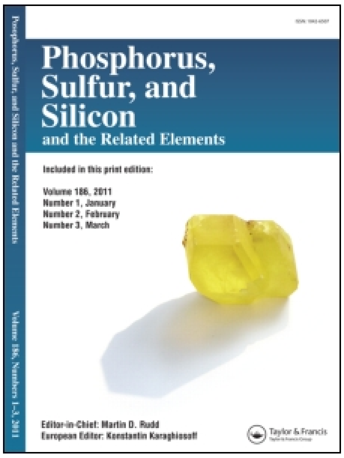

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Phosphonic analogues of morphactines

Roman Gancarz[a]; Paweł Kafarski[a]; Barbara Lejczak[a]; Przemysław Mastalerz[a]; Jan Sylwester Wieczorek[a]; Elzbieta Przybyłka[b]; Witold Czerwinski[b]
[a] Institute of Organic and Physical Chemistry, Technical University of Wrocław, Wrocław, Poland [b] Institute of Plant Biology and Biophysics, Agricultural Academy, Wrocław, Poland

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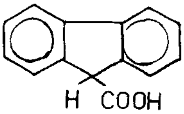
PHOSPHONIC ANALOGUES OF MORPHACTINES

ROMAN GANCARZ , PAWEŁ KAFARSKI , BARBARA LEJCZAK ,
PRZEMYSŁAW MASTALERZ , JAN SYLWESTER WIECZOREK ,
Institute of Organic and Physical Chemistry,Technical
University of Wrocław,50-370 Wrocław,Poland

ELŻBIETA PRZYBYŁKA and WITOLD CZERWIŃSKI
Institute of Plant Biology and Biophysics,Agricultural Academy,
50-375 Wrocław,Poland

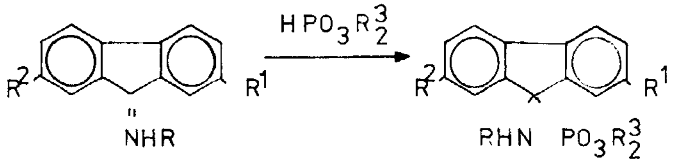
Abstract Derivatives of 9-aminofluorene-9-phosphonic acid and 9-aminofluorene-9-phosphinoxides,the phosphonic analogues of morphactines,were synthesized.All the obtained compounds showed marked morphactin-like activity against test plants: Spirodela oligorrhiza and Lepidium sativum.

Derivatives of fluorenecarboxylic acid 1,known as morphactines[1], appear to be one of the most interesting,synthetic plant growth regulators.They show strong influence on plant morphogenesis and development,and usually exhibit synergism with known herbicides or natural plant hormones.



1

Studying the effect of replacement of carboxylic moiety in amino acids by phosphonic group on their activity against chosen plant systems we focused our interest on derivatives of 9-aminofluorene-9-phosphonic acid - phosphonic analogues of morphactines 2.They were prepared[2] by known addition of dialkyl phosphites to imines according to the scheme:



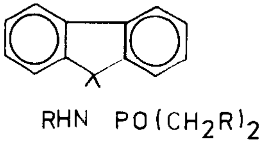
$R = H, Ph, Bu^n, Bu^s, Hep^n$
$R^1, R^2 = H, Cl, Br, NO_2$
$R^3 = Me, Et, Bu^n$

2

It is worth noticed that the dialkyl esters of 9-aminofluorene-9-phosphonic acid as well as their N-alkyl derivatives underwent partial decomposition during hydrolysis with concentrated hydrochloric acid or acidolysis with hydrogen bromide in glacial acetic acid solution,yielding fluorenone.The reaction rates strongly depended on the nitrogen substituent.For example,aromatic substituents strongly promoted the decomposition reaction while dialkyl 9-aminofluorene-9-phosphonates were quite stable.

The physiological activity of the derivatives 2 was tested against Spirodela oligorrhiza and Lepidium sativum.Nearly all of the tested compounds affected the growth of both tested plants. Esters of 9-/N-butylamino/fluorene-9-phosphonic and 9-/N-heptylamino/fluorene-9-phosphonic acids were the most effective.They inhibited the growth of Spirodela by 50% in concentrations of 0,5-1,5 10^{-5} mole per liter.Also most of the tested analogues showed strong synergism with 2,4-D and mecoprop.Phosphonate if applied with sublethal dose of herbicide caused lethal effect on Spirodela oligorrhiza within 10-20 hours.

In order to explain the mechanism of action of phosphonic analogues of morphactines,which may consist in active transport of dialkyl phosphonate 2 into the plant tissues followed by its hydrolysis yielding phosphonic acid which is responsible for herbicidal action,we synthesised a series of phosphinoxides 3.In these compounds the ester oxygen of 2 is replaced by methylene fragment yielding "non-hydrolysable" analogue.



$R = H, Bu^n, Bu^i, Bu^s, Am^n, Am^i$

$R^1 = Pr^n, Bu^n, Pr^i$

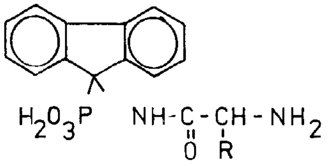
3

The activity of the obtained phosphinoxides 3 against *Lepidium sativum* was nearly the same as activity of the corresponding esters 2, while against *Spirodela oligorrhiza* concentrations of 3 in order of magnitude lower than 2 caused the same lethal effect.This clearly indicates that the ester group is not hydrolysed during herbicidal action.Surprisingly,the phosphinoxides 3 exhibited antagonistic effect if applied with mecoprop,i.e.the opposite effect to compounds 2.

Trying to improve the activity of 9-aminofluorene-9-phosphonic acid we synthesized its P-terminal peptides 4 assuming that they could be better transported into the plant tissue.The peptides were prepared by coupling diethyl 9-aminofluorene-9-phosphonates with N-benzyloxycarbonylamino acids using standard mixed carboxylic-carbonic anhydride procedure,followed by removal of blocking groups with hydrogen bromide in glacial acetic acid solution.The sieries of phosphonopeptides 4 containing N-terminal alanine,leucine,valine, phenylalanine,proline,threonine,glutamine,lysine,methionine and glycilglycine was prepared in this manner.Also in this case we have noticed the carbon-phosphorus bond cleavage under basic conditions during peptide synthesis as well as during deblocking step.

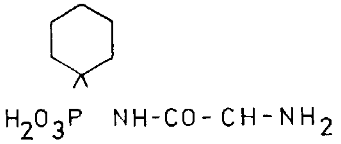
Preliminary biological tests performed using *Lepidium sativum* showed interesting properties of the obtained peptides.They exhibited typical morphactin-like activity influencing plant morphology.

The kind of the morphological changes of the plant strongly depended on the N-terminal fragment of the peptide 4.



4

The observed effects were quite similar to those found for the peptides of known herbicide 1-aminocyclohexanephosphonic acid 5. This data,and similarity between structure-activity relationship for aminophosphonates 2 and derivatives of 1-aminocyclohexanephosphonate 6 /among which the most effective is herbicide Trakephon[3], where $R = R^1 =$ Bu-n/ suggest the same mechanism of action of these two groups of aminophosphonates.



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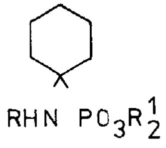

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