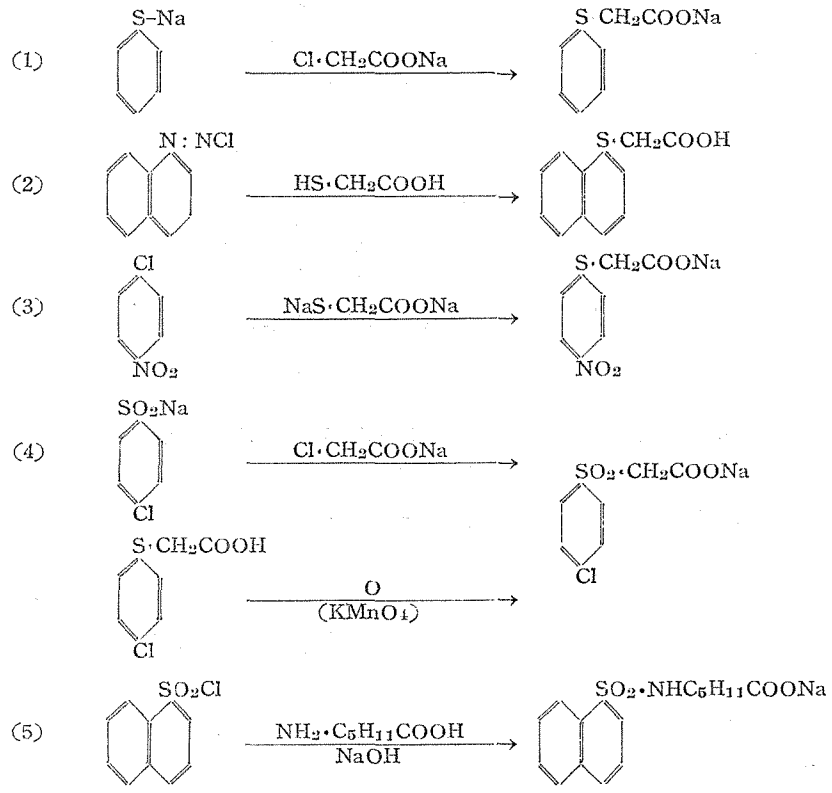
Michiyasu SUGII and Atsushi SUGII*

(Ogiu and S. Takagi Laboratories)

Received May 12, 1952

Substituted phenoxy and benzoic compounds for regulating the growth of plants have been reported by P. W. Zimmerman *et al.* We synthesized forty-seven derivatives of aryl thioglycolic and aryl sulfon acetic acids, for the purpose of testing the growth promoting activity for plant.

These compounds were prepared by the following usual methods.



The activities of these substances were detected by epinasty experiment with tomato plant (Zimmerman). (Figs. 1 and 2).

---

* 杉井通泰, 杉井篤

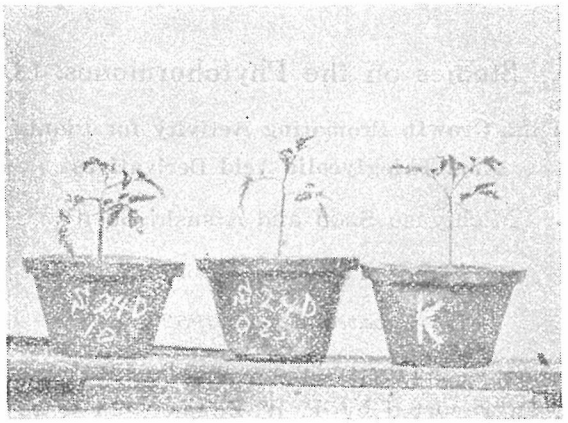


Fig. 1. Control (right) and two tomato plants responding to local treatment with lanolin preparation of S-(2.4-dichlorophenyl) thioglycolic acid 10 and 0.25 mg./g. (Three hours after treatment).

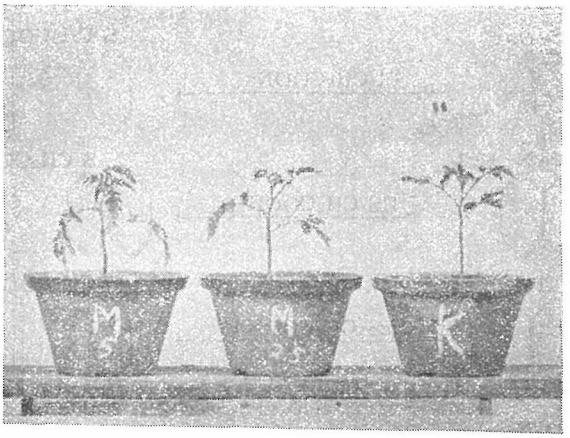
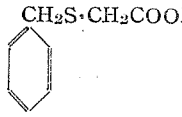
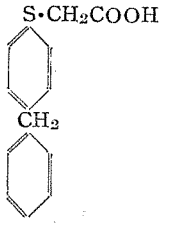
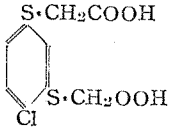
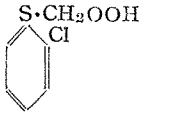
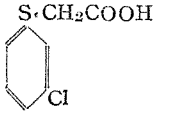
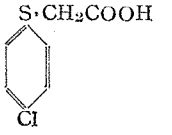
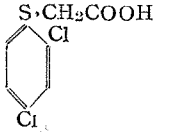
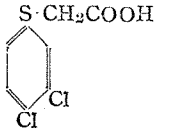
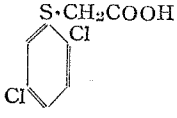
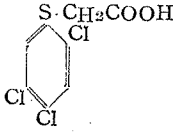
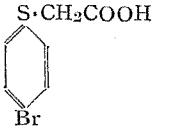


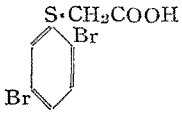
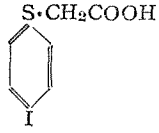
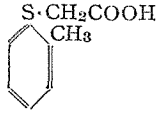
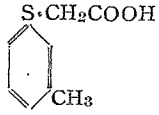
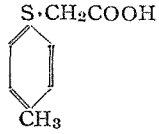
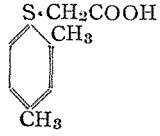
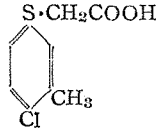
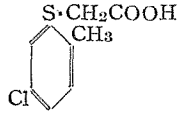
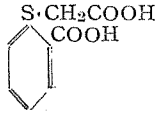
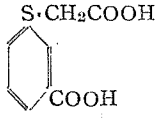
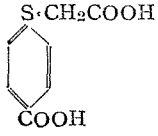
Fig. 2. S-(*o*-methylphenyl) thioglycolic acid 5 and 2.5 mg./g., control (right). (Three hours after treatment).

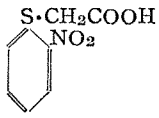
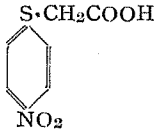
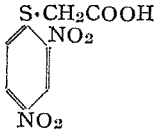
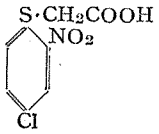
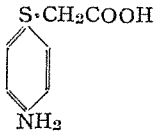
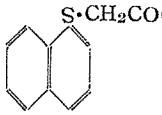
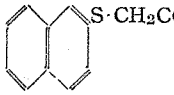
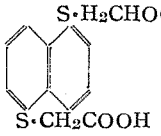
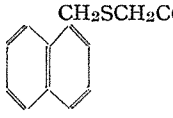
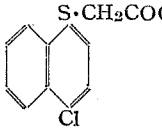
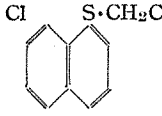
Activities of test substances and melting point are shown in Table 1.

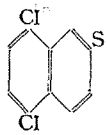
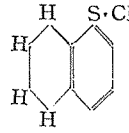
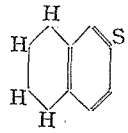
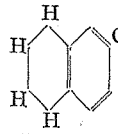
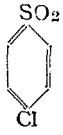
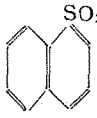
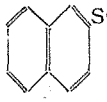
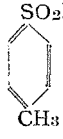
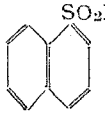
Table 1.

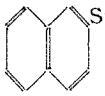
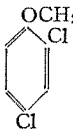
Aryl thioglycolic acid derivatives	Lowest concentration producing epinasty mg./g.	Melting point
 S-phenylthioglycolic acid	inactive	61–62°
 Dithioresorcin-S, S-diacetic acid	inactive	130–132°

	S-benzylthioglycolic acid	inactive	58–59°
	S-(*p*-benzylphenyl) thioglycolic acid	inactive	89–91°
	4-chloro-dithioresorcin-S, S-di-acetic acid	inactive	159–160°
	S (*o*-chlorophenyl) thioglycolic acid	3.0	112°
	S-(*m*-chlorophenyl) thioglycolic acid	1.0	81–82°
	S (*p*-chlorophenyl) thioglycolic acid	1.0	105°
	S (2.4-dichlorophenyl) thioglycolic acid	0.25	121–122°
	S (3.4-dichlorophenyl) thioglycolic acid	0.5	124–125°
	S (2.5-dichlorophenyl) thioglycolic acid	0.25	130°
	S (2.4.5-trichlorophenyl) thioglycolic acid	1.0	110–111°
	S-(*p*-bromophenyl) thioglycolic acid	10.0	111°

	S-(2 5-dibromophenyl) thioglycolic acid	0.5	120–121°
	S-(*p*-iodophenyl) thioglycolic acid	inactive	123°
	S-(*o*-methylphenyl) thioglycolic acid	2.5	108–109°
	S-(*m*-methylphenyl) thioglycolic acid	2.5	60–62°
	S-(*p*-methylphenyl) thioglycolic acid	5.0	95°
	S-(2.4-dimethylphenyl) thioglycolic acid	1.0	115–116°
	S-(3-methyl-4-chlorophenyl) thioglycolic acid	1.0	96–97°
	S-(2-methyl-5-chlorophenyl) thioglycolic acid	5.0	98–99°
	S-(*o*-carboxyphenyl) thioglycolic acid	inactive	215°
	S-(*m*-carboxyphenyl) thioglycolic acid	inactive	188–189°
	S-(*p*-carboxyphenyl) thioglycolic acid	inactive	267–269°

 S-(*o*-nitrophenyl) thioglycolic acid	inactive	161°
 S-(*p*-nitrophenyl) ycolic acid	inactive	155°
 S-(2.4-dinitrophenyl) thioglycolic acid	inactive	167°
 S-(2-nitro-4-chlorophenyl) thioglycolic acid	inactive	205–207°
 S-(*p*-aminophenyl) thioglycolic acid	15.0	196–197°
 S-(*α*-naphthyl) thioglycolic acid	inactive	94–95°
 S-(*β*-naphthyl) thioglycolic acid	5.0	90–91°
 Naphthalene-1.5-dithioglycolic acid	inactive	251°
 S-(*α*-menaphthyl) thioglycolic acid	inactive	110–112°
 S-(4-chloronaphthyl-1) thioglycolic acid	inactive	122-124°
 S-(7-chloronaphthyl-1) thioglycolic acid	inactive	131–132°

 S-(5.8-dichloronaphthyl-2) thioglycolic acid	inactiue	138–139°
 S-(α-tetrahydronaphthyl) thioglycolic acid	inactive	133–135°
 S-(β-tetrahydronaphthyl) thioglycolic acid	15.0	73–74°
 S-(β-tetrahydromenaphthyl) thiog'ycolic acid	inactive	107–110°
 P-chlorophenyl sulfon acetic acid	inactive	122°
 α-naphthyl sulfon acetic acid	inactive	168°
 β-naphthyl sulfon acetic acid	inactive	90°
 P-chlorophenyl sulfon-ξ-amino capronic acid	inactive	127–123°
 O-methylphenyl sulfon-ξ-amino capronic acid	inactive	70–73°
 P-methylphenyl sulfon-ξ-amino capronic acid	inactive	104–108°
 α-naphthyl sulfon-ξ-amino capronic acid	inactive	88–89°

	β-naphthyl sulfon ξ-amino capronic acid	inactive	108–110
	2,4-D	0.025	138–139°

From the results of experiments, it is showed that the test substances have the same activities as the corresponding Zimmerman's substituted phenoxy compounds. That is, the S-phenylthioglycolic acid is inactive, but halogen-substituted compounds are activated according to the position and the number of substituted groups in the nucleus of the molecule. For example, S-(*o*-chlorophenyl)thioglycolic acid is slightly active. The substitution by the chlorine atom in the para and meta positions increases the activity. The substitution in the 2,4 and 2,5 positions brings very active compounds, but 2, 4, 5-trichloro-compound is less active than 2,4 and 2,5-dichloro compounds. Although the presence of chlorine atom is effective for growth activity, the presence of dicarboxylic acids appears to abolish the activity. Example of inactive dicarboxylic acid is 4-chloro-dithioresorcin-S,S-di-acetic acid.

Bromo-substituted compounds showed the same activity, though less active, as the corresponding chloro-substituted compounds. *p*-Iodo substituted compounds do not act in the same way as chloro-substituted compounds. S-(*p*-iodophenyl) thioglycolic acid is inactive.

Methyl groups are also active. Carboxy- or nitro-substituted compounds in the nucleus are inactive. *p*-Amino compound is active.

S-(β-naphthyl) thioglycolic and S-(β-tetrahydronaphthyl) thioglycolic compounds are active, but S-(α-naphthyl) thioglycolic and their chloro derivatives are inactive. All sulfon compounds are inactive in cell elongation.

The authors wish to thank Prof. Seishi Takagi for the guidance and to Prof. Joji Ashida for his kind advice in this work.