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## Effect of the action of some chemical substances on the degree of injury caused by SO<sub>2</sub>\*

Numerous studies concerning the effect of gaseous emissions from industry aim at the discovery of methods that would allow lowering the injury to plants by these emissions and at the identification of mechanisms by which the gases injure plants and plants defend themselves from such injury. So far most commonly solutions of salts were used which are cations of heavy metals such as Ag, Hg, Cd and Ni (Obydiennyj, 1977). These are sprayed on plants to neutralize them against gases on the plant surface. On the other hand, in order to establish the mechanism by which gases injure plants and plants defend themselves use is made of some chemical compounds which reduce injuries by changing the metabolism of the plants. Koiwai et al. (1974). have used several chemical compounds which are derivatives of methylenedioxyphenyl and other compounds such as amino acids, vitamins, cytokinins etc. The spraying of leaves with solutions of these compounds have in several instances reduced the injury caused by O<sub>3</sub> compared to untreated control plants.

Studies on the effect of chemical compounds causing changes in the metabolic process of plants and thereby reducing their injury by gases appear to be a good means of establishing the mechanisms of plants injury and of the defence mechanisms that plants possess.

A. Effect of the action of several inorganic salts on the lowering of the degree of damage to needles of Scots pine by SO<sub>2</sub>.

Needles of detached shoots from one of the individuals of Scots pine have been treated with 2 mM solutions of silver nitrate, thorium nitrate, vanadium pentoxide, cobalt nitrate by means of dipping in the solutions. The wetted twigs were then placed in vials, with the cut surfaces in water, and the wetted needles were allowed to absorb the salt solutions. One part of the shoots constituted the control, while the other was treated with gas. Degree of injury to needles of shoots treated with the solutions

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and untreated, both fumigated with  $\text{SO}_2$  and controls have been listed in Table 1.

It was established that the degree of injury caused by  $\text{SO}_2$  to needles was reduced by the treatment with  $\text{AgNO}_3$ ,  $\text{Th}(\text{NO}_3)_4$  and  $\text{V}_2\text{O}_5$  relative to the untreated control (where only water was used). In the case of plants treated with  $\text{AgNO}_3$  without  $\text{SO}_2$  fumigation there were injuries caused by the salt which was probably used at a too high concentration.

B. Effect of benzimidazol and  $\alpha, \alpha'$ -dipyridyl on the degrees of injury by  $\text{SO}_2$  to two varieties of *Weigela*.

Table 1

Mean values of injury to needles of Scots pine shoots treated with solutions of chemical compounds following fumigation with  $\text{SO}_2$

Compound used	Concentration of $\text{SO}_2$ used in ppm	
	4.0	0.0
	degrees of injury	
$\text{AgNO}_3$	1.14 a	0.83 b
$\text{Th}(\text{NO}_3)_4$	1.75 ab	0.24 a
$\text{Co}(\text{NO}_3)_2$	1.83 ab	0.12 a
$\text{V}_2\text{O}_5$	2.45 bc	0.00 a
Water	2.97 c	0.14 a

Detached shoots of two *Weigela* varieties, the more resistant *W. Van Houtte*' and the less resistant *W. florida*, have been placed in containers with water. Half of the shoots were placed into containers with solutions of benzimidazol and  $\alpha, \alpha'$ -dipyridyl and the leaves were covered with the solutions of these compounds. The wetting of the leaves with the solution of benzimidazol and  $\alpha, \alpha'$ -dipyridyl was performed twice, immediately after cutting the shoots and two days later, and on the third day after cutting the shoots were fumigated with sulphur dioxide. Simultaneously another batch of the plants which were held for the whole time, that is from the moment of cutting, dipped with cut surfaces in solutions of benzimidazol and  $\alpha, \alpha'$ -dipyridyl, were likewise fumigated. The shoots which were held in water only and those which had their leaves treated with water only were considered as controls, and were not fumigated with  $\text{SO}_2$ . In order to establish whether the solutions of benzimidazol and  $\alpha, \alpha'$ -dipyridyl do not injure the leaves shoots held in these solutions and those in water but with the leaves treated were transferred to control conditions without  $\text{SO}_2$ .

The concentration of solutions of benzimidazol and of  $\alpha, \alpha'$ -dipyridyl were 2.5, 5.0 and 7.5 mM. The shoots were exposed to the action of sulphur dioxide for two days 6 hours daily at concentrations of 2.0 ppm  $\text{SO}_2$ . Results of the experiment are present in Table 2.

On the basis of the evaluation of injuries to leaf surfaces it was established that the used solutions of benzimidazol did not reduce injuries in the case of the susceptible variety *W. florida* compared to untreated leaves. In the case of more resistant variety even an increase  $\text{SO}_2$  injury was observed following treatment of shoots with solutions of this compound at all concentrations used and treatment of the leaves only at the concentration 7.5 mM compared with the controls.

Table 2

Effect of benzimidazol and  $\alpha, \alpha'$ -dipyridyl on the degree of injury to leaves of *Weigela'van Houtte'* and *W. florida*, subjected to the action of 2.00 ppm of  $\text{SO}_2$  for 12 hours

Method of treatment and millimolar conc. of compounds used.	<i>Weigela</i>				
	<i>'Van Houtte'</i>	concentration of $\text{SO}_2$		<i>florida</i>	
		2.0	0.0	2.0	0.0
	degree of injury				
Shoots in solution of benzimidazol					
2.5	2.74 cd*	0.20 a	3.97 ef	0.17 a	
5.0	2.84 cd	0.41 a	4.20 f	0.34 a	
7.5	2.70 cd	0.31 a	3.65 def	0.29 a	
Leaves covered with benzimidazol					
2.5	1.78 abc	0.60 a	2.64 cd	0.35 a	
5.0	1.39 ab	0.36 a	3.07 de	0.51 a	
7.5	2.27 bcd	0.30 a	3.74 def	0.34 a	
Shoots in solution of $\alpha, \alpha'$ -dipyridyl					
2.5	2.60 cd	0.27 a	0.48 a	0.08 a	
5.0	3.35 d	0.23 a	1.59 abc	0.23 a	
7.5	1.01 a	0.41 a	3.00 de	0.35 a	
Leaves covered with $\alpha, \alpha'$ -dipyridyl					
2.5	1.90 abc	0.46 a	1.78 bc	0.12 a	
5.0	2.10 abc	0.22 a	0.71 ab	0.20 a	
7.5	1.05 a	0.56 a	1.58 abc	0.25 a	
Untreated leaves					
0.0	2.01 abc	0.27 a	3.18 def	0.23 a	

\*The letters a, b, c, d, e and f indicate that the results belong to a common undifferentiated group at 0.05 level. In grouping the data use was made of the Duncan test.

A significant reduction in the injury to leaves was observed in the sensitive variety where shoots were treated with solutions of  $\alpha, \alpha'$ -dipyridyl at the three concentrations used and leaves were treated with 5.0 and 7.5 mM.

For the more resistant variety *W.'Van Houtte'* a reduction in the damage to leaves was not observed following treatment with a solution of  $\alpha, \alpha'$ -dipyridyl whether of whole shoots of leaves only. In this case only an increase in injury to plants can be observed following some of the treatments. The use of lower concentrations of  $\alpha, \alpha'$ -dipyridyl, 2.5 and 5.0 mM has caused even significant increases in the injuries of leaves of shoots placed in these solutions.

## DISCUSSION OF RESULTS

The results obtained appear to indicate that dipyriddy acts protectively on the plants whereas benzimidazol increases the injuries caused by fumigation with  $\text{SO}_2$  in the experimental conditions described above.

$\alpha, \alpha'$ -dipyriddy is a compound that inhibits hydroxylation of proline to hydroxyproline, while benzimidazol is a promoter of the synthesis of hydroxyproline (Giebel and Krenz, 1975). Cell walls contain glycoproteids characterized by a high content of hydroxyproline (Lampert and Northcote, 1960; Lampert, 1965). Young rapidly growing tissues have a low level of hydroxyproline associated with polysaccharides of cell walls in contrast to old tissues (Lampert, 1967).

The action of industrial gases hastens ageing of assimilation organs. In wilted and drying leaves even a several-fold increase in the content of proline is observable (Britikow, 1975), and the increase in proline content is correlated with the resistance of plants to draught (Ling et al., 1972) after Britikow (1975). Thus it appears possible that the higher resistance of plant to the action of gases is associated with a higher content of proline in leaves. A shift in the balance between hydroxyproline and proline in the direction of the latter amino acid, following the action of dipyriddy, would explain the increase in the resistance of plants following treatment with this solution.

Hsiao (1973), after Britikow (1975) suggests that proline may be oxidized to  $\text{CO}_2$  when carbohydrates are lacking, which is what happens in plants under the toxic action of gases.

After the action of gases that are acid in nature, as is the case with  $\text{SO}_2$ , there may result in the plants a liberation of ammonia similarly as during draught. In proline synthesis, similarly as in the synthesis of amides the toxic ammonia is bound Procenko et al., 1968, after Britikow, 1975).

The action of toxic gases on plants causes in them a substantial degradation of chlorophyll. The possibility of rebuilding chlorophyll as suggested by Gusiew and Gordon (1968) after Britikow (1975) by the decarboxylation of proline into pirolidine, which subsequent rearrangement into pyrol that is a component of chlorophyll might also explain the defensive influence of  $\alpha, \alpha'$ -dipyriddy which causes a relative increase in the level of proline in plants.

## SUMMARY

In the study the effect of some chemical compounds (salts, oxides and two organic compounds benzimidazole and  $\alpha, \alpha'$ -dipyriddy) on the lowering of plant injury by sulphur dioxide was investigated.

The spraying of needles of detached Scots pine shoots by  $\text{AgNO}_3$ ,  $\text{Th}(\text{NO}_3)_4$ ,  $\text{V}_2\text{O}_5$  and  $\text{Co}(\text{NO}_3)_2$  has caused a lowering of needle injury (in declining order respectively) by  $\text{SO}_2$  compared to plants that were also fumigated with  $\text{SO}_2$  but not pretreated.

The use of benzimidazole and  $\alpha, \alpha'$ -dipyridil as sprays or dips has resulted in the latter compound reducing leaf injury of two *Weigela* varieties ('*Van Houtte*' and *florida*) by  $\text{SO}_2$ .

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### Wpływ działania niektórych związków chemicznych na stopień uszkodzenia roślin przez $\text{SO}_2$

#### Streszczenie

W pracy przedstawiono wpływ niektórych związków chemicznych typu soli i tlenków nieorganicznych oraz dwóch związków organicznych: benzimidazolu i  $\alpha, \alpha'$ -dwupirydyli na obniżenie uszkodzenia roślin przez dwutlenek siarki.

Opryskiwanie igieł odciętych pędów sosny zwyczajnej roztworami  $\text{AgNO}_3$ ,  $\text{Th}(\text{NO}_3)_4$ ,  $\text{V}_2\text{O}_5$  i  $\text{Co}(\text{NO}_3)_2$  powodowało (w podanej kolejności) obniżenie stopnia uszkodzenia igieł przez  $\text{SO}_2$  w porównaniu z roślinami nietraktowanymi tymi związkami a tylko  $\text{SO}_2$ .

Stosowanie roztworów benzimidazolu i  $\alpha, \alpha'$ -dwupirydyli (opryskiwanie liści lub umieszczanie pędów w roztworach) powodowało w przypadku roztworu  $\alpha, \alpha'$ -dwupirydyli redukcję uszkodzenia liści dwóch odmian *Weigela*: '*Van Houtte*' i *W. florida*.

ПЕТР КАРОЛЕВСКИ

Влияние действия некоторых химических соединений на степень повреждаемости растений SO<sub>2</sub>

Резюме

В работе проверялось влияние некоторых химических соединений типа солей и неорганических окисей, а также двух органических соединений: бензимидазола и α,α'-дипиридила на уменьшение повреждений растений сернистым ангидридом.

Обработка хвон срезанных побегов сосны обыкновенной растворами AgNO<sub>3</sub>, Th(NO<sub>3</sub>)<sub>4</sub>, V<sub>2</sub>O<sub>5</sub> и Co(NO<sub>3</sub>)<sub>2</sub> вызывала (в выше указанной последовательности) уменьшение повреждений хвон SO<sub>2</sub> по сравнению с побегами не обработанными этими соединениями.

Применение растворов бензимидазола и α, α'-дипиридила (опрыскивание листьев или погружение оснований побегов в раствор) вызывало, в случае применения α,α'-дипиридила, уменьшение повреждений листьев двух разновидностей Weigela 'Van Houtte' и W. florida.