Syntheses and Biological Activities of Analogs of Absciscic Acid†

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Selenium dioxide oxidation of methyl α -ionylideneacetate (IIb) in ethanol afforded methyl 1'- and 4'-hydroxy- α -ionylideneacetate (IIIb and IV), methyl 3'-hydroxy- β -ionylideneacetate (V) and crude dihydroxy-ionylideneacetate (VI). The latter was oxidized with active manganese dioxide to give methyl abscisate (Ib). The growth and germination-inhibitory activity of compounds related to abscisic acid on Azuki bean seedlings and some species of seeds were examined.

In previous papers^{1,2)} the authors reported that analogs of 2-*cis*, α - and β -ionylideneacetic acids, having the same skeleton as abscisic acid (ABA), possess strong growth-inhibitory activities on rice seedlings, but their homologs with shorter side-chains³⁾ and longer side-chains⁴⁾ do not. Recently Popoff *et al.*⁵⁾ suggested that a skeleton of citrylideneacetic acid (C_{12} -acid), rather than of ionylideneacetic acid is sufficient for growth inhibition by structures related to ABA on the basis of experiments with barerooted Black Valentine seedlings (*Phaseolus vulgaris* L.). Generally the activity of growth regulators may differ by species and variety of test plants, as the case of analogs of gibberellic acid (GA_3). In rice seedling tests, the activity of ABA analogs found by us was similar to that obtained by Tamura *et al.*⁶⁾ despite the use of different varieties. In the case of *Phaseolus vulgaris*, the difference of activity due to varieties is still not clear. Furthermore, it was known that the activity of the ester form of α -ionylideneacetic acid, which was used as a standard sample by Popoff *et al.*, was weaker than that of the free acid (IIa) on rice seedlings, so we re-examined the activity of compounds related to ABA on two varieties of *Phaseolus vulgaris* L. seedlings, pea and

soybean seedlings. The data⁷⁾ on their inhibitory activities showed that compounds having an ionylideneacetic acid skeleton were generally more active than their lower homologs ($C_{10\sim13}$ compounds) and the activities of compounds related to ABA vary considerably with variety of *Phaseolus vulgaris* L. Here, the authors describe syntheses of some hydroxy-ionylideneacetic acids, and the biological activity of compounds related to ABA on Azuki bean seedlings (*Phaseolus angularis* L.) and some species of seeds. It was also demonstrated that analogs of ionylideneacetic acids are more effective than their lower homologs for germination inhibition of seeds.

Syntheses

Previously the oxidation of methyl 2-*cis*- α -ionylideneacetate (IIb) with selenium dioxide in dioxane¹⁾ was attempted, giving a mixture of methyl keto- and hydroxy-ionylideneacetates. The separation of each hydroxy-ionylideneacetates from this mixture was difficult. Here, selenium dioxide oxidation of IIb in ethanol was successfully carried out to give a separable mixture of methyl hydroxy-ionylideneacetates as follows. IIb was oxidized with selenium dioxide in ethanol at room temperature for 6 days and the products was separated by silica-gel column chromatography, yielding methyl 2-*cis*-1'-hydroxy- α -ionylideneacetate (IIIb),⁸⁾ a small amount of methyl 2-*cis*-4'-hydroxy- α -ionylideneacetate (IV)²⁾ and mainly

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allylic rearrangement products, methyl 3'-hydroxy- β -ionylideneacetate (V), the latter consisting of 2-*cis* and *trans* form (stereoisomers). At the refluxing temperature of ethanol, IIB gave a crude methyl dihydroxy-ionylideneacetate (VI) in addition to the above mono-hydroxy-esters. The dihydroxy-ester (VI) was further oxidized with active manganese dioxide in chloroform to give methyl abscisate (Ib).

Biological activity

Growth-inhibitory activity on Azuki bean seedlings

As shown in Table I, analogs of ionylideneacetic acids showed stronger growth inhibition of the second and third internodes (terminal meristem) than of the first internode. Probably this indicates inhibition of cell fission and cell elongation of the terminal meristem rather

SCHEME 1.

Also, 2-*cis*-epoxy- β -ionylideneacetic acid (IXa), which has strong growth inhibitory activity on rice seedlings,⁶⁾ was prepared by photo-isomerization of 2-*trans*-epoxy- β -ionylideneacetic acid (VIII), which was easily prepared by epoxidation of methyl 2-*trans*- β -ionylideneacetate (VII) with perbenzoic acid followed by alkaline hydrolysis. Further, as one of the lower homologs (C_{12} -acid), methyl epoxy- β -cyclocitrylideneacetate (XXVII) was prepared by epoxidation of methyl β -cyclocitrylideneacetate (XXVIb) in chloroform. Other compounds tested for biological activity are listed in Fig. 1.

than of the first internode, which almost completed cell fission. Analogs of ionylideneacetic acids showed stronger growth inhibitory activity than their lower homologs on Azuki bean seedlings, and ABA showed the strongest inhibitory activity among analogs of ionylideneacetic acids.

Interaction of some inhibitors with GA_3 on rice seedlings

The growth of rice seedlings (*Oryza sativa* L. var. Honenwase) was promoted by GA_3 (10^{-4} M) and this growth-promoting action of GA_3 was suppressed by IIa as well as ABA at

FIG. 1.

concentrations of $10^{-4} \sim 10^{-7} \text{M}$, as shown in Fig. 2. On the other hand, XXVIa did not suppress this action, but slightly promoted it. Therefore, it was considered that the mechanism of weak inhibition of XXVIa may differ from those of analogs of ionylideneacetic acids.

Germination-inhibitory activity

Lettuce (*Lactuca sativa* L. var. Great Lakes). Germination of lettuce seeds was strongly inhibited in light rather than in the dark by analogs of ionylideneacetic acids (Table II). Interestingly, 2-*trans* isomers (XII, XIII) showed the strong inhibition in light. The homologs with shorter side chains ($\text{C}_{10} \sim \text{C}_{13}$ compounds) showed weak or almost no activity. The increase of activity in light was considered probably due to activation of some enzyme converting the inhibitors into active

forms in light. Farnesol (XVI), a precursor of ABA, showed weak activity in light.

Leaf mustard (*Brassica juncea* Coss.). Analogs of 2-*cis*-a-ionylideneacetic acid and their 2-*trans* isomers (XII, XIII) showed inhibition of germination, but analogs of cyclocitrylideneacetic acid did not, as shown in Table II.

French marigold (*Tagetes patula* L.). ABA itself, among the analogs of ionylideneacetic acids, showed the strongest inhibition of germination. Some lower homologs (XXVIa, XXVII and XXIX) showed weak activity at 10^{-4}M , as shown in Table II.

Radish (*Raphanus sativus* L. var. Nerima) and Oat (*Avena sativa* L. var. Zenchin). The germination of both radish and oat seeds was weakly inhibited by analogs of 2-*cis*-ionylideneacetic acids, but scarcely inhibited by analogs of cyclocitrylideneacetic acid and

FIG. 2. The Growth of Rice Seedlings (*Oryza sativa* L. var. Honen-Wase) in 0.7% Agar Medium with GA₃ (10^{-4}M) and Containing Inhibitors.

—, After growth at 28°C (2000 lux) for 5 days (---, without GA₃ for 6 days), the length of the second leaf sheath was measured.

○, abscisic acid (Ia); ×, 2-*cis*-a-ionylideneacetic acid (IIa); △, β-cyclocitrylideneacetic acid (XXVIa).

other lower homologs. However, the growth of both seedlings was strongly inhibited by analogs of ionylideneacetic acids, but scarcely inhibited by some of their lower homologs, as shown in Table III. Two compounds, 2-*cis*-3-methyl-phenylpentadienoic acid (XI) and 1'-hydroxy-4'-keto- α -cyclocitrylideneacetic acid (XXII), showed weak growth-promoting activity on radish seedlings.

Generally in the above bioassay tests, the methyl or ethyl esters of oxygenated ionylideneacetic acids showed stronger activity than

their free acids. However, methyl α -ionylideneacetate (IIb), which does not possess an oxygen function except for the carboxylic group, showed weaker activity than its free acid (IIa). Generally ABA showed the strongest activity among analogs of ionylideneacetic acids in the above bioassay tests. This probably means that analogs of ionylideneacetic acids may become effective as a result of enzymatic conversion into ABA in plants, as suggested in another paper.⁷⁾ The conversion of IXa into ABA in plants has already been

TABLE I. THE GROWTH-INHIBITORY ACTIVITY OF COMPOUNDS RELATED TO ABA ON *Phaseolus angularis* L. SEEDLINGS

% Inhibitory activity (control=0, Complete inhibition=100)

Concn. Compound No.	10 ⁻³ M		10 ⁻⁴ M		10 ⁻⁵ M	
	F ^{b)}	S ^{b)}	F	S	F	S
I (ABA)	100 ^{c)}	100	55	94	35	47
IIa	65	99	25	30	2	15
IIb	35	45	0	0	0	0
IIIa	45	60	0	5	0	0
IIIb	90	98	5	85	40	0
V	40	85	0	10	0	0
IXa	90	100	30	45	0	0
IXb	20	50	10	30	0	0
X	5	65	0	15	0	0
XI	3	34	0	10	0	0
XII	15	80	0	0	0	0
XIII	45	90	10	0	0	0
XIV	0	5	0	0	0	0
XV	0	5	0	0	0	0
XVI	0	15	0	0	0	0
XVII	10	35	0	4	0	0
XVIII	0	6	0	0	0	0
XIX	10	10	0	0	0	0
XX	5	20	0	0	0	0
XXI	10	60	0	30	0	0
XXII	10	60	0	10	0	0
XXIII	47	60	0	20	0	0
XXIV	48	70	10	35	0	0
XXV	6	15	0	0	0	0
XXVIa	40	90	0	20	0	0
XXVIb	7	50	0	5	0	0
XXVII	30	80	0	40	0	0
XXVIII	5	40	0	5	0	0
XXIX	70	90	0	10	0	5
XXX	15	20	0	0	0	0
XXXI	10	30	0	0	0	0

a) F: Growth inhibition of the first internode.

b) S: Growth inhibition of the second internode plus the third.

c) After growth at 28°C (2000 lux) for 5 days, the effects on epicotyl elongation were measured.

TABLE II. THE GERMINATION-INHIBITORY ACTIVITY OF COMPOUNDS
RELATED TO ABA ON SOME SPECIES OF SEEDS% Germination-inhibitory ratio (control=0, complete inhibition=100) at concn. of 10^{-4} M.

Compound No.	Leaf mustard	French Marigold	Lettuce	
			light	dark
I (ABA)	90 ^{a)} gi ^{b)}	100	100	100
IIa	75	70	100	95
IIb	60	35	85	10
IIIa	20	35	85	40
IIIb	100	98	100	80
V	0	20	90	40
IXa	0	25	95	80
IXb	35 gi	80 gi	98	95
X	40 gi	95	90	40
XI	0	20	20	15
XII	75 gi	25	100	25
XIII	45	20	75	0
XIV	0	30	0	0
XV	0	0	0	0
XVI	0	0	35	0
XVII	0	5	0	0
XVIII	0	5	5	0
XIX	0	10	0	0
XX	5	0	0	0
XXI	5	0	30	20
XXII	0	0	0	10
XXIII	0	0	30	0
XXIV	0	0	0	0
XXV	0	0	0	0
XXVIa	0	20 gi	30	20
XXVIb	0	0	20	0
XXVII	0	30 gi	10	0
XXVIII	0	0	0	0
XXIX	0	20 gi	20	10
XXX	0	5	0	0
XXXI	0	0	50	0

^{a)} After germination at 28°C (2000 lux) for 2 (leaf mustard), 3 (French Marigold), 5 (lettuce in light) and 3 days (lettuce in the dark), % germination-inhibitory ratios were measured.^{b)} gi: strong growth inhibition of seedlings.

demonstrated by Milborrow *et al.*⁸⁾ and this is considered to support the above view. Probably the low activity of methyl 3'-hydroxy- β -ionylideneacetate (V) indicates difficulty in converting it into ABA in plants.

EXPERIMENTAL

Syntheses of test compounds

1) *Selenium dioxide oxidation of methyl 2-cis- α -ionylideneacetate (IIb).* To a stirred solution of IIb (1.2 g) in 250 ml of 95% ethanol was added dropwise

an ethanolic SeO₂ solution (prepared from 1.0 g of SeO₂ and 150 ml of ethanol) at room temperature for 1 hr and the mixture was further stirred for 6 days at room temperature. After evaporation of the ethanol the residual oil was chromatographed on silica-gel. Elution with benzene gave 120 mg of crude IIb. Further elution with benzene-ethyl acetate (4:1) gave 195 mg of methyl 2-cis-1'-hydroxy- α -ionylideneacetate (IIIb) as the first fraction (*R_f*: 0.85 on silica-gel TLC Merck H, developing with benzene-ethyl acetate (4:1)), a mixture of methyl 2-cis-4'-hydroxy- α -ionylideneacetate (IV) and methyl 2-cis- and *trans*-3'-hydroxy- β -ionylideneacetates as the second fraction (300 mg) and

TABLE III. THE GERMINATION AND GROWTH-INHIBITORY ACTIVITIES OF COMPOUNDS RELATED TO ABA ON SEEDS OF RADISH AND OAT

% Inhibitory ratio (control=0, complete inhibition=100) at concn. of 10^{-4} M

Compound No.	Radish		Oat	
	Germ ^{a)}	Growth ^{b)}	Germ	Growth
I (ABA)	50 ^{a)}	100	60	100
IIa	25	60	0	89
IIb	15	40	0	75
IIIa	0	30	0	25
IIIb	70	100	0	0
V	10	60	20	8
IXa	20	40	10	98
IXb	30	60	10	100
X	10	60	10	98
XI	0	p ^{d)}	0	18
XII	10	70	0	90
XIII	0	35	0	35
XIV	0	0	0	0
XV	0	0	0	0
XVI	0	0	0	0
XVII	0	0	0	0
XVIII	5	0	0	5
XIX	10	25	0	10
XX	0	0	0	0
XXI	0	0	10	20
XXII	0	p	0	0
XXIII	0	0	0	0
XXIV	0	0	0	10
XXV	0	0	0	0
XXVIa	0	0	10	0
XXVIb	5	0	15	0
XXVII	0	0	0	20
XXVIII	0	0	0	0
XXIX	0	0	0	0
XXX	0	0	0	0
XXXI	0	0	0	0

^{a)} Germ: The germination-inhibitory ratio.^{b)} Growth: The growth-inhibitory ratio of germinated seedlings.^{c)} After germination and growth at 28°C (2000 lux) for 3 (radish) and 5 days (oat), % inhibitory ratios were measured.^{d)} p: Growth-promoting action on germinated seedlings.

360 mg of methyl 2-*cis*-3'-hydroxy- β -ionylideneacetate (V). Preparative silica-gel TLC (Merck PF₂₅₄) of the second fraction (100 mg) afforded 11.5 mg of IV and then a mixture of methyl 2-*cis* and *trans*-3'-hydroxy- β -ionylideneacetates (about 1:2). *Rf* values on TLC as described above: 0.62 for IV, 0.36 for V, 0.43 for the 2-*trans* form of V. Similar oxidation of IIb (1.2 g) with SeO₂ (800 mg) in ethanol under reflux for 16 hr gave 350 mg of IIb, 465 mg of the monohydroxy-esters and 130 mg of the dihydroxy-esters, which were separated by silica-gel column chromatography, developing

with benzene-ethyl acetate (4:1~1:1). The latter fraction contained three components on TLC as described above (*Rf*: 0.13, 0.19 and 0.28) and was oxidized with active MnO₂ (7.0 g) in 20 ml of CHCl₃ for 2 days to give 25 mg of methyl abscisate (Ib), which was separated by silica-gel column chromatography and identified with an authentic sample. IIIb, NMR (CCl₄) δ : 0.88 (*s*, 3H), 0.98 (*s*, 3H), 1.61 (*s*, 3H), 2.00 (*s*, 3H), 3.63 (*s*, 3H), 5.45 (1H), 5.55 (*s*, 1H), 6.05 (*d*, 1H, *J*=15 Hz), 7.50 (*d*, 1H, *J*=15 Hz). IV, NMR (CCl₄) δ : 0.90 (*s*, 3H), 1.0 (*s*, 3H), 1.65 (*s*, 3H), 2.00 (*s*, 3H),

3.65 (s, 3H), 6.00 (d, 1H, $J=15$ Hz), 7.68 (d, 1H, $J=15$ Hz), 5.53 (2H). IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3520, 1720, 1630, 1600, 1380, 1230, 1160, 1045, 920. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 276.5. V, NMR (CCl_4) δ : 1.05 (s, 3H), 1.08 (s, 3H), 1.82 (s, 3H), 2.05 (s, 3H), 3.60 (s, 3H), 3.82 (1H), 5.55 (s, 1H), 6.42 (d, 1H, $J=16.5$ Hz), 7.58 (d, 1H, $J=16.5$ Hz).

2) *2-cis-Epoxy- β -ionylideneacetic acid (IXa)*. Methyl 2-*trans*- β -ionylideneacetate (VII), prepared from β -ionone (XX), was epoxidized with perbenzoic acid in chloroform and then hydrolyzed with aqueous potassium hydroxide to give 2-*trans*-epoxy- β -ionylideneacetic acid (VIII), mp 105~107°C. Irradiation of VIII (1.0 g) in 25 ml of ethyl acetate with an ultra violet ray lamp (100 W) for 2 hr gave a mixture of the 2-*cis* and *trans* acids (1:1). Recrystallization of the mixture from acetonitrile afforded 2-*cis*-epoxy- β -ionylideneacetic acid (IXa), mp 146~147°C. Similar irradiation of ethyl 2-*trans*-epoxy- β -ionylideneacetate, followed by silica-gel column chromatography, afforded ethyl 2-*cis*-epoxy- β -ionylideneacetate (IXb) as an oil. NMR (CCl_4) δ : 0.92 (s, 3H), 1.08 (s, 3H), 1.13 (s, 3H), 1.25 (t, 3H), 1.97 (s, 3H), 4.02 (q, 2H), 5.47 (s, 1H), 6.00 (1H, d, $J=15$ Hz), 7.35 (d, 1H, $J=15$ Hz).

3) *Methyl epoxy- β -cyclocitrylideneacetate (XXVII)*. Epoxidation of methyl β -cyclocitrylideneacetate (XXVIb), which was obtained by methylation of β -cyclocitrylideneacetic acid (XXVIa), mp 102~103°C (from *n*-hexane) with diazomethane, in chloroform at 5°C gave XXVII as an oil, which was purified by silica-gel column chromatography. NMR (CCl_4) δ : 0.92 (s, 3H), 1.13 (s, 3H), 1.15 (s, 3H), 3.68 (s, 3H), 5.90 (d, 1H, $J=16$ Hz), 7.05 (d, 1H, $J=16$ Hz). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 222 ($\epsilon_{\text{cm}}^{1\%}=5250$).

4) *Ethyl 2-cis and trans-farnesoates (XV and XVI)*.⁹⁾ Wittig reaction of *trans*-geranylacetone with carbethoxymethylenetriphenylphosphorane at 170~180°C for 2 hr afforded ethyl 2-*cis* and *trans* farnesoates (about 1:1 mixture), which were chromatographed on silica-gel. Elution with benzene gave ethyl 2-*trans* farnesoate (XVI) as an oil, followed by ethyl 2-*cis* farnesoate (XV) as an oil. Gas chromatographic analysis with 30% SE-30 on celite 545 (1.5 m $\times$ 3 mm), column temp. 214°C, He flow rate: 15cc/min (1.6 kg/cm²), retention time: 8.2 min for XV and 7.2 min for XVI. XV, NMR (CCl_4) δ : 1.25 (t, 3H), 1.56 (s, 3H), 1.85 (s, 3H), 1.95 (s, 3H), 4.05 (q, 2H), 5.00 (2H), 5.55 (s, 1H). IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1725, 1644, 1375, 1220, 1145. XVI, NMR (CCl_4) δ : 1.25 (t, 3H), 1.56 (s, 3H), 1.65 (s, 3H), 1.95 (s, 3H), 2.10 (s, 3H), 4.05 (q, 2H), 5.00 (2H), 5.55 (s, 1H). IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1725, 1642, 1355, 1220, 1155.

5) *Other test compounds*. ($\pm$)-Absciscic acid (Ia), and racemic analogs of IIa, XIX, XXIV and XXX were used for growth assay. ($\pm$)-Ethyl 4'-keto- α -ionylidene-

acetate (X) a stereoisomeric mixture of 2-*cis* and *trans* forms (1:1) was prepared by *tert*-butyl chromate oxidation of ethyl 2-*cis* and *trans*- α -ionylideneacetates (4:6 mixture) and purified by preparative silica-gel TLC (Merck PF₂₅₄) for growth assay. Farnesol (XVI) was purchased from Firmanich Co. Ltd.

Bioassay procedure

Azuki bean seedling growth. Azuki bean seedlings were grown in sunny fields under natural conditions (mainly from May 1 to June 25, 1973, average temperature: 15~20°C) before the following test. In winter, Azuki bean seedlings were grown from seeds in moist Vermiculite at 25°C (2000 lux). Better results were obtained using the former seedlings than the latter. Azuki bean seeds (*Phaseolus angularis* var. Dainagon) were sown in moist soil and grown for about two weeks and uniform seedlings were selected for the tests. Average length of seedlings before the test: Epicotyl 5.5~6.0 cm. Two barerooted seedlings were grown per 200 ml beaker, which contained 20 ml of a 10⁻¹ M acetone solution, prepared from 0.1% Hyponex nutrient solution and test compounds (10⁻³~10⁻⁴ M), at 27~28°C under continuous illumination (2000 lux) for 5 days. The effect on stem elongation between the cotyledonary node and terminal meristem (the length of the epicotyl) was measured on 2~3 replicas for each compound. Length of the control test: Length of the first internode; 14.0~15.0 cm, length of the second internode plus the third internode; 6.0~6.5 cm. The average inhibitory activity found is shown in Table I in terms of percent growth inhibition (control=0%, complete inhibition=100%).

Rice seedling test. Rice seedlings (Honen-Wase, an ordinary variety of *Oryza sativa* L.), which were sterilized with 0.1% HgCl₂ solution and germinated in water for 3 days at 27°C, were grown on 40 ml of 0.7% agar medium in 7.0 cm Petri plates (10 seedlings per dish). After growing at 27~28°C for 5~6 days, the length of the second leaf sheath (distance from the coleoptile joint to the second leaf joint, in the previous report¹¹ the distance from the first leaf tip to the second leaf joint) was measured, as shown in Fig. 2.

Seed germination test. Seeds: Radish (Nerima, an ordinary variety of *Raphanus sativus* L.), French Marigold (*Tagetes patula* L.) and leaf mustard (*Brassica juncea* Coss) were germinated in 7.0 cm Petri plates lined with three disks of filter paper soaked in 10 ml of test solution (10⁻⁴ M). Each experiment was carried out with 2~3 replicates of fifty seeds for lettuce and leaf mustard, and twenty seeds for radish or French Marigold. Emergence of the radicle from the seed coat was taken as the criterion of seed germination. Germination was carried out in a humid box at 27~28°C in the light (2000 lux) and the number of seeds

which germinated was counted. The activities were expressed as a percentage compared to the control (Table II). Also, the growth-inhibitory activity of hypocotyls for germinated radish seeds was measured as shown in Table III.

Growth-inhibitory activity and seed germination test of oat. Seeds (Zenshin, an ordinary variety of *Avena sativa* L.) were germinated and grown in 7.0 cm Petri plates lined with two disks of filter paper soaked in 10 ml of test sample solution (10^{-4} M) at 27°C (2000 lux) for 5 days. The number of germinated seeds was counted and the length of the leaf sheath was measured, as shown in Table III.

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