GROWTH-REGULATING ACTIVITY OF BIS-QUATERNARY SALTS OF PYRROLIZIDINE ALKALOIDS AND THE PRODUCTS OF THEIR TRANSFORMATION

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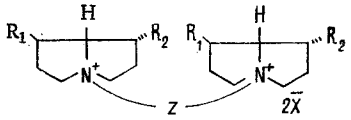
The growth-regulating activity of bis-quaternary salts of the pyrrolizidine series has been studied. It has been established that they possess a retardant activity which depends on the presence of the quaternary nitrogen atom, the acid residue of the molecule, and its configuration.

Many quaternary salts possess retardant properties. The first information on the retardant AMO-1618 is connected with Mitchell's investigation [1].

At the present time the most widely used retardant is chlorocholine chloride (the preparation CCC or TUR). The preparation TUR has found wide use for combatting the lodging of wheat. When the wheat stem is treated with chlorocholine chloride, it shortens and thickens, as a result of which it does not lodge, and its resistance to frost and to drought increases. Chlorocholine chloride also considerably lowers the lodging tendencies of the cotton plant (in a concentration of 0.02% at a rate of consumption of 500 liters/ha) [2]. Consequently, the search for retardants among bis-quaternary ammonium salts of pyrrolizidine alkaloids and some products of their transformation is of theoretical and practical interest. Bis-quaternary ammonium derivatives in general and those based on alkaloids in particular have not been considered as retardants. This class of compounds with the following general formula has been synthesized previously [3-5]:



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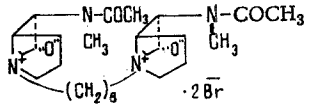

VIII

I. R_1 = H, R_2 = CH_2OH, Z = $(CH_2)_{10}$, X = Br

II. R_1 = H, R_2 = $CH_2OCONHCH_3$, Z = $(CH_2)_{10}$, X = Br

III. R_1 = H, R_2 = $CH_2OCOCH=CH-C_6H_5$, Z = $(CH_2)_{10}$, X = Br

IV. R_1 = $OCOCH=C(CH_3)_2$, R_2 = CH_3, Z = $(CH_2)_5$, X = Br

V. R_1 = $OCOC_6H_4OCH_3$, R_2 = CH_3, Z = $(CH_2)_{10}$, X = Br

VI. R_1 = H, R_2 = $CH_2OCOC(OH)-CH(OH)CH_3$,
$CH(CH_3)_2$

Z = $-CH_2-O$ > $-(CH_2)_2-$ < $O-CH_2-$, X = Cl
$-O$ $O-$

VII. R_1 = H, R_2 = $CH_2OCOC(OH)-CH(OH)CH_3$,
$CH(CH_3)_2$

Z = $-CH_2-O$ > $-CH=CH-$ < $O-CH_2-$, X = Cl
$-O$ $O-$

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TABLE 1. Influence of Bis-quaternary Salts of the Pyrrolizidine Series on the Growth of the Seeds of Plants, % on the Control (Dose of the Preparations 5 kg/ha)

Compound	Cucumber		Barley		Cabbage		Radish	
	roots	shoots	roots	shoots	roots	shoots	roots	shoots
I. Decamethylenebislindelofidinium dibromide	−12	−37	+8	−16	−10	+15	−8	−34
II. Decamethylenebis(0-methylcarbamoyllindelofidinium) dibromide	−8	−34	+4	0	−10	0	−21	−34
III. Decamethylenebis(0-β-phenylacryloyllindelofidinium) dibromide	−40	−34	+8	−10	−20	−39	−21	−51
IV. Pentamethylenebis(0-β,β-dimethylacryloylheliotridanium) dibromide	+4	−17	+8	0	−30	0	0	−28
V. Decamethylenebis(0-4-methoxybenzoylheliotridanium) dibromide	−48	−50	−68	−34	−60	−54	−71	−73
VI. Ethylenebis(N-dioxolanylmethyllindelofine) dichloride	−8	−3	0	0	0	0	+7	+5
VII. Vinylenebis(N-dioxolanylmethyllindelofine) dichloride	+4	−10	−12	−4	−10	0	−22	−17
VIII. Octamethylenebislolininium dibromide	+16	−4	−4	−4	−20	−8	−22	−6
IX. Viridifloric acid	−4	0	+12	−7	−10	0	−8	−23
X. Trachelanthamic acid	+8	+3	+40	+6	−10	−8	+7	−23
XI. Lindelofine	0	−17	+8	−10	+10	+7	+35	+6

Note. +) stimulation; −) inhibition; 0) at the level of the control (water).

The bis-quaternary salts of the pyrrolizidine series have been studied in four tests: cucumber, barley, cabbage, and radish. Different species of plants behave differently under the action of these compounds. Thus, the substances suppress the growth of the roots and shoots of cabbages and radishes. Under the action of N,N'-pentamethylenebis (0-β,β-dimethylacryloylheliotridanium) dibromide (IV) the growth of barley and cucumber roots is stimulated and that of their shoots is suppressed. Thus, the retardant effect of this substance consists in a stimulation of the root system at the expense of the stem part of the shoot.

A derivative of compound (IV) having a β-phenylacryloyl residue — N,N'-decamethylenebis(0-β-phenylacryloyllindelofidinium) dibromide (III), as was assumed, possesses a strongly inhibiting action, suppressing the growth of all the plants. An exception is barley, for which a slight stimulation of the root system is observed. The strongest inhibitor proved to be N,N'-decamethylenebis(0-4-methoxybenzoylheliotridanium) dibromide (V), having residues of hydroxyheliotridane (an isomer of lindelofidine) and also of a plant-growth inhibitor — 4-methoxybenzoic acid. Octamethylenebislolininium dibromide (VIII) stimulates the growth of the root and suppresses the growth of the stem of the shoot in the test on cucumbers.

Thus, experiments have shown that the bis-quaternary salts possess a retardant activity due to the presence of the quaternary nitrogen atom. An important role in inhibition is played by the acid residue of the molecule. It is just this part that may lead to an increase or decrease of the inhibiting action (Table 1).

It is interesting to note that the configuration of the acids present in the alkaloids also plays a role in the stimulation of plants. Thus, while trachelanthamic acid (X) stimulates their growth and development, its erythro isomer viridifloric acid (IX) is an inhibitor and is effective as a retardant in the barley test. It is likely that in the case of trachelanthamic acid, interaction with the enzyme responsible for this activity is more favorable and takes place through the carbonyl and hydroxy groups.

The alkaloid lindelofine (XI) possesses a stimulating activity in all the tests, suppressing only the growth of cucumber shoots.

EXPERIMENTAL

The alkaloid lindelofine was isolated by a modified method from the plant Lindelofia anchusoides [6]. It had mp 105-106°C (from acetone).

Viridifloric acid was obtained by the alkaline hydrolysis of the alkaloid viridiflorine [7], mp 119-121°C (from chloroform), and trachelanthamic acid by the hydrolysis of the alkaloid lindelofine or trachelanthamine, mp 94-95°C (from a mixture of chloroform and petroleum ether).

The symmetrical bis-quaternary ammonium salts (I-VIII) were synthesized by a known method [3-5].

Determination of Inhibiting and Stimulating Activities. The preparations were tested in an agar medium on four test plants sensitive to inhibiting and stimulating activities: cucumber, barley, cabbage, and radish.

Seeds of the test plant were sown in a Petri dish containing 50 ml of a 1% solution of agar-agar with the addition of 0.5 ml of a 0.4% aqueous solution of the preparation, and were kept in a thermostat at 27°C for seven days. After this, the lengths of the rootlets and shoots of the test plants were measured in each experiment and their mean values were calculated. Inhibition or stimulation was determined by comparison with control plants. The experiments were performed in duplicate. The results of the tests are given in Table 1.

SUMMARY

It has been shown that bis-quaternary salts of pyrrolizidine alkaloids and the products of their transformation possess a retardant activity which depends on the presence of the quaternary nitrogen atom and of the acid residue of the molecule and on the configuration of the latter.

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