New auxin-type plant growth regulators

A. Merkys,
L. Novickienė,
V. Gavelienė

Institute of Botany,
Žaliųjų ežerų 49,
LT-2021 Vilnius, Lithuania

V. Daukšas,
Z. Šaltytė

Department of Chemistry,
Vilnius University,
Naugarduko 24,
LT-2006 Vilnius, Lithuania

New compounds – N-alkyl-N-[2-(2,4-dichlorophenoxyacetoxy)ethyl]morpholinium chlorides were synthesized. They enhance tuber number and mass formation in potatoes. N-Allyl-N-[2-(2,4-dichlorophenoxyacetoxy)ethyl]morpholinium chloride is the most active compound. It is more active potato growth regulator than its naphthalene analogue. All synthesized compounds exhibit also a retardant activity for kidney beans.

Key words: plant growth regulators, patatoes, synthesis, 2,4-dichlorophenoxyacetic acid derivatives, N,N-dialkylmorpholinium salts

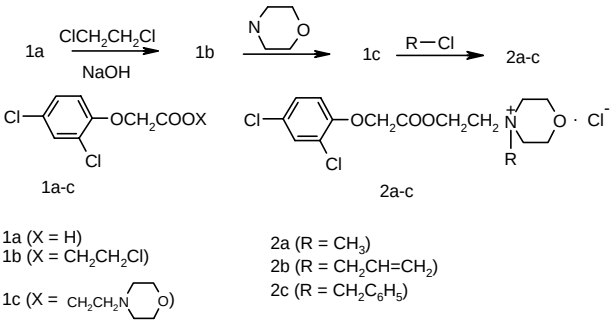
INTRODUCTION

Over the last decades the number of organic synthetic compounds exhibiting growth-regulating properties has increased significantly, however, only a small part of them (about 100) have become employed in plant growing worldwide [1]. Their common feature is that most frequently they influence the whole plant by suppresing or stimulating its growth. However, this can be achieved by modern agrotechnical and agrochemical means depending on the peculiarities of plant (species, sort) and soil. At present, attention is focused on the search of physiological analogues of phytohormones and other types of regulatory compounds, on their investigation and employment in plant cultivation.

The aim of the present work was to search for new chemical and physiological analogues of auxin-1-naphthylacetic and 2,4-dichlorophenoxyacetic acids of selective action, applicable in agricultural practice.

METHODS OF SYNTHESIS

New N-alkyl-N-[2-(2,4-dichlorophenoxyacetoxy)ethyl]morpholinium chlorides (2 a–c) were synthesized by N-alkylation of N-[2-(2,4-dichlorophenoxyacetoxy)ethyl]morpholine (1c) with chloromethane, 3-chloropropene or chloromethylbenzene. The O-alkylation of 2,4-dichlorophenoxyacetic acid (1a) with 1,2-dichloroethane led to 2-chloroethyl 2,4-dichlorophenoxyacetate (1b) which was converted to the compound 1c by the action of morpholine.



The compounds 1b and 1c were used in the synthesis without isolation in a pure state. The postulated structures of newly synthesized compounds (2 a–c) are in agreement with their UV, IR and ^{1}H NMR spectral and elemental analysis data. The compound 1a is a commercial product.

A mixture of 2,4-dichlorophenoxyacetic acid (22.1 g, 0.1 mol), NaOH (4.0 g, 0.1 mol), $ClCH_2CH_2Cl$ (30.0 g, 0.3 mol) and dimethylformamide (50 ml) was heated under reflux for 3 h, cooled to 20 °C, the precipitate filtered off, the filtrate concentrated in vacuum, the residue extracted with hot hexane, and the extract was concentrated to give a crude compound 1b. A mixture of the crude com-

pound 1b, ethyl acetate (50 ml) and morpholine (26.1 g, 0.3 mol) was heated under reflux for 10 h, cooled to 20 °C, the precipitate was filtered off, the filtrate concentrated, the residue extracted with hot hexane and the extract was concentrated to give a crude compound 1c. A mixture of crude compound 1c, ethyl acetate (50 ml) and corresponding R-Cl (0.3 mol) was heated under reflux for 200 h (R = = allyl) or 75 h (R = benzyl) or heated in an autoclave for 150 h at 100 °C (R = CH_3), cooled to 10 °C, the precipitate was filtered off, washed with anhydrous ether, dried in a vacuum and recrystallized from a mixture of anhydrous ethanol with anhydrous ethyl acetate (1:4) to give the compounds 2 a–c as white crystals very soluble in water and hot ethanol and insoluble in benzene, ether and hexane.

N-[2-(2,4-Dichlorophenoxyacetoxy)ethyl]-N-methylmorpholinium chloride (2a), yield 29.3 g (76% on compound 1a), m. p. 104–106 °C, UV: λ_{max} (nm) 209, 226, 281, 290, lgε 3.07, 2.95, 2.28, 2.24. IR ν (cm^{-1}) 1748 (CO). Found, %: C 46.98; H 5.35; Cl 27.51; N 3.75. $C_{15}H_{20}C_{l3}NO_4$. Calculated, %: C 46.83; H 5.24; Cl 27.65; N 3.64.

N-Allyl-N-[2-(2,4-dichlorophenoxyacetoxy)ethyl]morpholinium chloride (2b), yield 30.8 g (75% on compound 1a), m. p. 90–92 °C, UV: λ_{max} (nm) 208, 226, 281, 290, 312, lgε 3.46, 3.26, 2.47, 2.45, 2.02. IR λ (cm^{-1}) 1745 (CO). ^{1}H NMR: δ (ppm) 4.14 (6H, m, CH_2O), 4.80 (10H, m, CH_2N^+ and OCH_2CO), 5.67 (3H, m, CH_2=CH), 6.80 (3H, m, ArH). Found, %: C 49.90; H 5.55; Cl 25.97; N 3.51. $C_{17}H_{22}Cl_3NO_4$. Calculated, %: C 49.75; H 5.39; Cl 25.88; N 3.40.

N-Benzyl-N-[2-(2,4-dichlorophenoxyacetoxy)ethyl]morpholinium chloride (2c), yield 32.7 g (71% on a compound 1a), m. p. 145–147 °C, UV: λ_{max} (nm) 210, 226, 250, 255, 261, 267, 281, 290, lgε 3.82, 3.19, 2.35, 2.46, 2.48, 2.43, 2.25, 2.21. IR ν (cm^{-1}) 1740 (CO). Found, %: C 54.66; H 5.35; Cl 23.19; N 3.10. $C_{21}H_{24}Cl_3NO_4$. Calculated, %: C 54.74; H 5.25; Cl 23.08; N 3.04.

The UV spectra were recorded on a Specord UV-VIS (Carl Zeiss, Germany) in 95% ethanol and the IR spectra on a Specord M 80 (Carl Zeiss, Germany) in Nujol mulls, ^{1}H NMR spectrum – at 80 MHz on a BS 587A (Tesla, Czech Republic) in CF_3COOH with HMDSO as an internal reference.

METHODS OF BIOLOGICAL INVESTIGATIONS

The aim of primary screening is to investigate the biological efficiency of compounds 2 a–c. A biotest system with kidney bean hypocotyls was worked out. Hypocotyl segments were used to find out whether the compounds show an auxin or retardant activity. Hypocotyls (10 samples) were kept into glasses with water solutions of test compounds ($1 \cdot 10^{-5}$–$1 \cdot 10^{-4}$ M) for 2 days. A variant had four replications. Then, after washing the hypocotyls with water, they were kept in glasses with water for 6 days. The length of hypocotyls was measured before the test and after it.

Field trial on potato (*Solanum tuberosum* L.) second early variety '*Nida*' was carried out at the Vokė Branch of the Lithuanian Institute of Agriculture. Potatoes were grown in turf-podzol soil, applying 50 t/ha of manure in autumn and mineral fertilizer ($N_{70}P_{70}K_{80}$) in spring. The field area was 14.7 m^2, each variant had 4 replications. Potatoes were effected with water solutions of the test compounds at optimum doses and optimal time – organogenesis stage IV.

We defined the compounds' activity by the effect on potato tuber formation, tuber mass and yield.

RESULTS AND DISCUSSION

N-Alkyl-N-[2-(1-naphthylacetoxy)ethyl]morpholinium halogenides increase the number of potato tubers and their mass [2]. So, as an extension of our interest in structure–activity relationships of auxin-type plant growth regulators, the present study dealt with the synthesis of new the compounds 2 a–c, which are the synthetical analogues of the compounds mentioned above but contain a 2,4-dichlorophenoxy group instead of a 1-naphthyl group. The new compounds 2 a–c also increase the number and mass of

Table 1. **Effect of compounds 2 a–c on potato 'Nida' tuber yield (average for 1 plant)**

Variants of the experiment	Number of potato tubers		Mass of potato tubers		Tuber yield, t/ha	
	n	%	g	%	total	extra
Control (H_2O)	8.2	100	850	100	24.0	–
Compound 2a (580 g/ha)	9.9*	120	860	101	24.5	0.5
Compound 2b (615 g/ha)	10.2*	124	952*	112	27.1	3.1
Compound 2c (690 g/ha)	10.0*	122	870	102	24.2	0.2

The data are statistically reliable at $p \leq 0.05$. *R% = 0.22.

Table 2. **Effect of compounds 2 a–c on kidney bean hypocotyl growth and rootage***

Variants of the experiment	Hypocotyl increment		Number of roots	
	cm	%	n	%
Control (H_2O)	4.0 ± 0.32	100	18 ± 0.80	100
Compound 2a ($1 \cdot 10^{-4}$ M)	2.4 ± 0.14	60	26 ± 0.92	144
Compound 2b ($1 \cdot 10^{-4}$ M)	3.0 ± 0.25	75	27 ± 0.88	150
Compound 2c ($1 \cdot 10^{-4}$ M)	2.6 ± 0.12	65	25 ± 1.02	139

*6 days after application; initial hypocotyl length 10 cm.

potato tubers formation (Table 1). The most active compound, II b, is more active than its naphthalene analogue [3]. Moreover, the compounds 2 a–c exhibit a retardant activity for dicotyledonous plants (kidney bean hypocotyl) growth but induced root taking (Table 2).

CONCLUSIONS

1. New biologically active N-alkyl-N-[2-(2,4-dichlorophenoxyacetoxy)ethyl]morpholinium chlorides were synthesized.

2. The synthesized compounds increase the number and mass of tubers in potatoes. The allyl derivative is the most active. All the compounds exhibit also the retardant activity for kidney beans.

3. The same allyl derivative is a more active potato growth regulator than its naphthalene analogue known before.

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A. Merkys, L. Novickienė, V. Gavelienė, V. Daukšas, Z. Šaltytė

NAUJI AUKSINO TIPO AUGALŲ AUGIMO REGULIATORIAI

Santrauka

Iš 2,4-dichlorfenoksiacto rūgšties susintetinti N-alkil-N-[2-(2,4-dichlorfenoksiacetoksi)-etil]morfolino chloridai, didinantys bulvių gumbų skaičių ir masę. N-Alil-N-[2-(2,4-dichlorfenoksiacetoksi)etil]morfolino chloridas yra aktyviausias. Visi junginiai dar pasižymi retardantiniu aktyvumu pupelių hipokotilių augimui, tačiau skatina jų įsišaknijimą. Nurodytas junginys yra aktyvesnis bulvių augimo reguliatorius už naftaleno analogą.