STUDIES ON THE SYNTHESIS OF PLANT GROWTH SUBSTANCES

I. Growth Promoting Activity of the Mono-substituted N-Phenylglycines.

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Beside the well-known typical growth regulators like α-naphthylacetic acid and 2,4-dichlorophenoxyacetic acid, many other substances that exhibit growth regulating activities have now been found. Almost all of these compounds bear a resemblance in their chemical structure to natural regulators, i. e. auxin and heteroauxin. They are all ring-unsaturated cyclic compounds that have carboxyalkyl group or substituent convertible into carboxyalkyl group as the side chain. There are, however, such exceptions as C-(α-naphthyl)nitromethane (Veldstra, 1944) and C-(α-naphthyl)methanesulfonic acid (Veldstra, 1954).

Based on the result of the pea test, Koepfli, Thimann and Went (1938) generalized the minimum structural requirements for the cell elongation activity as a plant growth regulator as follows :

(1) a ring system as the nucleus ;
(2) a double bond in this ring ;
(3) side chain ;
(4) a carboxyl group or a structure readily convertible to a carboxyl on this side chain at least one carbon atom removed from the ring ;
(5) a particular space relationship between the ring and the carboxyl group.

It is noted, however, that the generalization is descriptive, so there are some physiologically inactive substances in spite of their compatibility to the above requirements and there are also some other ones which are incompatible to the above requirements in spite of their physiological activity. It has become clear that concerning aryloxyalkylcarboxylic acids and substituted benzoic acids there is a difference in physiological activity according to the character and the position of the substituent in the ring, and that only the compounds the ring of which is properly substituted are physiologically active (Zimmerman, 1942, 1944, 1945 and 1952). Consequently, the kind and the position of substituents are deemed to be the important factors influencing the physiological activity. And, this fact has given rise to the possibility of obtaining an active substance by the choice of proper substituents to be introduced into the ring structure of the compound, which, otherwise, has been regarded as inactive.

However, the physiological activity, as a whole, cannot be anticipated

only by the relationship between the ring structure and the activity hitherto elucidated since it has such a wide variation caused by the nature of the side chain as between that of substituted benzoic acid and that of substituted phenoxyacetic acid.

Zimmerman (1942 and 1952) found as the result of the tomato test that among substituted benzoic acids, 2-bromo-3-nitro, 2,6-dichloro-3-nitro and 2,3,6-trichloro derivatives stimulatd cell elongation. The activities of 2,4-dichloro and 2,4,5-trichlorophenoxyacetic acids were found to be the strongest of the substituted phenoxyacetic acids, while that of 2,5-dichlorophenoxyacetic acid was weaker than the above-mentioned acids, and 2,6-dichlorophenoxyacetic acid was inactive.

Based on the results of the *Avena* cylinder test, Hansch (1949, 1950, 1951*a* and 1951*b*) has concluded that it was essential for the physiological activity of substituted phenoxyacetic acids that one of the *ortho* positions remained unsubstituted, while in the case of substituted benzoic acids one or both of the *ortho* positions had to be substituted. Wain (1953) obtained similar results in the pea test as well as in the *Avena* cylinder test, although in the pea test, 2,6-dichlorophenoxyacetic acid and 2,3,6-trichlorophenoxyacetic acid as well as 2,4,6-trichlorophenoxyacetic acid exhibited, feeble as it was, response.

It is well known that like substituted phenoxyacetic acids, S-phenylthioglycolic acids, if properly substituted, exhibit strong physiological activity (Skoog, 1951 ; Sugii, 1953). This shows that for the physiological activity combination of carboxyalkyl group with benzene ring only by carbon atom is not always necessary, but oxygen or sulphur atom is usable in place of carbon in the side chain without injuring the activity.

N-Arylglycine, as well as aryloxyacetic acids and S-arylthioglycolic acids, is endowed both with the aromatic ring and the side chain of carboxyalkyl group in the structure. In spite of their meeting the minimum structural requirements, their physiological activity has been demonstrated neither by the pea test nor by other biological tests (Skoog, 1951), although Veldstra (1949) reported that N-(2,4-dichlorophenyl)glycine exhibited activity almost equal to that of 2,4-dichlorophenoxyacetic and α-naphthylacetic acid. Walker (1948) found in his test that N-(β-naphthyl)glycine had no effect in producing parthenocarpic fruits of tomato.

We can find no research study on the plant growth regulating activity of the glycines oher than the reports on N-arylglycine tested for their herbicidal action (Norman, 1946; Kraus, 1947).

It is of interest, therefore, to determine whether the imino group (-NH-) of glycines is useful as a linking group combining unsaturated ring system and side chain without injuring the activity.

In order to ascertain this on the basis of experimental facts, some of mono-substituted N-phenylglycines and related compounds, including

N-phenylglycine, were prepared and tested for the physiological activities by the methods which would be described later. The result showed that all of the glycines employed were active. Although N-phenylglycine had been reported as inactive (Skoog, 1951), it was found to exhibit a weak response in the three tests performed. The physiological activities of the following glycines for primary growth, which were inferred from the induced responses in the physiological testings, decreased in this order : 3-nitro, 4-chloro, 3-chloro, 2-methyl, 2-chloro and 4-methyl derivative. This means that growth activity is enhanced by the introduction of chlorine into the *para* position of the ring of N-phenylglycine, by the introduction of chlorine or nitro group into the *meta* position, while the activity is not much changed by the introduction of methyl group into the *para* position. Such an effect of ring substitution in mono-substituted N-phenylglycines corresponds to that in mono-substituted phenoxyacetic acids rather than to that in benzoic acid derivatives (Zimmerman, 1942, 1945 and 1952).

Generally speaking, the chemical structure of side chain has a very close connection with physiological activity (Skoog, 1951). As for N-arylglycines, the substitution of hydrogen attached to nitrogen affects the activity. That is to say, acetyl derivatives of N-phenylglycine and N-(4-chlorophenyl)glycine lack the growth activity for cell elongation, while properly substituted N-phenyl-N-carboxymethylglycine exerts activity, as will be described later. This means that for primary growth activity of substance the hydrogen attached to nitrogen must not always be free. It is possible that the introduction of substituents of electron-attracting character into the side chain of the active molecule nullifies the growth activity.

Both of the N-arylaminomethanesulfonates tested, which seemed not to be true sulfonates, lacked activity.

EXPERIMENTAL

Preparation of the Materials.

The following glycines were prepared in the same way as described by Schwalbe *et al.* (1908) except that one mole of both potassium cyanide and formaldehyde, instead of 0.5 mole, were used on one mole of corresponding anilines : N-(2-chlorophenyl)glycine, N-(3-chlorophenyl)glycine, N-(4-chlorophenyl)glycine, N-(*o*-tolyl)glycine and N-(*p*-tolyl)glycine. The reaction time seems to be an important factor to obtain a pure substance in the preparation. Refluxing was continued for four hours with 2-chloroaniline, two hours with 3-chloroaniline, one and half hours with 4-chloroaniline, two hours with *o*-toluidine and six hours with *p*-toluidine.

In Table 1, the melting point, the yield and the analysis are summarized.

TABLE 1

Mono-substituted N-phenylglycines

Substance, glycine	M.p., °C (decomposition)	Yield, % [g, h]	Formula	Nitrogen, % [f]	
				Calcd.	Found
N-(2-Chlorophenyl)-	169 [a]	43 (55)	$C_8H_8ClNO_2$	7.54	7.7
N-(3-Chlorophenyl)-	103–104 [b]	54 (43)	$C_8H_8ClNO_2$	7.54	7.6
N-(4-Chlorophenyl)-	141–142 [c]	78 (51)	$C_8H_8ClNO_2$	7.54	7.6
N-(*o*-Tolyl)-	151–152 [d]	50 (58)	$C_9H_{11}NO_2$	8.47	8.5
N-(*p*-Tolyl)-	119–121 [e]	61 (51)	$C_9H_{11}NO_2$	8.47	8.5

[a, b, c, d, e] The reported m.p. are (a) 171° (Schwalbe, *loc. cit.*), (b) 93° (Schwalbe, *loc. cit.*), (c) 141° (Schwalbe, *loc. cit.*), (d) 149-150° (Steppes, 1900) and (e) 120-121° (Steppes, *loc. cit.*), respectively. [f] Analysed by modified semi-micro Kjeldahl (Takeda, 1954*a*). [g] The yield based on consumed anilines. [h] The figures parenthesized are the percentages of recovered anilines.

The following compounds were prepared according to the statement of literatures : sodium N-phenylaminomethanesulfonate (Knoevenagel, 1904), N-phenylglycine (Mai, 1902), N-(3-nitrophenyl)glycine (Deutsch, 1907), N-phenyl-N-acetylglycine (Hausdörfer, 1892), N-phenyl-N-carboxymethylglycine (Vorländer, 1901) and ethyl N-(2,4-dichlorophenyl)oxamate (Chattaway, 1906). The properties of these compounds are summarized in Table 2.

TABLE 2

Substances	M.p., °C	Formula	Nitrogen, %	
			Calcd.	Found [f]
Sodium N-phenylaminomethanesulfonate	do not melt below 300°	$C_7H_8NNaO_3S$	6.73	6.6
N-Phenylglycine	128 dec. [a]	$C_8H_9NO_2$	9.28	9.3
N-(3-Nitrophenyl)glycine	161–162 dec. [b]	$C_8H_8N_2O_4$	14.28	14.1
N-Phenyl-N-acetylglycine	194–196 slit. dec. [c]	$C_{10}H_{11}NO_3$	7.25	7.3
N-Phenyl-N-carboxymethylglycine	near 155 dec. bubbling [d]	$C_{10}H_{11}NO_4$	6.69	6.7
Ethyl N-(2,4-dichlorophenyl)oxamate	118 [e]	$C_{10}H_9Cl_2NO_3$	5.35	5.4

[a, b, c, d, e] The reported m.p. are (a) 125-126°, (b) 156°, (c) 194-195°, (d) 150-155° dec. bubbling and (e) 119°. [f] By modified semi-micro Kjeldahl (Takeda, *loc. cit.*).

Since sodium N-(4-chlorophenyl)aminomethanesulfonate, N-(4-chlorophenyl)-N-carboxymethylglycine and N-(4-chlorophenyl)-N-acetylglycine are hitherto unknown compounds, the preparation has been described in some detail.

Sodium N-(4-chlorophenyl)aminomethanesulfonate. This compound was prepared by the sulfomethylation of 4-chloroaniline with a three molar solution of formaldehyde-sodium bisulfite. Refluxing 12.7 g. (0.1 mole) of 4-chlo-

roaniline with 50 ml. of a three molar aqueous solution of formaldehyde-sodium bisulfite for ten minutes yielded 22 g. (91%) of snow white crystals. This material do not melt below 300°.

Anal. Calc'd for $C_7H_7ClNNaO_3S$: N, 5.73. Found : N, 5.5.

N-(4-Chlorophenyl)-N-carboxymethylglycine. The mixed solution of 6.2 g. (1/30 mole) of N-(4-chlorophenyl)glycine and 3.2 g. (1/30 mole) of monochloroacetic acid in 50 ml. of a 5% aqueous sodium hydroxide was refluxed with stirring for six hours, during which the *p*H of the solution was maintained to weak alkali by adding a 20% aqueous solution of sodium hydroxide at intervals. The precipitation of the product was completed by acidifying the solution until pink coloration to thymol blue with dilute hydrochloric acid (1: 1), yield 6.2 g. (79%). It crystallized from warm water in fine, colorless needles, m.p. 189–190° (decomposition, bubbling).

Anal. Calc'd for $C_{10}H_{10}ClNO_4$: N, 5.75. Found : N, 5.6.

N-(4-Chlorophenyl)-N-acetylglycine. To the solution of 19 g. (0.1 mole) of N-(4-chlorophenyl)glycine in 20 ml. of acetic acid the mixture of 12 g. (0.12 mole) of acetic anhydride and 4 ml. of acetic acid was added. This solution was heated on a water bath for thirty minutes. After the addition of about 40 ml. of water the heating was continued for additional five minutes in order to decompose the excess of acetic anhydride. From the reaction mixture 20 g. (88%) of the crude product melting at 162–167° was separated at the room temperature, m.p. 174–174.5° dec. after two recrystallizations from dilute alcohol.

Anal. Calc'd for $C_{10}H_{10}ClNO_3$: N, 6.17. Found: N, 6.1.

The diethylamine salts of the acids were prepared by solely mixing the equimolar amounts of both components dissolved in a small quantity of ethyl alcohol. The yields were almost quantitative. The m.p. and the analysis of the salts are listed in Table 3. All of these are new compounds.

Methods for the Assessment of Growth Promoting Activity.

The first known function of auxin is the promotion of cell elongation of stems and coleoptiles. The following processes are all controlled by auxins (Thimann, 1937) : the initiation of roots on stems ; cell division both in the cambium and other stem tissues ; the growth of the ovary into a fruit ; the abnormal growth of parenchymatous tissues into tumors, so on.

The activity of substances is assessed from the observations of the above-mentioned auxin actions induced. Auxin action can be tested by such biological test methods as the *Avena* curvature test (Went, 1937), the *Avena* cylinder test (Bonner, 1933 ; Bentley, 1937), the pea test (Went, loc. cit. and 1934), the *Cephalaria* test (Söding, 1937) and the tomato test (Zimmerman, 1937). The *Avena* curvature test is generally applicable for the detection or the determination of natural auxins, but in this test only a feeble response is exhibited by such a series of synthesized substances as α-naph-

TABLE 3

Diethylamine salts of mono-substituted N-phenylglycines

Substance,[a] diethylamine salt of	M. p., °C (decomposition)	Formula	Nitrogen, % Calcd.	Found
N-Phenylglycine	142–143	$C_{12}H_{20}N_2O_2$	12.47	12.5
N-Phenyl-N-acetylglycine[b]	111–112	$C_{14}H_{22}N_2O_3$	10.50	10.4
N-Phenyl-N-carboxymethylglycine	176–177	$C_{18}H_{33}N_3O_4$	11.80	11.8
N-(2-Chlorophenyl)glycine	92–93	$C_{12}H_{19}ClN_2O_2$	10.82	10.9
N-(3-Chlorophenyl)glycine	120–121	$C_{12}H_{19}ClN_2O_2$	10.82	10.7
N-(4-Chlorophenyl)glycine	162	$C_{12}H_{19}ClN_2O_2$	10.82	10.9
N-(*o*-Tolyl)glycine	106	$C_{12}H_{22}N_2O_2$	11.75	11.7
N-(*p*-Tolyl)glycine	145–147	$C_{12}H_{22}N_2O_2$	11.75	11.7
N-(4-Chlorophenyl)-N-acetylglycine[c]	117–120	$C_{14}H_{21}ClN_2O_3$	9.30	9.2
N-(3-Nitrophenyl)glycine	127–132	$C_{12}H_{19}N_3O_4$	15.61	15.6
α-Naphthylacetic acid	98–102	$C_{16}H_{21}NO_2$	5.41	5.4
2,4-Dichlorophenoxyacetic acid	176–177	$C_{12}H_{17}Cl_2NO_3$	4.77	4.8
N-(4-Chlorophenyl)-N-carboxymethylglycine	179	$C_{18}H_{32}ClN_3O_4$	10.76	10.8

[a] Crystals soluble in water, alcohol and benzene. All the compounds listed here are new.
[b, c] Very hygroscopic substance.

thylacetic acid and 2,4-dichlorophenoxyacetic acid which have aromatic nucleus in the molecule (Bonner, 1950). For the assessment of the activities of these substances, therefore, the pea test and the *Avena* cylinder test are more beneficially employed because of their conspicuous responses. These tests, however, require the water-soluble samples for the observation of the primary growth activity, that is, the promotion of cell elongation. The tomato test is therefore preferable for this purpose, since the above-mentioned processes controlled by auxins can be conveniently observed by this method.

The present author proposed to apply the Aduki beans curvature test (Takeda, 1954*b*) for the same purpose. As will be described later, this test is not only as good in sesitivity as the tomato test but also the testing procedures are simpler than the tomato test and can be completed within a shorter period.

In this experiment, the physiological activities of N-arylglycine and its derivatives were tested by three different test methods, viz. the pea test, the *Avena* cylinder test and the Aduki test. The procedures of testing are as follows.

The pea test. The testing was carried out in the usual manner. In each of a 50-ml. Petri dish containing 30 ml. of one of the serial dilutions of the sample to be tested, five of split sections of *Alaska* peas were put and kept in a dark room for 24 hours at 25°. The curvatures induced were then observed.

Activity in this test is indicated by the threshold minimum concentra-

tion to induce the inward curvature. In our experiment, that of diethyl amine salt of 2,4-dichlorophenoxyacetic acid was assessed to be 0.04-0.06 mg./*l* and that of diethylamine salt of α-naphthylacetic acid as 0.5 mg./*l*.

The Avena cylinder test. Commercial seeds of oats (var. Victory) were used for the test and the testing was carried out as usual. In this test, however, cylinders of 20 mm. long were used as the test objects.

Ten coleoptile cylinders floated in each solution for the test as in the case of the pea test, were kept in darkness at 25° for 24 hours and then their lengths were measured. For the control, cylinders were, however, floated in distilled water. The rate of increases in length were recorded as the percentage of the corresponding control. The activities of substances were represented graphically by the elongation-concentration curve.

The Aduki test (*the Aduki beans curvature test*). A large bean variety of *Phaseolus angularis* W. F. WIGHT (Aduki beans) called "Dainagon" was used. The seeds were soaked in water and kept in the darkness for 30 hours at 25°. The seeds with more or less elongated hypocotyls were then planted in wet saw-dust medium regularly with the radicules downward. Six days after the planting the etiolated plants become 3 to 3.5 cm. high. Among these plants, uniformly grown ones whose stems were straight and about 3 cm. long were used for the test.

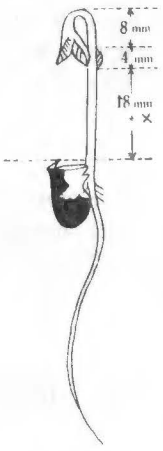

Fig. 1.

As seen in Fig. 1, about 20mg. of lanolin paste was placed on the point 1 cm. down from the winding portion and at the opposite side of the hypocotyl against the terminal bud. At least ten plants were used for each treatment. Five out of ten were cut 24 hours after the treatment, at 15 mm. upward and 25 mm. downward from the center of treated portion and the curvature was measured.

The curvature toward the treated side is called positive and represented by plus sign, while the curvature toward the opposite side is called negative and represented by minus sign. The former is regarded to be indicative of growth inhibition and the latter, of growth promotion.

About 72 hours after the treatment, it was examined with the aid of a microscope how the cell division in the treated portion was promoted. The formation of adventitious roots or tumours and the total length of plants were observed 5 to 6 days after the treatment.

The activities of the tested substances were indicated by the minimum concentration necessary for inducing negative curvature. The concentrations of the diethylamine salt of 2,4-dichlorophenoxyacetic acid and the diethylamine salt of α-naphthylacetic acid, for instances, were found to be 0.001-0.005 % and 0.0001-0.0005 %, respectively.

Biological Assay.

It was known in the above-mentioned three tests for primary growth activity that the diethylamine salts of all these glycines exhibited activity, though it was much less than those of 2,4-dichlorophenoxyacetic acid and of α-naphthylacetic acid.

Table 4 shows the results of the pea test concerning them. Seven of 12 compounds are active.

TABLE 4

Activity of mono-substituted N-phenylglycines in the pea test

Compound[a]	Threshold minimum concentration to induce inward curvature	
	mg./l (p.p.m.)	mol./l 10^{-4}×
N-Phenylglycine	46.9	2.09
N-Phenyl-N-acetylglycine	inactive (196.0)[b]	—
N-Phenyl-N-carboxymethylglycine	inactive (140.0)[b]	—
N-(2-Chlorophenyl)glycine	57.5	2.23
N-(3-Chlorophenyl)glycine	3.0	0.12
N-(4-Chlorophenyl)glycine	1.0—2.5	0.04—0.10
N-(4-Chlorophenyl)-N-acetylglycine	inactive (238.0)[b]	—
N-(4-Chlorophenyl)-N-carboxymethylglycine	2.8	0.07
N-(3-Nitrophenyl)glycine	0.85—1.67	0.031—0.062
N-(*o*-Tolyl)glycine	23.3—46.5	0.95—1.95
N-(*p*-Tolyl)glycine	49.5—99.0	2.08—4.15
Sodium N-phenylaminomethanesulfonate	inactive (100)[b]	—
Sodium N-(4-chlorophenyl)-aminomethanesulfonate	inactive (100)[b]	—
α-Naphthylacetic acid	0.5	0.0194
2,4-Dichlorophenoxyacetic acid	0.04—0.06	0.0014—0.0021

[a] The diethylamine salts of the glycines were employed for the testing. [b] The upper limit of concentration to which the testing was performed.

Figure 2 shows the exhibited activity of glycines in the *Avena* cylinder test.

The effects of the glycines observed in the Aduki test are summarized in Table 5. N-Arylglycines exhibited not only primary growth activity in the tests but also such hormone-like effects as the promotion of cell division and the formation of adventitious roots. That is to say, it was observed both in microscopical and macroscopical examinations that all the glycines caused plants unusual cell elongation which was followed by the increased cell division in the treated site of plants. The situation is illustrated by the following photographs for N-(4-chlorophenyl)glycine.

TABLE 5

Activity of mono-substituted N-phenylglycines in the Aduki test

Substance[a]	Concentration range[b] inducing negative curvature, %
N-Phenylglycine	0.5—2.0
N-Phenyl-N-acetylglycine	inactive[c]
N-Phenyl-N-carboxymethylglycine	inactive
N-(2-Chlorophenyl)glycine	0.5—4.0[d]
N-(3-Chlorophenyl)glycine	0.1—2.0
N-(4-Chlorophenyl)glycine	0.01—0.5
N-(4-Chlorophenyl)-N-acetylglycine	inactive[e]
N-(4-Chlorophenyl)-N-carboxymethylglycine	0.05—2.0
N-(3-Nitrophenyl)glycine	0.05—1.0
N-(*p*-Tolyl)glycine	0.5—4.0[f]
N-(*o*-Tolyl)glycine	0.01—4.0[f]
Sodium N-phenylaminomethanesulfonate	inactive
Sodium N-(4-chlorophenyl)aminomethanesulfonate	inactive
α-Naphthylacetic acid	0.0005—0.5
2,4-Dichlorophenoxyacetic acid	0.001—0.1

[a] The diethylamine salts of the glycines were employed for the testing. [b] The preparation having the concentration over the upper limit induced a positive curvature and promoted thereafter remarkably the formation of adventitious roots. [c] The preparations of the compound having the concentration over 1.0% induced a positive curvature but the promotion of the adventitious root formation could not be observed. [d, f] The experiment to difine the upper limit of the concentration was not conducted. [e] The lanolin preparation of the compound having the concentration over 0.5 % induced positive curvature. They did not promote the formation of adventitious roots likewise.

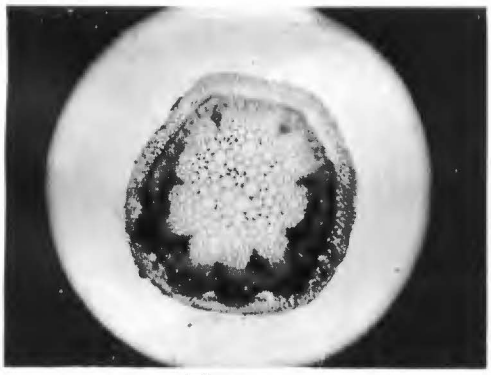

Fig. 3. (A)

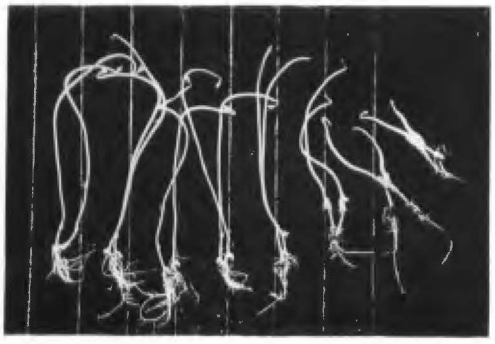

Fig. 3. (B)

Fig. 3. Responses of the etiolated plant of *Phaseolus angularis* W.F. Wight (Aduki beans) to N-(4-chlorophenyl)glycine. (A) shows the cross-secton of the treated site three days after the treatment with a 0.5 % lanolin preparation and (B) the growth of plants six days after the treatment. Left to right : control ; 0.005 % ; 0.01% ; 0.05% ; 0.1% ; 0.5% ; 1.0% and 2.0%.

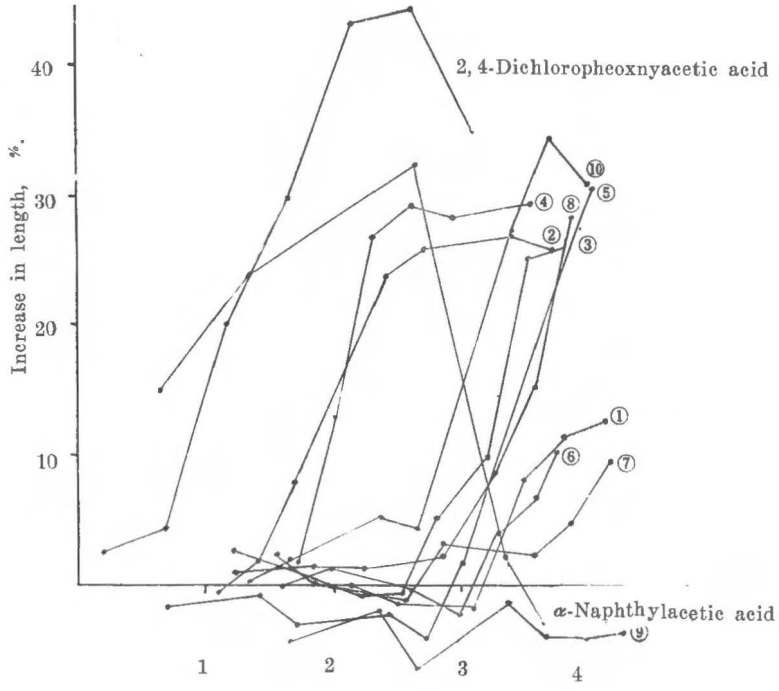

Fig. 2. Relative activity of mono-substituted N-phenylglycines in the *Avena* cylinder test : (1) N-phenylglycine ; (2) N-(3-nitrophenyl)glycine ; (3) N-(3-chlorophenyl)-glycine ; (4) N-(4-chlorophenyl)glycine ; (5) N-(*o*-tolyl)glycine ; (6) N-(*p*-tolyl)-glycine ; (7) N-phenyl-N-acetylglycine ; (8) N-phenyl-N-carboxymethylglycine ; (9) N-(4-chlorophenyl)-N-acetylglycine ; (10) N-(4-chlorophenyl)-N-carboxymethylglycine. Diethylamine salts of these compounds were employed for the testing. The sections 20 mm. long were used as test objects. C : concentration (mol./*l*).

SUMMARY

Some of the mono-substituted N-phenylglycines and relating compounds were prepared and tested for their growth promoting activity in plant.

The highest activity was shown by the 3-nitro and 4-chloro derivatives. It is concluded that N-arylglycine as well as aryloxyacetic acid can be active plant growth substance if the ring is properly substituted.

The results of the biological tests for the assessment of plant growth promoting activity are described. A new method using the seedlings of Aduki beans (*Phaseolus angularis* W. F. WIGHT) was proposed.

Acknowledgments. — The authors wish to thank Doctors K. Sisido and H. Nozaki of Kyoto University for their kind guidance.

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