

An evaluation of the physiological activity of 9-amine-9-fluorenephosphonic acid derivatives

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Abstract

The physiological activity of eleven 9-amine-9-fluorenephosphonic acid derivatives, synthesized at the Wrocław Polytechnic, was examined. The test plant was *Spirodela oligorrhiza*. The effect of these compounds on the increase of the dry matter of this plant was tested in eight-day experiments. The activity of the compounds was varied. The most toxic were nos. 2, 4, 9, 8, 5 and 6 which were lethal in low concentrations. Somewhat less toxic were nos. 7, 10 and 11; nos. 1 and 3 were the least toxic.

INTRODUCTION

Derivatives of 9-amine-9-fluorenephosphonic acid are newly synthesized compounds with a structure and activity similar to morphactins. Fluorene derivatives, of which morphactins are typical examples, exert a strong influence on plant physiological processes, especially on morphogenesis (Mohr and Ziegler, 1969; Schneider, 1970; Bopp, 1972; Katsumi, 1973). An interesting property of some morphactins is their synergistic interaction with herbicides (Pieniążek and Saniewski, 1969; Schneider, 1970; Jindal and Singh, 1976). The addition of morphactins to herbicides increases their weed-killing effectivity which, in agricultural practice, allows the herbicide dose to be lowered, thereby decreasing environmental pollution. The physiologic activity of morphactins is highly dependent on the type of substituent in position 9 of fluorene (Mohr and Ziegler, 1969). During 1980-1981, fluorene derivatives substituted at position 9 with amine or phosphonic groups were studied in our Department from the point of view of their physiologic activity in plants (Czerwiński et al., 1982).

The purpose of this study was to determine the physiologic activity of a new group of fluorene derivatives having different substituents in

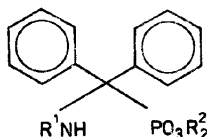
position 9. These compounds were synthesized at the Institute of Organic and Physical Chemistry of the Wrocław Polytechnic by a team headed by Doc. J. S. Wieczorek (Gancarz and Wieczorek, 1980; Czerwiński et al., 1982; Gancarz et al., 1983).

MATERIAL AND METHODS

Studies on the physiologic activity of the investigated compounds were done on *Spirodela oligorrhiza* (duckweed great). This plant has been used for many years in our Department for studies on the activity of herbicides and other tested compounds (Knypl et al., 1976; Czerwiński, 1982; Skrabka et al., 1984). It is an aquatic, flowering plant which quickly reproduces vegetatively. This species is very sensitive to toxic substances and reacts quickly and distinctly by changes in leaf (frond) color, arrest of divisions, growth and dry weight increases.

The plants were cultivated on a special, sterile medium, under constant external conditions, in 100 cm³ Erlenmeyer flasks containing 50 cm³ of medium. A modified Hoagland's medium was used (Czerwiński et al., 1982). Solutions of the studied compounds were added to sterilized mineral nutrient solutions. The final concentrations of the studied compounds (after addition to and mixing with the medium) were: 0.5×10^{-5} M, 2×10^{-5} M, 8×10^{-5} M, 32×10^{-5} M and 64×10^{-5} M. Two *Spirodela* plants (2 trifronds) were placed in a sterile way into each flask. Plants growing on mediums with no additional additives served as controls. The experiment was run in triplicate. Vegetation time was 8 days. The plants remained in the photostat all day, illuminated by artificial lighting of approx. 5000 lux and at a temperature of 26°C. After 8 days, the dry weight of all of the plants was determined.

A list of the 11 studied 9-amine-9-fluorenephosphonic acid derivatives, differing by the substituent in position 9 of fluorene, is presented below.



RESULTS

Distinct differences in the activities of the studied compounds were evident. These compounds can be divided into 3 groups. The derivatives numbered 2, 4, 9, 8, 5 and 6 (Figs. 1 and 2) fall into the first group. They are characterized by a strong inhibitory effect on the dry matter increase of *Spirodela*; at the relatively low concentration of 8×10^{-5} M,

Numeration of fluorene derivatives (morphactins)	Substituents in position at 9-fluorene	
	R ₁	R ₂
1	-NH ₂	-P(O) (OEt) ₂
7	-NH ₂	-P(O) (OisoPr) ₂
8	n-Butyl-NH-	-P(O) (OBu) ₂
9	n-Butyl-NH-	-P(O) (OisoPr) ₂
3	iso-Butyl-NH-	-P(O) (OH) ₂
2	iso-Butyl-NH-	-P(O) (OEt) ₂
10	iso-Butyl-NH-	-P(O) (OBu) ₂
5	sec-Butyl-NH-	-P(O) (OMe) ₂
4	sec-Butyl-NH-	-P(O) (OisoPr) ₂
6	sec-Butyl-NH-	-P(O) (OBu) ₂
11	$\begin{array}{c} \text{H} \\ \\ \text{Ph-N-C-NH-} \\ \\ \text{O} \end{array}$	-P(O) (OisoPr) ₂

about 16 ppm, they already inhibit growth by almost 90% and almost totally destroy the plants. Compounds numbered 7, 10 and 11 (Figs. 2 and 3) are in group 2 — they exhibited a lower toxicity, nonetheless, it was still evident. They inhibited plant growth by 80% at a concentration of 32×10^{-5} M (110-150 ppm), a much higher concentration than the compounds in group 1. Compounds numbered 1 and 3 (Fig. 3) with a relatively low activity, are assigned to group 3. When used in high concentrations, 64×10^{-5} M, (225 ppm), they inhibited growth by 30-40%.

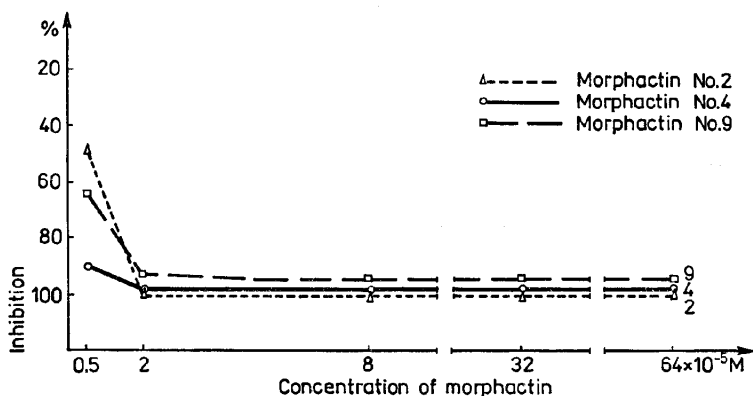


Fig. 1. The effect of 9-amine-9-fluorene phosphonic acid derivatives Nos. 2, 4, 9 on the increase of dry matter of *Spirodela* plants in 8-day long experiments, expressed in percent of inhibition

An important aspect of studies of this kind is the correlation of the phytotoxicity of compounds with their chemical structure, especially of the R₁ and R₂ substituents in position 9 of fluorene. However, on the

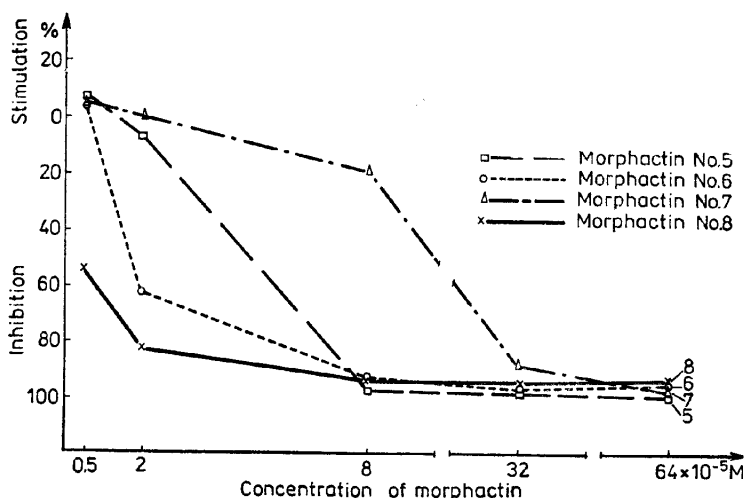


Fig. 2. The effect of 9-amine-9-fluorenephosphonic acid derivatives Nos. 5, 6, 7, 8 on the increase of dry matter of *Spirodela* plants in 8-day long experiments, expressed in percent of stimulation or inhibition

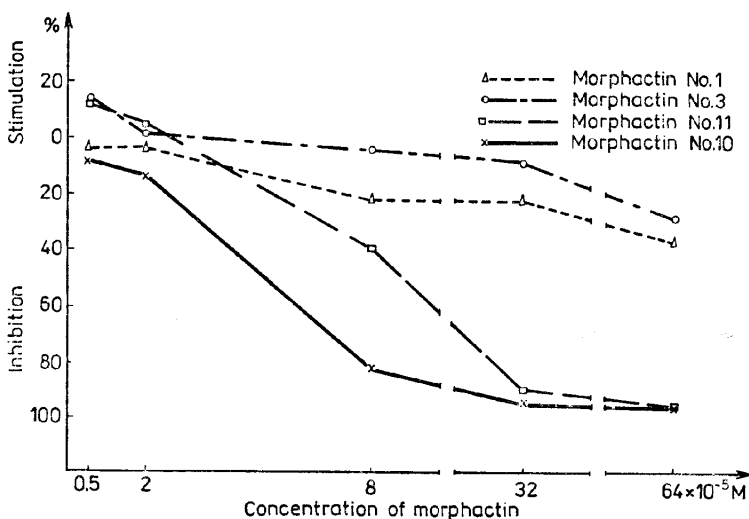


Fig. 3. The effect of 9-amine-9-fluorenephosphonic acid derivatives Nos. 1, 3, 11 and 10 on the increase of dry matter of *Spirodela* plants in 8-day long experiments, expressed in percent of stimulation or inhibition

basis of these experiments, it is difficult to find an unequivocal relationship between structure and phytotoxicity. Certain dependencies were found in respect to compounds 8 and 9; they have the same substituent — n-Butyl-NH-, and a similar activity. A similar relationship exists between compounds 5 and 6 (substituent R_1 sec-Butyl-NH-) and 8 and 6 (substituent R_2 — $-P(O)(OBu)_2$).

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OCENA AKTYWNOŚCI FIZJOLOGICZNEJ POCHODNYCH KWASU
9-AMINOFLUORENO-FOSFONOWEGO-9

Streszczenie

Przebadano aktywność fizjologiczną 11 pochodnych kwasu 9-aminofluoreno-fosfonowego-9 zsyntetyzowanych na Politechnice Wrocławskiej. Rośliną testową była *Spirodela oligorrhiza*. Badano wpływ tych związków na przyrost suchej masy rośliny testowej w 8-dniowych doświadczeniach. Badane związki charakteryzowały się różną aktywnością. Najbardziej toksyczne były związki nr 2, 4, 9, 8, 5 i 6 [w niskich stężeniach niszczyły rośliny]. Nieco mniej toksyczne były związki nr 7, 10 i 11, a mało toksyczne — nr 1 i 3.