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Preparation of Phytoactive Polymers Derived from Mono- and Bispiperidols with Growth-Stimulating Properties

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Abstract—Optimal conditions for the synthesis of phytoactive polymers from mono- and bispiperidols and maleic anhydride copolymers were found. The growth-stimulating activity of these polymers was tested on arid cultures.

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To improve the germinating capacity of seeds and enhance the resistance of plants to natural stress factors, synthetic biologically active substances (BASs) improving the formation of the root system and accelerating the growth and development of plants are used along with phytohormones. It is apparently preferable to use polymeric growth regulators exhibiting prolonged effect, high biological efficiency at small dosages, and single action in the vegetation period.

In this study, with the aim to obtain phytoactive polymers stimulating the growth of plants, including arid cultures, we examined the immobilization of 1,4-bis[*N*-(2-ethoxyethyl)-4-hydroxypiperid-4-yl]buta-1,3-diyne (Kaz-4) and 1,2,5-trimethyl-4-dimethoxyphosphorylpiperid-4-ol (Fospinol, ASA) with 1,4-bis-(1,2,5-trimethyl-4-hydroxypiperid-4-yl)buta-1,3-diyne (Akpinol, AE) on maleic anhydride copolymers. It is known that Fospinol affects to a greater extent the growth of tops, whereas Akpinol stimulates the root formation; therefore, the development of a polymeric plant growth regulator containing both these piperidols is of interest from both scientific and practical viewpoint.

Biologically active polymers were prepared by polymer-analogous transformations in a dimethyl sulfoxide solution. As starting polymers we used copolymers of maleic anhydride with styrene (Styromal, StMA) and with acrylic acid (AAMA). These copolymers, which are mainly alternating [1], allow immobilization of a BAS uniformly along the macromolecular chain. This feature allows prediction of the properties of phytoactive polymers being synthesized and facilitates further standardization and certification of agricultural agents based on them.

EXPERIMENTAL

To prepare a mixed polymeric monoester of Akpinol, Fospinol, and Styromal, a 1.212-g portion of StMA (0.006 mol) was charged into a two-necked flask equipped with a stirrer and was dissolved in 9.5 ml of DMSO at 60°C within 5–10 min. After the StMA dissolved completely, the temperature was raised to 90°C, and 0.7532 g (0.003 mol) of Fospinol and 0.4 ml (0.003 mol) of triethylamine (TEA) were added. Two hours later, 0.996 g (0.003 mol) of Akpinol, 9.1 ml of DMSO, and 0.4 ml (0.003 mol) of TEA were added. The reaction mixture concentration was 15 wt %, and total reaction time, 4.5 h. After the lapse of the prescribed time, the synthesis was stopped, and the polymer solution was slowly poured while hot into a precipitant mixture (150 ml of acetone, 30 ml of isopropyl alcohol, and 20 ml of 8% KOH solution in isopropyl alcohol). The mixture was allowed to stand for 15 min, after which the precipitate was filtered off at reduced pressure, washed on the filter with isopropyl alcohol, and filtered once more. The precipitate was transferred into a Petri dish and dried first at room temperature and then in a vacuum oven at 35°C

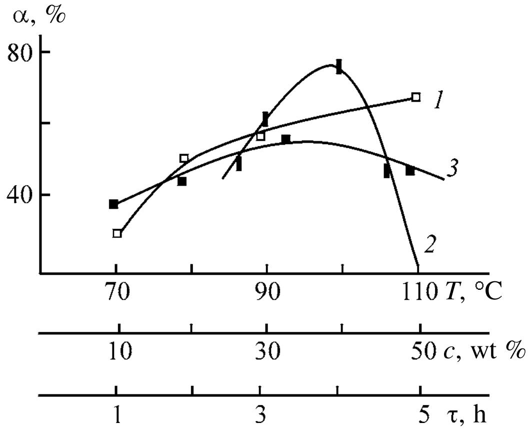


Fig. 1. Degree of immobilization α of a BAS on the copolymer as a function of the (*1*) reactant concentration *c*, (*2*) temperature *T*, and (*3*) reaction time τ.

to constant weight. Yield 2.701 g. The degree of immobilization determined by potentiomeric titration was 75 mol %. The IR spectrum contained a new band at 1710 cm^{-1} (ester groups).

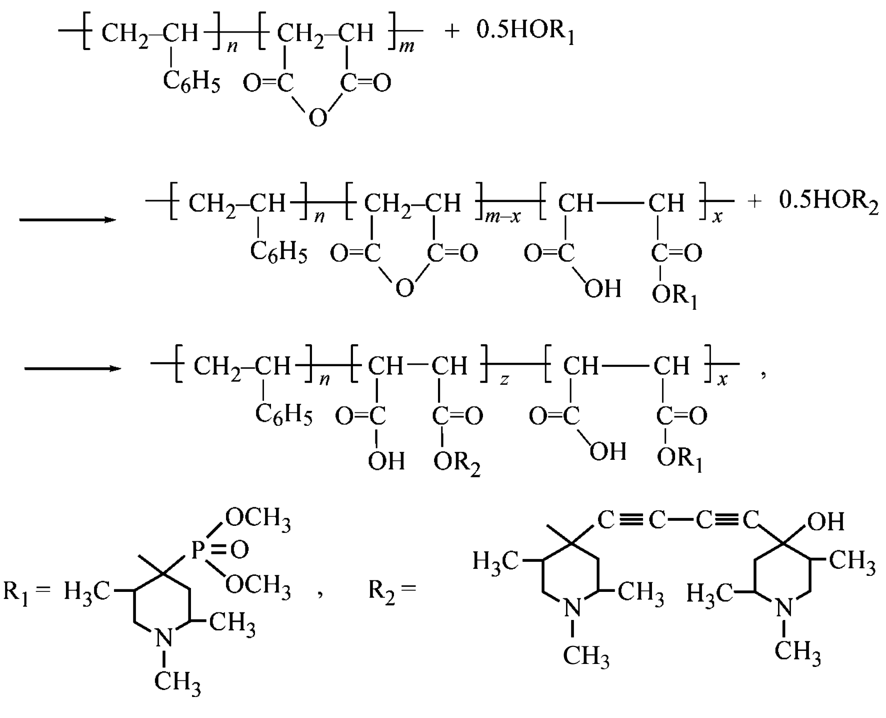
The biologically active polymers derived from Kaz-4 and Akpinol were prepared similarly.

The styrene–maleic anhydride copolymer (Kaustik Research and Production Association, molecular weight 40 000) was purified to remove residual monomer by reprecipitation from cyclohexane into petroleum ether and then was subjected to additional anhydridization in a vacuum at 200°C. The IR spectrum contained bands at 1770–1850 and 1080–1220 cm^{-1} (anhydride ring). The content of anhydride groups was 39 mol %.

Akpinol and Fospinol (submitted by the Laboratory of Chemistry of Physiologically Active Compounds, Bekturov Institute of Chemical Sciences, Ministry of Education and Science of Kazakhstan Republic) were used without additional purification. The physical constants agreed with the published data [2].

The amount of anhydride groups and degree of immobilization were determined by procedures described in [3].

The IR spectra of the starting and synthesized compounds were recorded on a Jasco IR-810 spectrometer (Japan) in KBr pellets against pure KBr pellet in the range 4000–400 cm^{-1}. The reactions of StMA with Fospinol and Akpinol followed the scheme



The reactant ratio was calculated per mole of elementary unit containing anhydride ring: copolymer : ASA : AE = 1.0 : 0.5 : 0.5. The IR spectrum confirmed the formation of an ester bond, and elemental analysis confirmed the presence of P and N.

To determine the optimal synthesis conditions, we examined the effect of various factors on the degree of immobilization of BAS on the copolymer.

Figure 1 shows how the degree of immobilization of ASA and AE on StMA depends on the temperature, reaction time, and concentration of the reactants. With an increase in the concentration of the reaction solution to 30 wt %, the BAS content increases to 67.4 mol % (curve *1*). However, at this concentration the mixture becomes viscous, which prevents complete removal of the unchanged reactants. Therefore, it is not appropriate to use higher concentrations. The temperature dependence (curve *2*) passes through a maximum, and this point is shifted toward higher temperatures compared to experiments on immobilization of each BAS taken separately [2]. The highest degree of immobilization, 77.1 mol %, is attained at 100°C. An increase in the reaction time (Fig. 1, curve *3*) leads to a gradual increase in the BAS content. The maximal degree of immobilization is attained in the 4-h reaction.

The influence exerted on the degree of immobilization of phytoactive substances by the reaction time in the presence and in the absence of a catalyst and at different temperatures was examined in more detail; the results are shown in Fig. 2. The molar ratio of the reactants, copolymer : BAS : catalyst, was 1 : 1 : 1; the concentration, 15 wt %; and the temperature, 75 and 90°C.

At 75°C (Fig. 2, curve *1*), the maximal degree of immobilization (35.6%) is attained in 4 h. As the temperature is raised to 90°C (curve *2*), the degree of immobilization increases to 51.3%, and the effective time of BAS binding decreases to 3 h. Addition of TEA as catalyst (curve *3*) increases the degree of BAS immobilization to 57.3 mol %. The difference between the BAS amounts in the absence and in the presence of TEA is minor, which confirms the previously revealed capability of piperidols (in particular, ASA) for autocatalysis [2]. Figures 1 and 2 show that the temperature dependence of the degree of BAS immobilization passes through a maximum. A decrease in the content of immobilized BAS with an increase in the temperature above the optimal level is caused by the fact that esterification is an equilibrium process, and on reaching the maximal conversion the reverse process starts to prevail.

We determined the degree of immobilization of each piperidol separately. The results are given in the table. It is seen that addition of TEA increases the binding of the first component: ASA reacts almost completely within 4 h, and the degree of immobilization is 48.3 mol %, whereas the AE content is as low as 9.0%. In the absence of TEA, as seen from the table, the maximal content of ASA in the polymer decreased to 31.5%, but the degree of AE immobilization increased to 19.8 mol %. At 75 and 90°C, in the absence of the catalyst, the trend was similar; in the initial period (1–2 h), the content of both BASs was comparable, but in the subsequent period the amount of bound ASA increased and that of bound AE decreased. Thus, by varying the reaction conditions, it is possible to control the BAS ratio in the bioactive polymer.

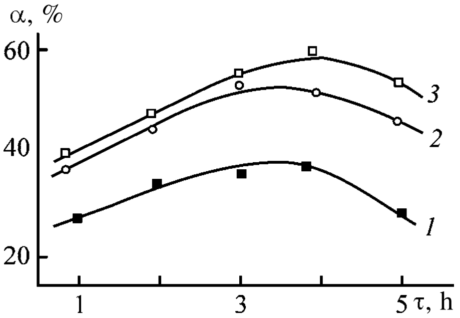


Fig. 2. Degree of immobilization α as a function of the reaction time τ at (*1*) 75 and (*2*, *3*) 90°C (*1*, *2*) in the absence and (*3*) in the presence of the catalyst.

The immobilization of Kaz-4 on StMA was studied similarly. The optimal conditions appeared to be as follows: copolymer : BAS ratio 1 : 1, 85–90°C, 3.5 h, concentration of the reactants 15–20 wt %. Under these conditions, the degree of immobilization determined by potentiometric titration was 35.4%. Addition of 1 mol of TEA per anhydride group increased this parameter to 54.0 mol %.

The use of AAMA as polymeric carrier allowed

Influence of the reaction temperature and time on the degree of BAS immobilization

T, °C	τ, h	Degree of immobilization, mol %		
		Fospinol	Akpinol	total
75	1	13.8	27.6	41.4
	2	19.1	33.3	52.4
	3	20.7	34.6	55.3
	4	25.3	35.6	60.9
	5	15.0	28.9	43.9
90	1	21.4	47.1	68.5
	2	30.6	50.5	81.1
	3	31.5	51.3	82.8
	4	28.9	47.9	76.8
	5	22.2	40.0	62.2
90 (in the presence of TEA)	1	38.4	39.3	77.7
	2	43.8	42.3	86.1
	3	48.5	48.6	97.1
	4	56.0	49.3	105.3

preparation of a water-soluble Kaz-4 polyester. We found that binding of Kaz-4 with AAMA occurs under milder conditions: concentration of the reactants 15–20 wt %, 75°C, 2.5 h; the maximal BAS content was 80.6 wt %, which is 1.5 times higher compared to the immobilization on StMA.

We also examined the influence of the TEA content on the degree of immobilization of Akpinol on AAMA. We found that, in the absence of a catalyst, the amount of the active substance did not exceed 46.0%. With introduction of the catalyst into the reaction mixture, the degree of BAS binding increased and reached 98.0% on adding 1 mol of TEA per mole of anhydride groups. At larger amounts of the catalyst, the degree of immobilization calculated from the nitrogen content exceeds 100%, which can be due only to binding of the catalyst with the carboxy group of the copolymer. Therefore, in the next step of our study we examined how the copolymer : BAS ratio affects the degree of binding of Akpinol which also contains tertiary nitrogen. We found that maximal immobilization of Akpinol (58.5 mol %) was attained at the AAMA : Akpinol ratio of 1 : 2.5. Then we examined how the amount of the immobilized substance depends on the reaction mixture concentration, temperature, and time. We found that the biopolymer with the maximal degree of binding of Akpinol with AAMA is obtained at 90–100°C in 3 h at the reaction mixture concentration of 30 wt %.

The IR spectrum of this polymer suggests the formation between the piperidol and copolymer of an ester bond (1717 cm^{-1}) and an ionic bond (absorption bands of the carboxylate ion at 1573 cm^{-1} and of the quaternary nitrogen moiety at 2528 cm^{-1}).

The character of BAS bonding with the polymer matrix suggests that, when this preparation will be used as aqueous solutions, the active agent will be released in time. The process will start with fast hydrolysis of the ionic bond (since the initial acid and base are relatively weak), which will be followed by slow hydrolysis of the ester bond. Furthermore, in contrast to Styromal-based polymeric BASs, the AAMA-based substances are soluble in water, apparently due to carboxy groups present in the copolymer. This fact makes it unnecessary to convert the polymeric BASs into potassium salts (this procedure is done with polymeric biostimulants based on maleic anhydride copolymers, in particular StMA, to make them water-soluble).

The biopolymers prepared were tested for the germination energy and germinating capacity of corns. The polymeric growth regulators showed higher, compared to the monomeric analogs, biological activity; the highest germination capacity was attained upon treatment with a 0.001% solution of polymeric Akpinol (87.3%).

The field tests showed that the biopolymer containing two growth regulators is more active than polymeric Akpinol. The polymeric growth regulators developed can be used for presowing treatment of seeds in cultivation of arid cultures (crops, saxaul) under semidesert conditions on alluvial sandy soils.

CONCLUSIONS

(1) Phytoactive polymers derived from 1,4-bis[*N*-(2-ethoxyethyl)-4-hydroxypiperid-4-yl]buta-1,3-diyne and 1,2,5-trimethyl-4-dimethoxyphosphorylpiperid-4-ol (Fospinol) with 1,4-bis(1,2,5-trimethyl-4-hydroxypiperid-4-yl)buta-1,3-diyne (Akpinol) were prepared. The optimal conditions for immobilization of these compounds on copolymers of maleic anhydride with styrene and methacrylic acid were found: copolymer : BAS : catalyst ratio 1 : 1 : 1, reation time 2.5–4 h, concentration of the reactants 15–30 wt %, temperature 90–100°C depending on the nature of the starting compounds.

(2) Tests of the polymers synthesized showed that the biopolymer prepared by immobilization of Akpinol with Fospinol on maleic anhydride–styrene copolymer is the most active.

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